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Application of solid-phase microextraction to the analysis of volatile organic compounds in water

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Abstract

Solid-phase microextraction (SPME) was investigated as a solvent-free alternative method for the extraction and analysis of some volatile organic compounds which can be present in industrial effluents. Such compounds are included in the hazardous pollutants list of the US National Institute for Occupational Safety and Health and the US Environmental Protection Agency. The performance of SPME fibres coated with two different stationary phases, such as poly(dimethylsiloxane) 100 μm and 7 μm film thickness and 85 μm poly(acrylic acid) were evaluated. Absorption times of 12 min for 100-μm poly(dimethylsiloxane) and 85-μm poly(acrylic acid) fibres and 5 min for 7-μm poly(dimethylsiloxane) were needed to reach the equilibrium and 2 min was enough for complete desorption of the analytes in the injection port of the gas chromatograph. High recoveries were obtained using the 100-μm poly(dimethylsiloxane) fibre, although for polar compounds better results were found using the 85-μm poly(acrylic acid) fibre. Linear dynamic ranges and a detection limit between 0.3 and 1.5 $\mu g\ l^{-1}$ were obtained using the 100-μm poly(dimethylsiloxane) fibre and flame ionization detection. The SPME–GC procedure gave good repeatability (R.S.D.=4.3–10.5%) and reproducibility (R.S.D.=6.6–12.9%). The proposed SPME–GC method was applied to determine some volatile organic compounds in spiked drinking water and in industrial effluent samples.

Keywords: Sample handling; Environmental analysis; Water analysis; Extraction methods; Volatile organic compounds

1. Introduction

Organic pollution of water is a common environmental problem. The complexity and diversity of environmental contaminants have resulted in the development of analytical techniques for their extraction and analysis. Sample pretreatment is often necessary to isolate the components of interest from sample matrices, and to purify and concentrate the analytes. Currently, volatile compounds are analyzed using either headspace [1,2] or purge-and-trap [3–5] techniques, while for a semi-volatile and non-volatile compounds liquid–liquid extraction [6,7] and solid-phase extraction [8,9] are commonly used. All these techniques are effective but have limitations [10–12]. Headspace analysis is largely confined to highly concentrated samples and purge-and-trap, although very sensitive, is expensive and prone to leaks, sample carryover and contamination. Liquid–liquid extraction requires large volumes of high-purity solvents and cannot be easily automated. Finally, solid-phase extraction (SPE) needs less solvent, but,

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for trace analysis, a large volume of sample is required and it is susceptible to high baseline blanks, channelling, and, if the sample contains particulate matter, plugging of the sorbent beds.

Solid-phase microextraction (SPME), recently developed by Pawliszyn and co-workers [13–16], is an excellent alternative to the aforementioned techniques. It is a rapid, inexpensive, solventless, and easily automated technique for the extraction of organic compounds from aqueous samples. SPME combines sampling and preconcentration into one step and allows direct transfer of the analytes to the chromatographic column through a standard split/splitless injector. The SPME fibre is a fused-silica needle coated with a stationary phase [17] fitted in a special syringe-type holder for protection and sampling. The fused-silica fibre is exposed to the aqueous solution to extract the organic compounds from their matrix. When sampling is completed, the silica fibre is inserted directly into the liner of a conventional split/splitless injector of a gas chromatograph for thermal desorption and analysis. Absorption of analytes is based on equilibrium partitioning between the coated fibre and the sample rather than exhaustive extraction. When the equilibrium is reached, the amount of each analyte extracted is directly related to its concentration in the aqueous sample [15]. High sensitivity can be reached by using a thick and selective stationary phase. The whole extraction and analyte transfer process usually takes only a few minutes [13] and it can easily be automated [18].

The SPME method coupled with GC has been applied to the analysis of different compounds in water [18–21], caffeine in beverages [22] and polyaromatic hydrocarbons, polychlorinated biphenyls [15,23], chlorinated hydrocarbons [10,16], phenols [24,25] and pesticides [26] in different matrices.

Volatile organic compounds have gained prominence in air and water pollution control over the past decade as a result of increased environmental and health concerns and the introduction of new regulations. This paper presents an evaluation of the SPME technique and the performance of SPME fibres, available commercially, coated with different stationary phases, such as poly(dimethylsiloxane) and poly(acrylic acid), for the determination of some volatile organic compounds that are often detected in industrial effluents and drinking waters and are included as hazardous pollutants in the list of the US National Institute for Occupational Safety and Health (NIOSH) and the US Environmental Protection Agency (EPA) [27–29]. The main objective of this work was to evaluate the SPME as a routine alternative technique for headspace and purge-and-trap.

2. Experimental

2.1. Standards and reagents

The volatile organic compounds studied were supplied with a purity higher than 99% by Fluka and Aldrich (both Buchs, Switzerland). Divinylbenzene (synthesis grade) was also purchased from Aldrich but three different ethylvinylbenzene isomers were detected as impurities. A stock standard solution mixture of these compounds at 1000 mg l^{-1} was prepared by mass in ethanol (Fluka). A secondary standard solution was prepared by dilution in ethanol of the primary standard to give concentrations of 10 mg l^{-1}. Water (HPLC grade) solutions of 6 ml were prepared by spiking with different amounts of the secondary standard and used for calibration. The concentrations of the volatile organic compounds in the aqueous calibration solutions ranged between 0.1 and 1000 μg l^{-1}. *n*-Decane was used as internal standard for calibration and quantification, and was added with a 50-μl Hamilton (Hamilton, Reno, NV, USA) syringe so that the concentration was 100 μg l^{-1} in the calibration solutions and water samples. For the extraction, the solutions were placed in 10-ml screw-cap vials equipped with stir bars and fitted with silicone/PTFE septa.

2.2. Chromatographic conditions

Gas chromatography was carried out on a Hewlett-Packard (Palo Alto, CA, USA) Model 5890 capillary gas chromatograph equipped with flame-ionization detection (FID) using nitrogen as make-up gas. A BPX 5 (modified 5% phenyl, 95% methyl siloxane) fused-silica capillary column (50 m×0.32 mm I.D.) (SGE, Australia) with a 1.0 μm film thickness was used with helium as carrier gas at a linear velocity of 31 cm s^{-1}. The temperature was held isothermically

at 35°C for 5 min, raised to 180°C at 6°C min^{-1} and maintained at 180°C for 1 min, then raised to 300°C at 20°C min^{-1}. The injector temperature was between 220 and 260°C, depending the fibre, and the detector was maintained at 300°C. The chromatographic data were analysed using an HP 3365 GC workstation data system.

For the identification of the studied compounds, GC–MS analyses were performed using a MD-800 mass quadrupole analyser coupled to a GC 8000 series gas chromatograph, both from Fisons Instruments (Manchester, UK). The GC capillary column and the chromatographic conditions were the same as described for the GC–FID determinations. The MS operating conditions were as follows: ion source and transfer line temperatures, 250 and 260°C, respectively; ionization energy, 70 eV (electron impact mode, EI); resolving power, 500; and mass range, 45–450 *m/z* at 1 s/scan using full-scan mode.

2.3. Solid-phase microextraction procedure

The studies were carried out with SPME devices purchased from Supelco (Ontario, Canada). Microextraction fibres were coated with poly(dimethylsiloxane) of 100 μm and 7 μm film thickness (bonded phase) and poly(acrylic acid) of 85 μm film thickness as stationary phases and were applied using a solid-phase microextraction syringe purchased from Supelco.

A SPME procedure which includes the following steps was developed: first, an amount of *n*-decane as internal standard was added to the sample vial using a 50-μl Hamilton syringe. The fibre was withdrawn into the syringe stainless-steel needle, which was used to penetrate the septum of the sample vial. When the needle was in the sample vial, the fibre was plunged into the sample so that the stainless-steel needle attachment was just below the meniscus. When equilibrium was reached, the fibre was again withdrawn into the needle and the syringe was removed from the vial. The last step was the thermal desorption of the analytes in the injection port of the gas chromatograph.

To determine the optimum penetration depth of the fibre in the GC injection port, the needle/fibre syringe was compared to a normal 10-μl GC syringe. The length comprising the stainless-steel needle and the silica fibre was adjusted to equal the length of a normal syringe needle (5 cm).

In order to stabilize the phase and remove all contaminants, the fibres were conditioned at 240°C for 100 μm poly(dimethylsiloxane) and at 280°C for 7 μm poly(dimethylsiloxane) and for 85 μm poly(dimethylsiloxane), before use. Conditioning was carried out for 2 h at these temperatures in the GC injector with the split vent open at 80–100 ml min^{-1} and the oven at 300°C. After conditioning, the fibre was desorbed for 5 min with the splitter vent closed and the analysis was performed in order to evaluate the blank. The conditioning procedure was carried out two or three times before use for a new fibre or for reconditioning a old one. It was found a fibre could be reused 50 times.

3. Results and discussion

In order to develop an SPME technique for the analysis of volatile organic compounds in water, it is necessary to optimize several parameters such as the stirring, the exposure time of the fibre to the aqueous sample and the desorption time in the GC injection port.

In order to minimize the time required for the volatile organic compounds to reach an equilibrium between the fibre stationary phase and the aqueous sample, the stirring speed of the aqueous solution during the SPME procedure was optimized. At stirring speed of 1000 rpm, the equilibrium time was reached after 5–15 min, whereas using lower speeds a time of 35–40 min was needed. Fig. 1 shows the example of the absorption time profiles for styrene, toluene and 2-methyl-1,3-butadiene at a concentration level of 200 $\mu g\ l^{-1}$ in water using the three different fibres. For the 100-μm poly(dimethylsiloxane) and the 85-μm poly(acrylic acid) fibres, the time required to reach the equilibrium was 12 min, while 5 min were enough with 7-μm poly(dimethylsiloxane) fibre.

To ensure that the exposure time of the fibre within the GC injector was long enough for the complete desorption of the compounds from the stationary phase the desorption time were studied. Fig. 2 shows the desorption time profile for three of the standard compounds using a 100-μm poly(di-

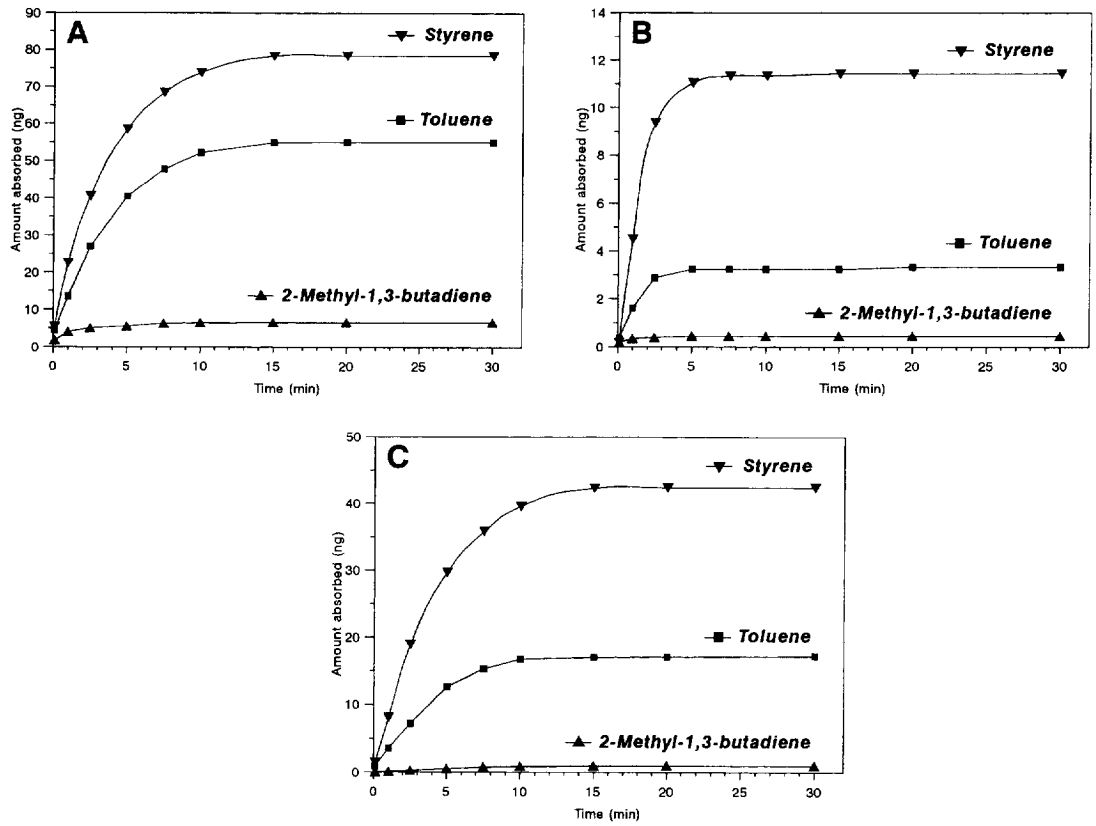

Fig. 1. Absorption time profiles for styrene, toluene and 2-methyl-1,3-butadiene under optimum conditions at a concentration level of 200 $\mu g\ l^{-1}$ for each compound using: (A) 100-μm poly(dimethylsiloxane) fibre; (B) 7-μm poly(dimethylsiloxane) fibre; and (C) 85-μm poly(acrylic acid) fibre.

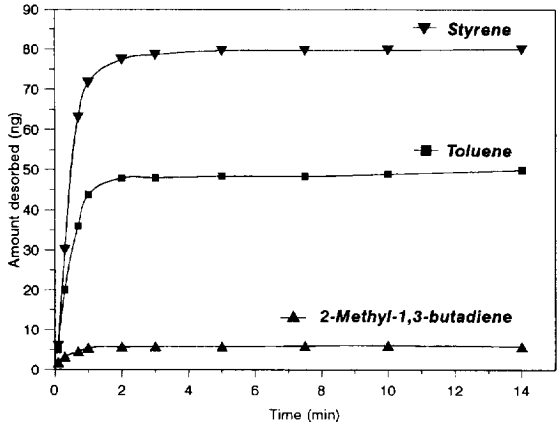

Fig. 2. Desorption time profiles for styrene, toluene and 2 methyl 1,3-butadiene under optimum conditions at a concentration level of 200 $\mu g\ l^{-1}$ for each compound using a 100-μm poly(dimethylsiloxane) fibre.

methylsiloxane) fibre. We set 5 min of desorption time in the GC injection port and the splitter was adjusted to 5 min. In order to determine whether the desorption was complete, the SPME fibre was again desorbed after each analysis. No carryover was observed, demonstrating that 5 min were enough. A GC–FID chromatogram of a standard mixture in water (200 $\mu g\ l^{-1}$ of each compound) using the 100-μm poly(dimethylsiloxane) SPME fibre is shown in Fig. 3. Sharp peaks and good chromatographic resolution for most of the compounds were obtained, although two isomers of divinylbenzene coeluted with the BPX 5 (modified 5% phenyl, 95% methyl siloxane) stationary phase.

The recoveries of the analytes using the three fibres were investigated and the values relative to the 85-μm poly(acrylic acid) fibre are given in Table 1. Polar compounds such as 2-propenenitrile, 2-methyl-

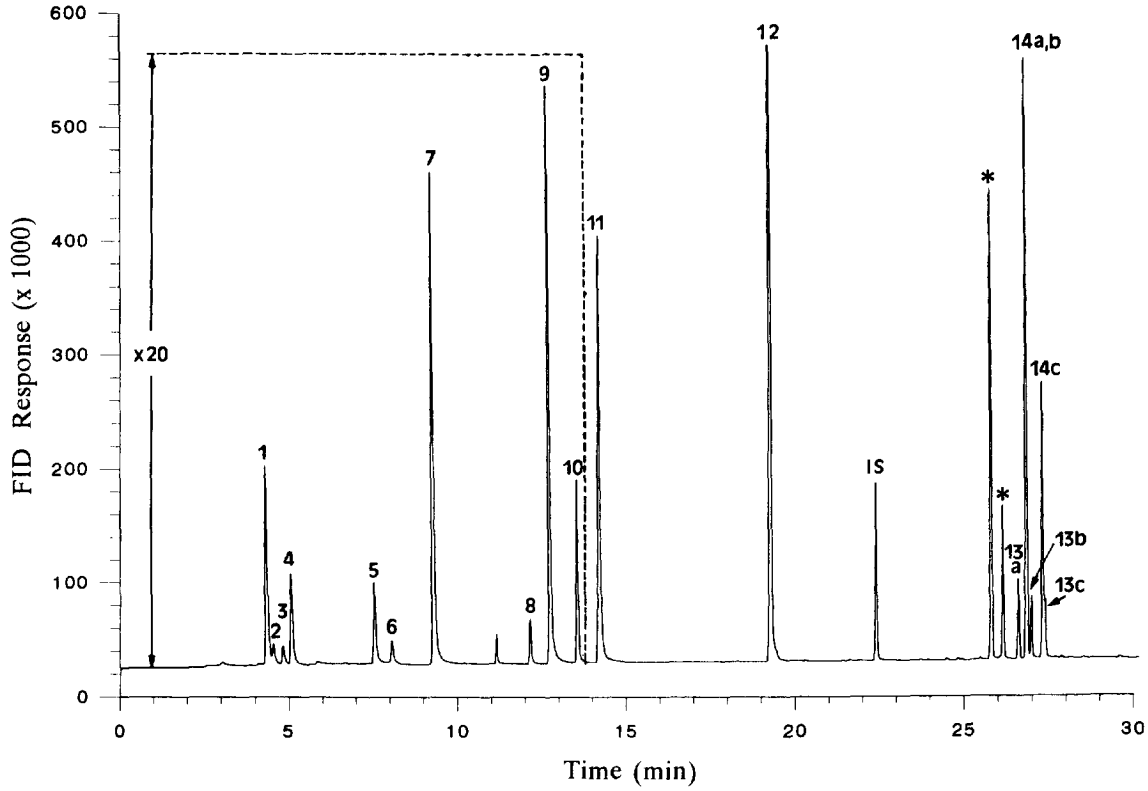

Fig. 3. GC–FID chromatogram of a standard solution in water at concentration level of 200 μg l^{-1} for each compound using a 100-μm poly(dimethylsiloxane) fibre. Peaks: 1=2-methyl-1,3-butadiene (t_R=4.33 min); 2=dimethoxymethane (t_R=4.52 min); 3=2-propenenitrile (t_R=4.81 min); 4=dichloromethane (t_R=5.06 min); 5=2-propenoic acid methyl ester (t_R=7.49 min); 6=2-methyl-1-propanol (t_R=8.01 min); 7=1,2-dichloroethane (t_R=9.24 min); 8=1-chloro-2,3-epoxypropane (t_R=12.09 min); 9=4-methyl-2-pentanone (t_R=12.67 min); 10=4-methyl-2-pentanol (t_R=13.48 min); 11=toluene (t_R=14.01 min); 12=styrene (t_R=19.12 min); 13a,b,c=isomers of 1,2,4-trivinylcyclohexane (t_R=26.46, 26.83 and 27.24 min, respectively); 14a,b=*o*- and *m*-divinylbenzene (t_R=26.71 min); 14c=*p*-divinylbenzene (t_R=27.17 min). I.S.: *n*-decane (t_R=22.22 min). *: isomers of ethylvinylbenzene. (Chromatographic conditions are described in Section 2).

1-propanol and 4-methyl-1-pentanol gave higher recoveries with the 85-μm poly(acrylic acid) fibre due to their better interactions with this polar stationary phase. Other compounds such as dimethoxymethane and divinylbenzene isomers were also better recovered with the poly(acrylic acid) stationary phase. The remaining compounds gave better recoveries with the 100-μm poly(dimethylsiloxane) fibre. Lower recoveries were obtained for the 7-μm poly(dimethylsiloxane) fibre due to its lower film thickness. The relative standard deviations of the recoveries using the 100-μm poly(dimethylsiloxane) fibre ranged between 4.2 and 7.1%, always lower than the values obtained with the other fibers, which ranged between 9.6 and 13.2%. Therefore, the 100-μm poly(dimethylsiloxane) fibre was preferred for the determination of these compounds.

After establishing the exposure time and the desorption time, the linear dynamic range of FID coupled with the SPME procedure for a 100-μm poly(dimethylsiloxane) was studied. The linearity was determined by plotting calibration curves of relative areas to internal standard (A_i/A_{IS}) versus relative concentrations (C_i/C_{IS}). The linear ranges and the correlation coefficients (r) for each compound are given in Table 2. For toluene, styrene, divinylbenzene isomers and 1,2,4-trivinylcychlohexane isomers the linear dynamic range was close to three orders of magnitude, and for the other analytes, the linear range was two orders of magnitude. The

Table 1
Recoveries (%) relative to the 85-μm poly(acrylic acid) fibre

Compound	100-μm poly(dimethylsiloxane) fibre		85-μm poly(acrylic acid) fibre		7-μm poly(dimethylsiloxane) fibre	
	Mean (%)[a]	R.S.D. (%)	Mean (%)[a]	R.S.D. (%)	Mean (%)[a]	R.S.D. (%)
2-Methyl-1,3-butadiene	641.0	4.8	100.0	11.5	35.9	10.1
Dimethoxymethane	95.2	6.5	100.0	8.3	8.3	10.9
2-Propenenitrile	90.7	6.8	100.0	7.4	6.6	12.6
Dichloromethane	150.4	5.3	100.0	8.9	10.1	11.7
2-Propenoic acid methyl ester	105.9	5.5	100.0	6.9	12.1	11.3
2-Methyl-1-propanol	71.8	6.8	100.0	6.2	7.0	13.2
1,2-Dichloroethane	132.5	5.1	100.0	7.4	8.0	12.1
1-Chloro-2,3-epoxypropane	234.7	4.2	100.0	12.8	17.4	10.4
4-Methyl-2-pentanone	111.9	5.6	100.0	9.3	9.5	11.7
4-Methyl-2-pentanol	88.6	7.1	100.0	8.6	5.0	13.5
Toluene	276.2	4.9	100.0	11.2	16.0	10.4
Styrene	174.8	5.6	100.0	8.2	24.0	9.6
1,2,4-Trivinylcyclohexane[b]	158.7	5.0	100.0	8.9	26.1	10.0
Divinylbenzene[c]	90.0	6.7	100.0	7.1	19.4	11.8

[a] Mean of three determinations.
[b] $\sum$ isomers.
[c] $\sum$ *o*-, *m*-, *p*-isomers.

loss of linearity might be related to the overload of the fibre capacity.

The repeatability and reproducibility of the SPME–GC procedure were studied by analyzing ten samples of HPLC water spiked at a concentration level of 50 $\mu g\ l^{-1}$ of each compound. The relative standard deviations for repeatability were between 4.3 and 10.5% and for reproducibility, between 6.6 and 12.9% (see Table 2). The detection limits (signal-to-noise ratio=3) of FID were also deter-

Table 2
Linear dynamic ranges, correlation coefficients (*r*), limit of detections (LOD), repeatability and reproducibility of the optimized SPME procedure using the 100-μm poly(dimethylsiloxane) fibre

Compound	Linearity range ($\mu g\ l^{-1}$)	Correlation coefficient (*r*)	Detection limit (LOD) ($\mu g\ l^{-1}$)	Repeatability ($n=10$)[a]		Reproducibility ($n=10$)[a]	
				Mean ($\mu g\ l^{-1}$)	R.S.D. (%)	Mean ($\mu g\ l^{-1}$)	R.S.D. (%)
2-Methyl-1,3-butadiene	2.4–845	0.9995	0.4	48.3	6.4	52.4	9.2
Dimethoxymethane	4.2–832	0.9996	1.5	47.6	9.2	46.5	10.6
2-Propenenitrile	4.3–774	0.9991	1.2	53.2	8.5	55.7	9.5
Dichloromethane	5.1–1414	0.9998	0.9	49.7	6.3	50.8	7.8
2-Propenoic acid methyl ester	4.4–1088	0.9996	0.9	48.1	7.6	47.2	9.7
2-Methyl-1-propanol	4.1–1042	0.9994	1.5	54.7	7.9	54.6	9.3
1,2-Dichloroethane	4.7–1545	0.9996	0.9	49.4	4.3	51.7	6.6
1-Chloro-2,3-epoxypropane	5.8–1356	0.9997	1.2	51.5	6.1	52.0	8.5
4-Methyl-2-pentanone	3.3–833	0.9998	0.6	50.8	5.8	51.5	7.3
4-Methyl-2-pentanol	3.2–868	0.9993	0.6	52.3	10.5	48.3	12.9
Toluene	1.7–945	0.9997	0.3	50.9	4.5	51.8	6.9
Styrene	1.2–981	0.9997	0.3	49.6	5.7	49.3	7.9
1,2,4-Trivinylcyclohexane[b]	1.1–928	0.9994	0.3	47.7	7.7	47.8	9.1
Divinylbenzene[c]	1.8–956	0.9993	0.3	51.2	7.8	52.7	9.6

[a] Concentration level of 50 $\mu g\ l^{-1}$.
[b] $\sum$ isomers.
[c] $\sum$ *o*-, *m*-, *p*-isomers.

Table 3
Spiking levels, estimated concentrations and relative standard deviations (%) of drinking water samples analyzed using a 100-μm poly(dimethylsiloxane) fibre

Compound	Spiking levels											
	10 $\mu g\ l^{-1}$			100 $\mu g\ l^{-1}$			500 $\mu g\ l^{-1}$			800 $\mu g\ l^{-1}$		
	Target ($\mu g\ l^{-1}$)	Mean[a] ($\mu g\ l^{-1}$)	R.S.D. (%)	Target ($\mu g\ l^{-1}$)	Mean[a] ($\mu g\ l^{-1}$)	R.S.D. (%)	Target ($\mu g\ l^{-1}$)	Mean[a] ($\mu g\ l^{-1}$)	R.S.D. (%)	Target ($\mu g\ l^{-1}$)	Mean[a] ($\mu g\ l^{-1}$)	R.S.D. (%)
2-Methyl-1,3-butadiene	12.1	11.6	5.8	112.1	119.2	5.8	515.1	525.3	6.2	824.3	853.1	6.4
Dimethoxymethane	11.6	10.3	7.8	108.6	101.3	7.9	499.4	514.2	7.6	812.6	825.0	7.8
2-Propenenitrile	10.9	9.8	7.2	105.4	110.6	7.4	508.6	498.6	7.5	816.9	785.1	7.6
Dichloromethane	8.8	9.4	3.8	99.8	105.1	4.1	488.6	512.1	4.8	808.6	833.3	5.1
2-Propenoic acid methyl ester	9.8	9.7	6.8	102.4	118.3	7.5	515.4	499.4	7.6	806.1	780.4	7.5
2-Methyl-1-propanol	10.8	11.4	7.6	115.2	121.2	7.8	517.6	528.6	7.7	809.6	827.2	8.1
1,2-Dichloroethane	9.9	10.5	4.3	107.4	100.2	4.6	492.3	516.4	5.1	805.6	863.4	5.2
1-Chloro-2,3-epoxypropane	11.3	10.8	6.8	109.5	101.4	7.1	512.6	537.2	7.2	795.4	828.3	7.8
4-Methyl-2-pentanone	13.4	12.7	6.2	110.3	118.3	6.8	514.2	529.1	7.1	812.6	736.6	7.6
4-Methyl-2-pentanol	10.5	11.2	7.7	104.6	98.6	8.0	498.8	520.4	7.9	816.4	836.4	8.0
Toluene	11.6	10.2	5.3	111.2	119.2	5.2	516.3	500.1	5.4	796.3	779.3	5.8
Styrene	10.5	11.0	5.1	105.5	104.3	5.8	518.4	531.4	5.6	805.3	824.4	6.2
1,2,4-Trivinylcyclohexane[b]	11.9	12.2	7.1	114.6	120.6	7.8	495.6	523.1	7.9	801.3	832.4	8.0
Divinylbenzene[c]	12.8	12.4	6.9	118.6	111.4	7.1	498.6	514.2	7.4	789.4	810.3	7.5

[a] Mean of three determination.
[b] $\sum$ isomers.
[c] $\sum$ *o*-, *m*-, *p*-isomers.

mined and are reported in Table 2. In order to estimate the detection limits, dilutions of the calibration standard were extracted with SPME fibres. Under these conditions the detection limits obtained were between 0.3 and 1.5 $\mu g\ l^{-1}$.

The SPME method proposed was applied for the determination of some volatile organic compounds in spiked drinking water and in industrial effluent samples. Duplicate analyses of four samples of drinking water spiked at concentrations between 10 and 800 $\mu g\ l^{-1}$ by addition of different amounts of standard mixtures were carried out in order to determine the accuracy and precision of the SPME method in water samples. Quantification was carried out using the calibration curve for each compound relative to the internal standard (*n*-decane). Spiking levels, estimated concentration and relative standard deviation are given in Table 3. The mean values obtained for all compounds agree with the target values and relative standard deviations were lower than 8.1%.

The volatile organic compounds selected in this work were also studied in samples of industrial effluents from chemical plants in the North of France. Six water samples collected in effluents from chemical industries were analyzed using the developed SPME procedure with 100-μm poly(dimethylsiloxane) fibres. All samples were diluted with HPLC-grade water in order to bring the concentration of the analytes down to the linear range. The chromatogram obtained with GC–FID of an effluent water sample is given in Fig. 4. Confirmation of the identified compounds was performed by GC–MS. High concentrations of dimethoxymethane, 1,2-dichloroethane, 4-methyl-2-pentanol and styrene were found. These concentrations are consistent with the observation that several production plants in the area drain their waste products directly into the river.

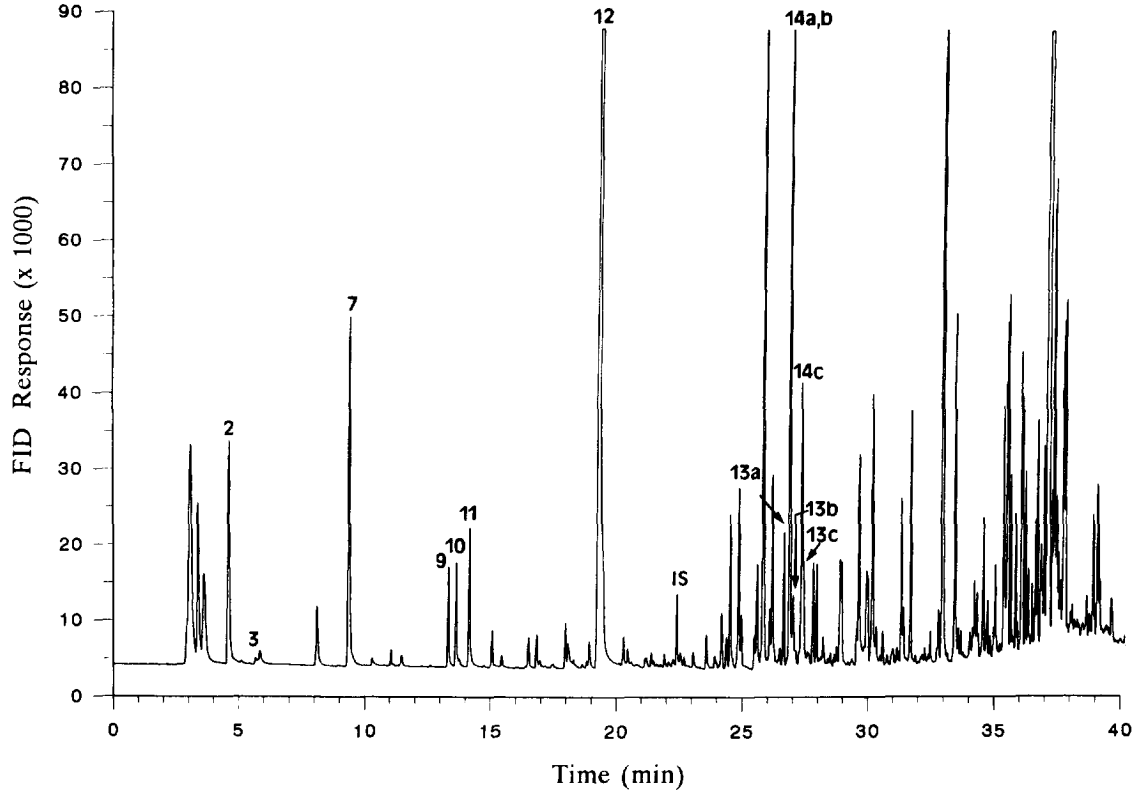

Fig. 4. GC–FID chromatogram of a effluent sample analyzed with a 100-μm poly(dimethyl siloxane) fibre. Peaks: 2=dimethoxymethane (6924 $\mu g\ l^{-1}$); 3=2-propenenitrile (680 $\mu g\ l^{-1}$); 7=1,2-dichloroethane (3154 $\mu g\ l^{-1}$); 9=4-methyl-2-pentanone (82 $\mu g\ l^{-1}$); 10=4-methyl-2-pentanol (8300 $\mu g\ l^{-1}$); 11=toluene (614 $\mu g\ l^{-1}$); 12=styrene (16 590 $\mu g\ l^{-1}$); 13a,b,c=1,2,4-trivinylcyclohexane isomers (240 $\mu g\ l^{-1}$); 14a,b,c=*o*-, *m*- and *p*-divinylbenzene (740 $\mu g\ l^{-1}$); I.S.: *n*-decane. Chromatographic conditions are described in Section 2.

Lower concentrations were obtained for 2-methyl-1,3-butadiene, 2-propenenitrile, dichloromethane, 4-methyl-2-pentanone, toluene, 1,2,4-trivinylcyclohexane isomers and divinylbenzene isomers, which are often produced in the area by the companies where the samples were collected. Duplicate analyses of effluent samples were carried out and the relative standard deviations obtained ranged between 6.8 and 10.6%.

4. Conclusions

The investigated SPME procedure is a fast, inexpensive and solvent-free method that has been proved to be precise and sensitive for analysis of volatile organic compounds in water samples. Compounds with a wide range of boiling points were studied and high recoveries were obtained using 100-μm poly(dimethylsiloxane) fibre, although the most polar compounds give higher recoveries with a 85-μm poly(acrylic acid) fibre. The SPME method using 100-μm poly(dimethylsiloxane) fibre allowed the quantitative analysis of a group of volatile organic compounds which can be present in water samples giving good reproducibility (R.S.D.=6.6 and 12.9%), and low detection limits (0.3 and 1.5 μg l^{-1}). The optimized SPME procedure can be proposed as a fast monitoring method for the analysis of volatile organic compounds in drinking waters and industrial effluents and can be used instead of the purge-and-trap technique which is more expensive and prone to leaks, sample carryover and contaminations. Further investigations on the SPME as an alternative method of analysis will concentrate for expanding the list of compounds and samples.

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