



ELSEVIER

Journal of Chromatography A, 824 (1998) 53–61

JOURNAL OF  
CHROMATOGRAPHY A

# Headspace solid-phase microextraction for the determination of volatile and semi-volatile pollutants in water and air

Maria Llompart<sup>a,\*</sup>, Ken Li<sup>b</sup>, Merv Fingas<sup>b</sup>

<sup>a</sup>*Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Química, Universidad de Santiago de Compostela, E-15706 Santiago de Compostela, Spain*

<sup>b</sup>*Emergencies Science Division, Environment Canada, Environmental Technology Centre, River Road, Ottawa, Ontario K1A 0H3, Canada*

Received 18 May 1998; received in revised form 21 July 1998; accepted 22 July 1998

## Abstract

In this work we report the use of solid-phase microextraction (SPME) to extract and concentrate water-soluble volatile as well as semi-volatile pollutants. Both methods of exposing the SPME fibre were utilised: immersion in the aqueous solution (SPME) and in the headspace over the solution (HSSPME). The proposed HSSPME procedure was compared to conventional static headspace (HS) analysis for artificially spiked water as well as real water samples, which had been, equilibrated with various oil and petroleum products. Both techniques gave similar results but HSSPME was much more sensitive and exhibited better precision. Detection limits were found to be in the sub-ng/ml level, with precision better than 5% R.S.D. in most cases. To evaluate the suitability of SPME for relatively high contamination level analysis, the proposed HSSPME method was applied to the screening of run-off water samples that had heavy oil suspended in them from a tire fire incident. HSSPME results were compared with liquid–liquid extraction. Library searches were conducted on the resulting GC–MS total ion chromatograms to determine the types of compounds found in such samples. Both techniques found similar composition in the water samples with the exception of alkylnaphthalenes that were detected only by HSSPME. A brief study was carried out to assess using SPME for air monitoring. By sampling and concentrating the volatile organic compounds in the coating of the SPME fibre without any other equipment, this new technique is useful as an alternative to active air monitoring by means of sampling pumps and sorbent tubes. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Solid-phase microextraction; Headspace analysis; Environmental analysis; Volatile organic compounds

## 1. Introduction

A recent advance in sample preparation for trace analysis is solid-phase microextraction (SPME) technology. In this solvent-free extraction technique, developed in 1989 by Pawliszyn [1–4], the analytes are adsorbed directly from an aqueous [2] or gaseous phase [5] onto a fused-silica fibre coated with a

liquid-polymeric phase. Hence sampling, extraction and concentration are accomplished in a single step. The entire assembly is mounted in a modified syringe needle which, after exposure to the sampling media (water or air), is inserted into a heated injector, and the chemicals adsorbed on the polymeric film are thermally desorbed and analyzed. The SPME fibre can also be suspended in the headspace above the water or solid sample (HSSPME), which eliminates interference problems because the fibre is

\*Corresponding author.

not in contact with the sample [6,7]. SPME has become very popular in the last two or three years, specially in environmental analysis [8–13]. SPME has been applied to the analysis of different water pollutants including volatile organic compounds (VOCs) [14], polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) [15,16], volatile chlorinated hydrocarbons [17], phenols [8] and pesticides [18].

Sample preparation for water analysis by traditional methods is usually time consuming and involves sophisticated instrumentation. Liquid partitioning is flexible but requires large amounts of ultrapure solvents, plus extraction is prone to contamination problems. Instrumental methods such as headspace (HS) are useful as a screening tool, using disposable vials, and adequate for relatively high contamination. Purge and trap (PAT) involves more sophisticated instrumentation and offers superior sensitivity, but suffers from high capital cost and is subject to crossover contamination due to the common trapping device. The proposed SPME technique, by comparison, operates by passive adsorption of the analytes on a polymeric coating and the subsequent desorption in the heated port of a gas chromatograph with suitable detector. For water analysis, other than stirring the sample in which the fibre is exposed to, no other external equipment is required and hence is much simpler to operate.

We report here the specific application of analysing soluble organic compounds in water, which constitutes an important aspect for routine environment monitoring as well as in emergency spill situations. For this evaluation, we have employed polydimethylsiloxane (PDMS) SPME fibres with film thickness of 100  $\mu\text{m}$ . With their universality of adsorption characteristics for most organic compounds, they should be good candidates for general analytical work. We have investigated the effect of immersing the fibre in the sample solution (SPME) as well as in the headspace over the sample (HSSPME). Also the effect of the addition of salt as well as the effect of temperature in the HSSPME response obtained were investigated. Extensive comparisons were carried out with static HS analysis on artificially spiked water samples as well as real water accommodated fraction (WAF) samples generated from crude oils. Both techniques gave similar results

but HSSPME was more sensitive and precise. The HSSPME method has also exhibited excellent linearity. To exploit the full potential of HSSPME as a quick field screening technique for dirty water samples, we have applied this technique to surface water samples heavily contaminated with the oily distillates resulting from a tire fire incident. HSSPME results were compared with liquid–liquid extraction (LLE). Library searches were conducted on the resulting gas chromatography–mass spectrometry (GC–MS) total ion chromatograms (TICs) to determine the types of organics found in such samples. Both techniques found similar composition in the water samples with the exception of alkylnaphthalenes that were detected only by HSSPME.

In the case of air analysis, the fibre is exposed to the sample media for a pre-determined amount of time and then thermally desorbed [5]. Used as a passive sampler, this technique is far simpler to implement than active pumping on collection of sorbent tubes. An evaluation was conducted on artificial air samples prepared with representative industrial chemicals. Because of the low cost and simplicity of deployment, perimeter monitoring of water- or airborne spilled chemicals can be carried out easily by SPME.

## 2. Experimental

### 2.1. Instrumentation

Static HS analysis was performed using a Hewlett-Packard HP19395A headspace sampler and a HP5890 Series II gas chromatograph equipped with a 5970 mass selective detector. Experimental parameters of the HS sampler were as follows: equilibration time, 30 min (nominal); bath temperature, 95°C; sample loop, 3-ml; valve/loop temperature: 110°C; valve operation sequence of pressurisation 10 s, venting and filling of loop 5 s, and injection 15 s. The carrier gas was helium at 80 ml/min; and auxiliary pressure of 1.5 bar. Conventional HS was run using the constant heating time accessory on the headspace sampler and each sample vial was equilibrated for the same amount of time, equivalent to one GC run (nominally 30 min).

A manual SPME holder was used with a 100- $\mu\text{m}$  PDMS fibre assembly (Supelco, Mississauga, Ontario, Canada). The analysis was performed on the above system with the HS transfer line detached from the injection port. GC conditions were the same in normal HS and in HSSPME analysis, and were as follows: inlet temperature, 225°C; inlet mode, split operation with split ratio 1:10 (splitless operation in SPME); split vent flow, 60 ml/min; oven temperature, 40°C hold 5 min, rate 7.5°C/min to final temperature 200°C; column, SPB-1 30 m $\times$ 0.53 mm I.D., 1.5  $\mu\text{m}$  film, column flow, 7.5 ml/min nominal; linear velocity, 40 cm/s at 100°C. An open-split interface was used to limit the flow to MS system to 0.7 ml/min. The MS system was operated in selected ion monitoring (SIM) mode using single-step acquisition monitoring ions. The ions monitored included  $m/z$  77 and 78 for benzene; 91 for toluene, ethylbenzene, *p*-xylene, propylbenzene and butylbenzene; 92 for toluene; 106 for ethylbenzene and *p*-xylene; 120 for propylbenzene; 134 for butylbenzene and 128 for naphthalene. The ions used for quantification were 78 for benzene, 91 for toluene, ethylbenzene, *p*-xylene, propylbenzene and butylbenzene, and 128 for naphthalene. The temperature of the source was 180°C, the autotune feature was selected, and the electron multiplier was set at a nominal value of 1400 V.

For the screening of tire fire water samples another GC–MS system similar to the one above was employed with a DB-5 GC column (30 m $\times$ 0.25 mm I.D., 0.25  $\mu\text{m}$  film). The MS system was operated in TIC mode scanning a mass range from  $m/z$  40 to 400. Both systems were controlled by a HPChem station (DOS series).

## 2.2. Reagents and chemicals

A multicomponent VOC standard was prepared from a Supelco hydrocarbon mixture D3710 with the addition of benzene, ethylbenzene and naphthalene to give a nominal concentration of 80 mg/ml. The target compounds for this study were benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, propylbenzene, butylbenzene and naphthalene. This stock solution was diluted in methanol 100-times to an intermediate stock solution. Appropriate amounts of the intermediate standard were added to water to

give final concentrations in the ng/ml level for SPME optimisation studies.

All the solvents (analytical grade) were purchased from Caledon (Belleville, Canada).

In this work, two oil samples were used: Alberta Sweet Mix Blend (ASMB) and diesel. The WAF samples were generated by simply mixing 1 g of oil with tap water in a 5-l glass bottle with a draw-off tap at the bottom. The low degree of mixing and a long equilibration time (several months) was assumed to generate samples containing only water-soluble species.

The tire fire water samples were from Saint Amiable, Quebec, Canada (1991).

## 2.3. Sampling procedure

HS sampling was performed as follows: 10 ml of water contaminated with VOCs were added into a headspace vial in 22 ml and then the vial was placed in the HS bath at 95°C for 30 min before analysis.

For SPME analysis an aliquot of 10 ml of contaminated water was added in a 22-ml vial. After placing a 0.8-cm long stir bar in each vial, it was sealed with a headspace cap with a PTFE-faced septum. SPME equilibration was either by immersing the fibre in the water or in the headspace at room temperature. The sampling time was 20 min with constant stirring to speed up phase equilibrium. Once sampling was complete, the fibre was immediately inserted into the GC injector for desorption. A desorption time of 3 min at 260°C was enough for a quantitative desorption of all the analytes studied and reinserting the fibre after the run did not show any carry over. Equilibration for the target VOCs occurred within 10 min, for consistency and to allow for different matrix effects, we worked with a sampling time of 20 min.

For the air monitoring experiments the samples were generated in an 80-l size tedlar bag filled with lab grade air. Known amounts of gasoline were injected via the sampling port and the bag was kneaded to evaporate the chemicals. A Gillian personal sampler pump HFS 513A was used to draw air samples through a 600-mg charcoal tube at 2 l/min for 10 min. Adsorbed VOCs were extracted using 2 ml of carbon disulphide. For SPME air monitoring, the fibre was inserted through the septum of an inlet

port in the tedlar bag and exposed to the sample for 20 min. Analyses were carried out on the same GC–MS system used for HS analysis.

### 3. Results and discussion

#### 3.1. Comparison between SPME and HSSPME

Two sample techniques were investigated. One involved immersing the 100- $\mu$ m PDMS-coated fibre in the aqueous phase (SPME) and, in the other, the fibre was suspended in the headspace above the water (HSSPME). The analyte concentration and the water sample size were the same in both cases. Results obtained are summarised in Fig. 1. Both techniques gave identical results for most of the compounds except for propylbenzene and butylbenzene. In HSSPME, propylbenzene showed a 25% and butylbenzene, a 200% increase in response over immersion. Sampling the headspace presents also a significant advantage in terms of selectivity because only volatiles and semivolatiles are released into the headspace. Since the fibre is not in contact with the sample, background adsorption and matrix effect are reduced, which also enhances the life expectancy of SPME fibre. All subsequent experiments were there-

fore performed with the fibre suspended in the headspace above the water (HSSPME).

#### 3.2. Effect of the addition of salt and effect of the temperature

The effect of the addition of salt to the water samples was studied. For this study, water samples were saturated with KCl before extraction. The responses obtained were similar to the ones obtained without the addition of KCl; the addition of salts did not produce any change in the response obtained in HSSPME. This is consistent with what we have reported in the case of normal HS analysis of water samples [19].

Since the first step of HSSPME involves the partitioning of VOCs from the aqueous layer to the headspace, an increase in temperature could enhance the final concentration of VOCs in the PDMS fibre. We conducted a series of experiments in which the equilibrium temperature was 60°C. No increase in the signal was observed. This is explained by the exothermic adsorption process by which the VOCs are partitioned between the headspace and the PDMS coating. A higher temperature increases the concentration of VOCs in the headspace by decreases the partition coefficient between the PDMS coating

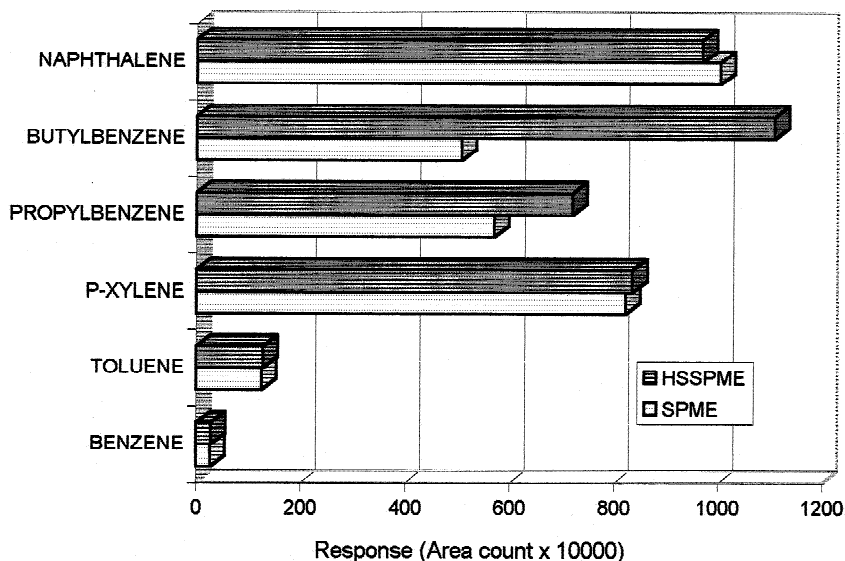


Fig. 1. Comparison between the responses obtained by SPME and HSSPME.

and the headspace. As a result of this, we found that the total amount of VOCs adsorbed into the fibre was the same at room temperature (20°C) and at 60°C.

### 3.3. Linearity, precision and sensitivity study

To evaluate the linearity of the HSSPME method a calibration study was performed by diluting the aromatic stock mixture in MeOH and using aliquots of 10 µl to spike 10 ml of water to give five concentration levels covering the range of 1 to 1000 ng/ml. At each concentration level, at least triplicate analyses were made. All the compounds studied were characterised by regression coefficients better than 0.999.

The precision of the HSSPME method was evaluated at two different concentration levels (1 and 1000 ng/ml) and was found to give a relative standard deviation (R.S.D.) between 6 to 15% for the low level and better than 3% for the high level (Table 1). The number of replicates was five.

The detection and quantification limits (signal-to-noise ratio of 3 and 10, respectively) were also determinate and are summarised in Table 1. Detection and quantification limits for all the target VOCs were in the ng/l level.

### 3.4. Analysis of WAF samples. Comparison with conventional HS

To eliminate the possibility of matrix effects, HSSPME studies were carried out by adding to the WAF samples different amounts of analytes to increase the water concentration in 10 and 100 ng/ml. After resting to the responses obtained the ones corresponding to the samples without addition, the

results agreed well with the same spiked levels in Milli-Q water, thus confirming no matrix effects were observed.

The WAF samples generated from two different oils, ASMB and diesel, were analysed by conventional HS and HSSPME. The concentrations of VOCs found by both techniques were in good agreement (Table 2). Also HSSPME showed better precision (Table 2). Fig. 2 shows the ion chromatogram 91 obtained by HS (a) and by HSSPME (b) for ASMB oil WAF sample. The sensitivity of the HSSPME method was in general much better than the sensitivity of the HS method (see Table 3). The responses obtained by HSSPME showed an enhancement by a factor of 1.8 to 22, and for butylbenzene the increase was even more significant (about 40 times). The only exception was benzene, which was less sensitive and the response obtained by HSSPME was about 50% of the response obtained by HS.

### 3.5. Comparison with LLE for the screening of water samples from a tire fire incident

Four water run-off samples collected from a tire fire incident were used for this comparison. They all had a heavy oily layer from the high temperature distillate of burning tires. Fifty ml of the water layer were extracted with 10 ml of hexane and an aliquot was injected onto a GC-MS system to determine the profile of organics in the water. The resulting library search of the major peaks indicated the presence of a wide range of aromatic compounds, predominantly alkylated benzenes and heterocyclics such as pyridines, benzonitriles and benzothiazoles. For HSSPME analysis, 1 ml of the water layer was diluted to 10 ml with Milli-Q water in a 22-ml vial.

Table 1  
Precision at two different concentration levels and detection and quantification limits of the HSSPME procedure

	Precision (R.S.D., %)		Detection limit (ng/l)	Quantification limit (ng/l)
	1 ng/ml	1000 ng/ml		
Benzene	15.2	0.3	273.9	913.0
Toluene	13.3	0.7	47.5	158.2
Ethylbenzene	9.7	0.7	10.7	35.5
<i>p</i> -Xylene	10.8	0.6	13.9	46.4
Propylbenzene	10.6	1.8	3.0	10.0
Butylbenzene	12.0	0.8	1.3	4.3
Naphthalene	5.6	0.5	7.8	26.0

Table 2

Mean concentration of VOCs found in the ASMB oil and diesel WAF samples using HSSPME and conventional HS

	ASMB oil WAF sample				Diesel WAF sample			
	HSSPME		HS		HSSPME		HS	
	Mean (ng/ml)	R.S.D. (%)	Mean (ng/ml)	R.S.D. (%)	Mean (ng/ml)	R.S.D. (%)	Mean (ng/ml)	R.S.D. (%)
Benzene	147.5	4.9	145.5	4.6	<0.3		<0.1 <sup>a</sup>	
Toluene	28.5	1.8	30.2	4.9	69.0	4.1	60.0	6.6
Ethylbenzene	121.2	0.8	141.2	4.4	32.0	3.5	25.6	4.9
<i>p</i> -Xylene	7.7	2.7	7.9	4.9	169.0	1.3	153.8	4.4
Propylbenzene	2.6	6.9	2.6	6.6	26.3	3.2	19.6	7.4
Butylbenzene	126.3	2.6	122.3	9.7	19.1	5.6	12.5	6.2
Naphthalene	9.7	2.2	8.8	8.5	24.9	3.0	17.5	9.7

The number of replicates was three.

<sup>a</sup> Approximated detection limit.

After closing the vial, the fibre was exposed to the headspace over the sample for 30 min before injection into the GC system. The resulting library search found in general the same chemical composition than for the LLE extract. As can be seen in

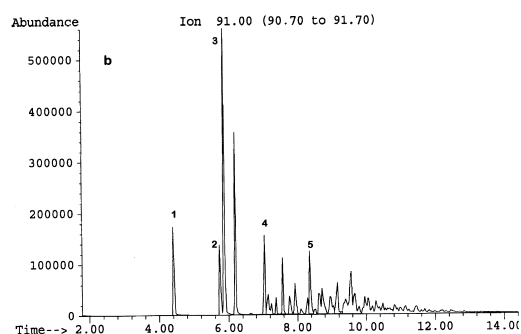
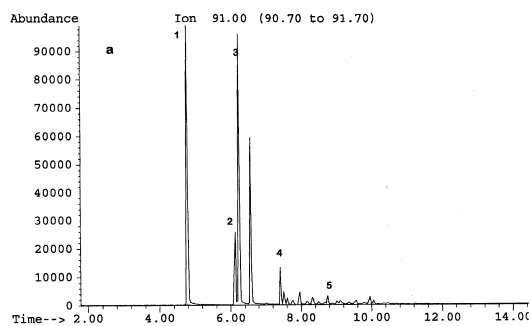


Fig. 2. Ion chromatogram 91 of the ASMB oil WAF sample by HS (a) and HSSPME (b). Peaks: 1=toluene, 2=ethylbenzene, 3=*p*-xylene, 4=propylbenzene, 5=butylbenzene.

Fig. 3, both chromatograms shown similar profile. Table 4 shows tentative peak identification by MS library searches. The responses for each compound are given in area counts. The area threshold was set in 10 000 counts. The majority of chemicals found by LLE and HSSPME were identical as shown in Table 4. This table also shows the ratio of responses. For some compounds the HSSPME response was lower than the LLE response, but for LLE the sample was concentrated five times (50 ml of water extracted with 10 ml of hexane) and for HSSPME the sample was diluted 10 times before sampling. The HSSPME technique showed different sensitivity depending on the compounds. This is mainly due to the different affinity of the analytes for the PDMS fibre. The sensitivity of the HSSPME technique was especially high for naphthalenes. The concentration of naphthalene and alkylnaphthalenes in the hexane extract was not high enough to show the presence of these compounds in the sample but these compounds could be identified by HSSPME.

Table 3

Comparison between the responses obtained by HS and HSSPME

	Ratio of responses (HSSPME/HS)
Benzene	0.5
Toluene	1.8
Ethylbenzene	5.2
<i>p</i> -Xylene	5.8
Propylbenzene	12.5
Butylbenzene	39.7
Naphthalene	22.0

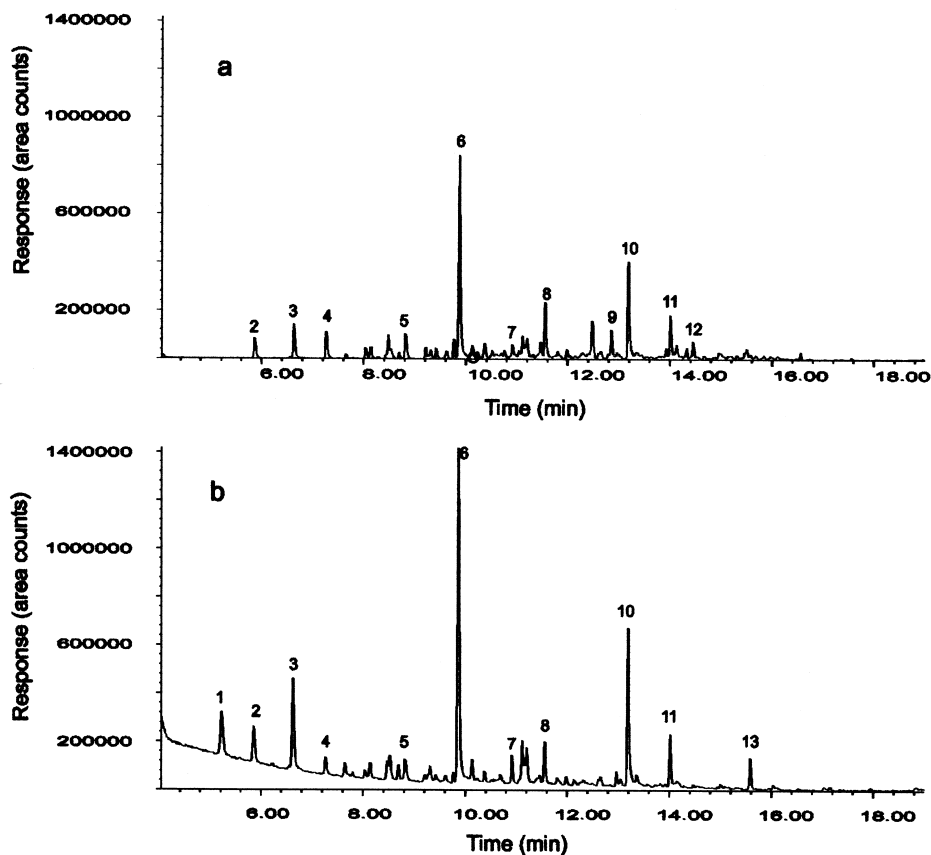


Fig. 3. Total ion chromatogram (TIC) of a tire fire water sample obtained by HSSPME (a) and LLE (b). Peaks: 1=2-buten-1-ol, 2=methyl isobutyl ketone, 3=cyclopentanone, 4=2-methylpyridine, 5=2,6-dimethylpyridine, 6=benzonitrile, 7=3-methylphenol, 8=4-methylbenzonitrile, 9=naphthalene, 10=benzothiazole, 11=2-methylbenzothiazole, 12=1-methylnaphthalene, 13=2,4-dimethylquinoline.

### 3.6. Application to air monitoring

The applicability of SPME for the air screening of aromatic contaminants was also tested. For this purpose, an 80-l tedlar bag filled with air was spiked with 2  $\mu$ l of gasoline. The SPME fibre was inserted through the septum of an inlet port and exposed for 20 min. Another identical air sample was prepared and a 10-min sampling was then carried out using a personal pump drawing air through a charcoal tube at 2 l/min. The charcoal was later desorbed with 2 ml of carbon disulphide and 1  $\mu$ l of the extract was analysed on a GC-MS system. Results are summarised in Table 5. The area threshold was set in 1000 counts. In comparison to a direct injection of a diluted gasoline sample (1:1000 in carbon disulphide), SPME did detect a broad

spectrum of VOCs ranging from toluene to the light PAHs. On the other hand, the mid-range substituted benzenes and light two-ring PAHs could not be detected with the sorbent tube method.

## 4. Conclusions

HSSPME at room temperature (20°C) was successfully applied to the analysis of dissolved VOCs in artificially spiked water as well as actual WAF samples from different oils. The HSSPME method has good linearity in a wide range of concentrations and also good precision. Detection limits in the sub-ng/ml level were obtained. Comparison between HSSPME at room temperature and conventional HS analysis at high temperature (95°C) showed good

Table 4

Tentative identification of the most abundant compounds found in the tire fire water sample using LLE and HSSPME

	Response (area count×10 000)		Ratio of responses HSSPME/LLE
	LLE	HSSPME	
2-Buten-1-ol	70	<1	
Methyl isobutyl ketone	53	27	0.5
Cyclopentanone	123	42	0.3
2-Methylpyridine	17	29	1.7
3-Methylpyridine	8	11	1.3
Hexanenitrile	14	13	0.9
2,6-Dimethylpyridine	15	35	2.3
2-Methyl-2-cyclopenten-1-one	15	6	0.4
2-Ethylcyclopentenone	20	8	0.4
Isoquinoline	17	5	0.3
2-Ethyl-6-methylpyridine	7	15	2.1
1,2-Benzenedicarbonitrile	13	10	0.8
Naphthalene	<1	22	
Benzonitrile	364	200	0.5
2,3,6-Trimethylpyridine	8	16	1.9
3-Methylphenol	22	14	0.6
Acetophenone	46	19	0.4
2,6-Diethylpyridine	25	12	0.5
4-Methylbenzonitrile	39	51	1.3
2-Ethyl-1,4-dimethylbenzene	15	11	0.7
Benzothiazole	158	95	0.6
2-Methylbenzothiazole	50	39	0.8
1-Methylnaphthalene	<1	15	
2-Methylnaphthalene	<1	9	
2,4-Dimethylquinoline	29	3	0.1
1,7-Dimethylnaphthalene	<1	12	

agreement between the two techniques but HSSPME exhibited better precision and offered a dramatic sensitivity enhancement. HSSPME was also applied to the screening of water samples from a tire fire

incident and compared to LLE. Both techniques offered similar sample profile with the exception of the alkylated naphthalenes that were only detected by the HSSPME method. Air monitoring using SPME

Table 5

Air monitoring using SPME and charcoal sorbent tubes

	Gasoline dil 1/1000	Air sampling	
		SPME	Sorbent tube
Ethylbenzene	58 167	3838	11 797
<i>p</i> + <i>m</i> -Xylene	175 705	13 130	34 712
<i>o</i> -Xylene	72 399	6391	11 683
1-Methyl-3-ethylbenzene	33 030	5373	4358
1,2,4-Trimethylbenzene	10 206	2787	<1000
1,2,3-Trimethylbenzene	12 619	4743	<1000
Naphthalene	27 958	26 236	<1000
2-Methylnaphthalene	14 521	34 238	<1000
1-Methylnaphthalene	6670	19 993	<1000

The responses are given in area counts.



pointed to a very sensitive technique, which was far simpler to use when compared with traditional solid sorbent techniques.

### Acknowledgements

The authors wish to thank Mike Goldthrope for his assistance in setting up the equipment in the air monitoring studies. One of the authors (M.L.) is indebted to Xunta de Galicia for a postdoctoral grant and to Environment Canada for its hospitality during the course of this work.

### References

- [1] C.L. Arthur, J. Pawliszyn, *Anal. Chem.* 62 (1990) 2145–2148.
- [2] C.L. Arthur, L.M. Killan, S. Motlagh, M. Lim, D.W. Potter, J. Pawliszyn, *Environ. Sci. Technol.* 26 (1992) 979–983.
- [3] A.A. Boyd-Boland, M. Chai, Y.Z. Luo, Z. Zhang, M.J. Yang, J. Pawliszyn, T. Gorecki, *Environ. Sci. Technol.* 28 (1994) 569A–574A.
- [4] Z. Zhang, M.J. Yang, J. Pawliszyn, *Anal. Chem.* 66 (1994) 844A–853A.
- [5] M. Chai, J. Pawliszyn, *J. Environ. Sci. Technol.* 29 (1995) 693–701.
- [6] Z. Zhang, J. Pawliszyn, *J. High Resolut. Chromatogr.* 16 (1993) 689–692.
- [7] J.B. Czerwinsky, B. Zygmunt, J. Namiesnik, *Fresenius J. Anal. Chem.* 356 (1996) 80–83.
- [8] K.D. Buchholz, J. Pawliszyn, *Anal. Chem.* 66 (1994) 160–167.
- [9] A.A. Boyd-Boland, S. Magdic, J. Pawliszyn, *Analyst* 121 (1996) 929–938.
- [10] H. Lakso, W.F. Ng, *Anal. Chem.* 69 (1997) 1866–1872.
- [11] T.K. Choudhury, K.O. Gerhardt, T.P. Mawhinney, *Environ. Sci. Technol.* 30 (1996) 3259–3265.
- [12] B.L. Wittkamp, S.B. Hawthorne, D.C. Tilotta, *Anal. Chem.* 69 (1997) 1204–1210.
- [13] J. Poerschmann, Z. Zhang, F.-D. Kopinke, J. Pawliszyn, *Anal. Chem.* 69 (1997) 597–600.
- [14] F.J. Santos, M.T. Galceran, D. Fraisse, *J. Chromatogr. A* 742 (1996) 181–189.
- [15] D.W. Potter, J. Pawliszyn, *Environ. Sci. Technol.* 28 (1994) 298–305.
- [16] M. Llompарт, K. Li, M. Fingas, *Anal. Chem.* (1998) in press.
- [17] M. Chai, C.L. Arthur, J. Pawliszyn, *Analyst* 118 (1993) 1501–1505.
- [18] R. Young, V. Lopez-Avila, *J. High Resolut. Chromatogr.* 19 (1996) 247–256.
- [19] K. Li, M.F. Fingas, P. Boileau, S. Blenkinsopp, J.R.J. Pare, J. Belanger, M. Llompарт, *Proceedings of the 19th Arctic and Marine Oilspill Program (AMOP) Technical Seminar, Environment Canada, Calgary, Vol. 1, 1996, pp. 89–111.*