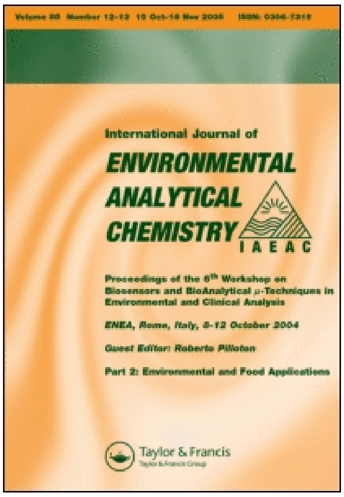

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Simultaneous analysis of 23 priority volatile compounds in water by solid-phase microextraction-gas chromatography-mass spectrometry and estimation of the method's uncertainty

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Simultaneous analysis of 23 priority volatile compounds in water by solid-phase microextraction–gas chromatography–mass spectrometry and estimation of the method's uncertainty

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Most water contaminations with volatile organic compounds (VOCs) are traceable to leaking underground fuel reservoirs, solvent storage vessels, agricultural practices, industrial residues, and deficient wastewater treatment and disposal. In order to perform effective monitoring of such organic micropollutants in a straightforward manner, a multiresidue method for the determination of 23 VOCs (trihalomethanes (THMs), BTEX and chlorinated solvents) in water has been developed using solid-phase microextraction (SPME) and capillary gas chromatography–mass spectrometry (GC–MS). This group includes also methyl-*tert*-butyl ether, epichlorhydrine, and vinyl chloride which present additional analytical difficulties. Three different fibres were assayed: 7-µm polydimethylsiloxane (PDMS), 100-µm PDMS, and 75-µm Carboxen-PDMS, and the extraction conditions were optimized. The best results for the majority of the analytes and mainly for those with the lowest signals were obtained using the Carboxen-PDMS fibre after 15 min of extraction in the headspace mode at a room temperature of $20 \pm 2°C$. The analytical sensitivity, linearity, precision, accuracy, and uncertainties have been studied for method validation in agreement with the international standard ISO/IEC 17025:2005. The limits of detection achieved with the proposed method (0.06–$0.17\,\mu g\,L^{-1}$) are adequate to determine the VOCs at the restrictive levels established by the European legislation. This was a decisive achievement to enable the analysis of all VOCs listed under the drinking-water directive in a single assay. The method exhibits performance capabilities suitable for routine analysis of VOCs in drinking-water by quality-control laboratories as enforced by EU Directives. The method is currently being used for this purpose, and participation in proficiency tests was assessed, with encouraging results.

Keywords: SPME; Water; VOCs; Epichlorydrine; Vinyl chloride; MTBE; GC-MS; Uncertainty

1. Introduction

Many volatile organic compounds (VOCs) are man-made chemicals mainly used as industrial solvents and cleaning agents, and in the manufacture of paints,

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pharmaceuticals, and refrigerants. They are also employed as fuel oxygenates (e.g. methyl-*tert*-butyl ether (MTBE)) and can be formed during drinking-water disinfection (e.g. chloroform, bromoform, dibromochloromethane, and dichlorobromomethane, so-called trihalomethanes (THMs)). VOCs are also components of petroleum fuels (benzene, toluene, ethylbenzene, and xylenes (BTEX)) [1].

THMs are widely present in most chlorinated drinking-water systems. Toxicological studies on animal models have shown that some of them have a potential for teratogenesis or carcinogenesis in humans. Epichlorhydrine is a raw material used in the production of epoxy resins, synthetic glycerol, and elastomers, and is also applied in article and pharmaceutical industries [2, 3]. In addition, it is widely employed as a composite in drinking-water pipes as well as in the synthesis of cationic polyelectrolytes, which are used in surface and wastewater clarification processes [4, 5]. Plastic materials employed in water storage and transport can also be an important source of contamination. Vinyl chloride is a water contaminant due to migration, since it is a constituent monomer of polyvinyl chloride (PVC) recognized as a human carcinogen [6]. MTBE is used in gasoline to reduce the emissions of carbon monoxide during the combustion process as well as an anti-detonator. Due to these applications, MTBE became the fuel oxygenate with the highest production volume worldwide [7]. In Europe, large amounts of MTBE ($2–3 \times 10^9$ kg) are produced each year, and its content in gasoline can comprise up to 12–14% (v/v) [8, 9]. As a result of its intense use, MTBE has become one of the most frequently detected VOCs in groundwater [10]. Even at low levels, MTBE may render drinking-water supplies undrinkable due to its offensive taste and odour.

To minimize the health risks associated with chlorine disinfection by-products, solvents, and tubing released chemicals, analytical methods are required to ensure that they do not exceed critical levels, if complete absence is not feasible. Presence of VOCs in waters intended for human consumption is regulated in the European Union by the 98/83/EC Directive that establishes the following maximum concentrations: $0.1\,\mu g\,L^{-1}$ for epichlorhydrine; $0.5\,\mu g\,L^{-1}$ for vinyl chloride; $1.0\,\mu g\,L^{-1}$ for benzene; $3.0\,\mu g\,L^{-1}$ for 1,2-dichloroethane; $10\,\mu g\,L^{-1}$ for the sum of tetrachloroethene and trichloroethene; and $100\,\mu g\,L^{-1}$ for total of THMs. These low levels and the large number of samples to be processed by the water control analytical laboratories demand the development of sensitive, fast, efficient, simple, and low-cost analytical methods [11].

Several sample-preparation techniques for the analysis of VOCs have been reported, such as liquid–liquid extraction, dynamic headspace technique (purge and trap) and solid-phase microextraction (SPME) [12, 13]. A comparison of a static headspace method with a purge-and-trap method of several chlorinated hydrocarbons showed similar results [14]. However, the purge-and-trap method is more time-consuming. A range of innovative techniques appeared in recent years, but demonstration of their applicability is still on the way. For the VOC analysis in water, high preconcentration factors are needed for trace analysis, making the applicability of the recent evolutions in DAI (direct aqueous injection) very much limited. Traditional liquid–liquid extraction (LLE) does not fit with current challenges of green analytical chemistry. There is a great tendency towards solvent microextraction, with steam distillation extraction (SDM), hydrophobic hollow fibre-liquid phase microextraction ((HF)-LPME), dispersive liquid–liquid microextraction (DLLME), single drop microextraction (SDME), and miniaturized membrane-assisted solvent extraction (MASE) being new interesting developments [15]. Solvent-free sorptive extraction techniques, such as stir bar sorptive extraction (SBSE) and solid-phase dynamic extraction (SPDE), are also receiving increased interest, as they require less operator handling and provide higher enrichment factors [15, 16].

The SPME technique developed by Pawliszyn and co-workers is an attractive technique for volatile compounds and has already found many applications in environmental analysis, since it is rapid, easily automated, and solvent-free [17]. Zhang and Pawliszyn demonstrated excellent results of SPME analysis for 28 volatile organo-halogenated compounds using headspace extraction and a 100-µm poly-dimethylsiloxane (PDMS) fibre [18]. The recently created Carboxen-PDMS fibre is recommended for the extraction of low molecular weight compounds. Popp and Paschke tested this fibre on several VOCs and obtained a significantly higher affinity compared with PDMS [19].

The present work describes the optimization and validation of an SPME–gas chromatograph–mass spectrometry system (GC–MS) method for the determination of 23 VOCs in water samples. Monitoring of many of these compounds in water is enforced by EU legislation, yet some of the substances present analytical difficulties that are not completely overcome. The challenge is to analyse in a single run compounds of different chemical families, extraction efficiency, and detector response in compliance with the disparate regulatory levels mentioned above. The newly developed Carboxen-PDMS fibre was compared with the well-established PDMS, and the method was adequately optimized and validated in order to achieve the required sensitivity, precision, and accuracy. Uncertainties of the calculated concentrations were also estimated to allow the implementation of this method in routine analysis in accordance to the international standard ISO/IEC 17025:2005 [20].

2. Experimental

2.1 *Chemical and materials*

A multicompound VOC standard mixture (EPA 524.2 VOC mixture 2000 µg mL^{-1}) was purchased from Supelco (Bellefonte, PA). Methyl-*tert*-butyl ether, vinyl chloride, and epichorhydrine were used as individual standards: MTBE and vinyl chloride were purchased from Supelco, both with a concentration of 2000 µg mL^{-1}, and epichlorhydrine was supplied by Riedel-de-Haën (Seelze, Germany). A stock standard solution of epichlorohydrine at 1 mg L^{-1} was prepared in methanol. An intermediate solution with all the compounds was prepared in water and was used in the preparation of the standards for the SPME optimization and in producing the calibration curves. This intermediate solution was prepared fresh whenever working standards were needed for the experiments, thus avoiding any errors caused by the high volatility of the compounds. Stock standard solutions were kept refrigerated at −18°C and in the darkness. SPME fibres of 100 µm PDMS, 7 µm PDMS, and 75 µm Carboxen-PDMS were supplied by Supelco.

2.2 *SPME extraction procedure*

The SPME fibres were conditioned in the injection port of the gas chromatograph according to the supplier's instructions. The SPME process was automated using a commercial auto-sampler (CombiPAL, CTC-Analytics, AG, Switzerland) equipped with a SPME unit connected to a GC–MS system. After the optimization process, which included the study of the SPME fibre coating and extraction time, the optimum conditions were established as follows: 10 mL of sample contained in a 20 mL vial were extracted at room temperature (20 ± 2°C) in the headspace for 15 min without agitation. No pH adjustment or ionic strength correction was needed to achieve the objectives of the analysis.

2.3 *Gas-chromatographic analysis*

The GC–MS system was composed of a Varian 3400 CX gas chromatograph coupled to an ion-trap mass spectrometer Varian Saturn 2000 (Varian Instruments, Sunnyvale, CA). The injection port was equipped with an insert designed for SPME and was kept at 250°C. The chromatographic separation was carried out on CP Select 624 CB (30 m × 0.25 mm i.d. × 1.4 µm film thickness). The column oven was set at 40°C for 2 min, ramped at $10^{\circ}\mathrm{C\,min^{-1}}$ up to 220°C, and held for 2 min. Helium (purity 99.9999%) was used as the carrier gas with a column flow rate of approximately $1.0\,\mathrm{mL\,min^{-1}}$. The MS transfer line temperature was kept at 170°C, and the ion source was kept at 150°C. The solvent delay time was set at 2 min. In order to improve the multiresidue characteristics of the method, MS using full scan acquisition mode (m/z 15–300) under electronic impact ionization (EI) was selected. The extracted ion chromatograms were used for quantification purposes using the peak area of each characteristic fragment (as given in table 1) at the respective analyte retention time.

Table 1. Characteristic ion of each individual compound used for quantification purposes and respective retention times.

Retention time (min)	Compound	Characteristic ion (m/z)
2.080	Vinyl chloride	62
3.814	Dichloromethane	49
4.106	MTBE	73
4.138	1,2-(*E*)-Dichloroethylene	61
4.578	1,1-Dichloroethene	63
5.243	1,2-(*Z*)-dichloroethylene	61
5.519	Bromochloromethane	49
5.583	Chloroform	83
6.241	Benzene	78
6.290	1,2-Dichloroethane	62
7.028	Trichloroethylene	130
7.320	1,2-Dichloropropane	76
7.704	Bromodichloromethane	83
8.133	Epichlorhydrine	57
8.658	Toluene	91
9.405	Tetrachloroethylene	166
9.746	Dibromochloromethane	129
9.945	1,2-Dibromomethane	107
10.629	Chlorobenzene	112
10.762	Ethylbenzene	91
10.942	*o*-Xylene	91
11.542	$m+p$-Xylene	91
11.827	Bromoform	173

3. Results and discussion

3.1 *Extraction optimization*

Three types of SPME fibres—7 µm PDMS, 100 µm PDMS, and 75 µm Carboxen-PDMS—were tested for the highest extraction efficiency. As illustrated in figure 1, the Carboxen-PDMS fibre achieved the best results for all the studied compounds. This fibre is as much as 43 times more efficient extracting bromochloromethane than the PDMS counterpart. It also adsorbs 1,2-(*E*)-dichloroethylene, 1,1-dichloroethene, and 1,2-dichloroethane about 20-fold more efficiently, but on average this fibre allows a ninefold improvement compared with 100-µm PDMS.

The Carboxen-PDMS fibre also has several advantages in terms of the number of compounds that can be analysed, since, at this intermediate optimization step, only vinyl chloride cannot be measured. The data presented clearly document the excellent extraction capabilities of the Carboxen-PDMS fibre for volatile compounds, so it was used in further optimization of the extraction time. Extractions periods between 5 and 20 min were tested, and the results obtained for each individual compound are displayed in figure 2. While for certain VOCs, a 15-min extraction is sufficient to obtain the maximum response, others require about 20 min. As can be seen in figure 3, a compromise was obtained with 15 min, since it allows high recoveries and at the same time improves the productivity of the method to about three samples per hour (including 5 min of fibre desorption in the GC injector). Figure 3 clearly documents that 15 min affords a considerable improvement in the extraction efficiency relative to 10 min (+14%), while 20 min adds only 2% extraction efficiency to the previous condition.

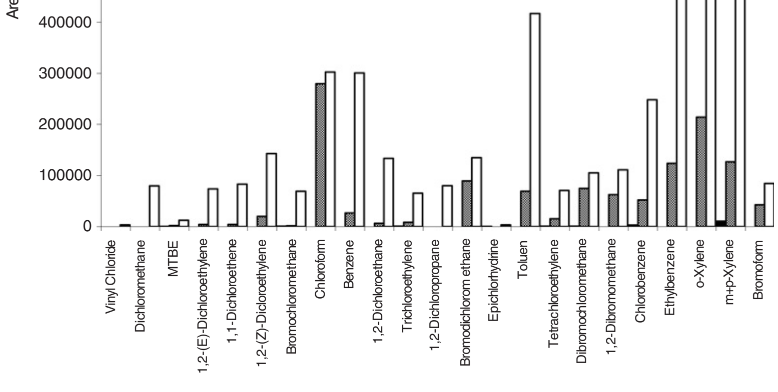

Figure 1. Comparative performance of the different tested SPME fibres using a VOCs standard solution at 1 µg L^{-1}.

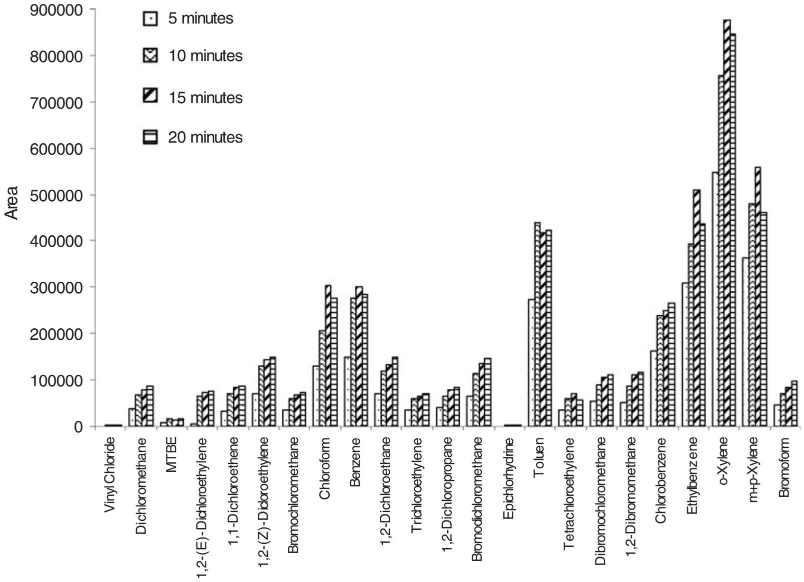

Figure 2. Influence of different extraction times in the analytical signal after SPME of an aqueous standard solution containing 1.0 μg L^{-1}.

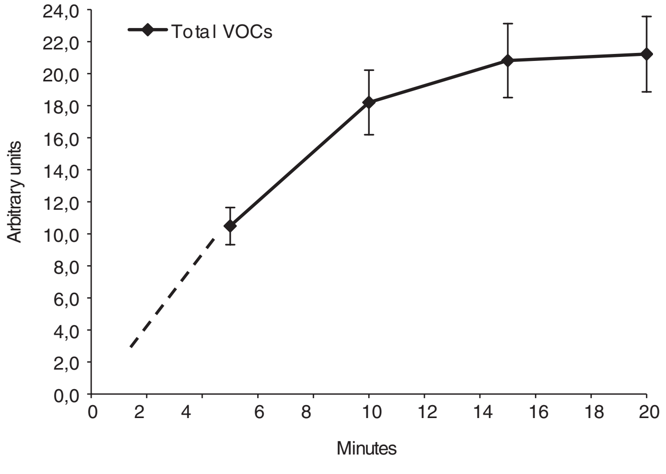

Figure 3. Extraction time profile of the selected volatile compounds represented as the sum of normalized areas at different extraction periods: 5, 10, 15, and 20 min. The error bars represent an overall precision of 11.1% (average intermediate precision).

The effect of different temperatures and the influence of the ionic strength of the sample on the SPME procedure were not studied, since, with the conditions described above, the method entirely fulfils the requirements of the current regulation. Besides, some authors have stated that such parameters are less important when extracting in the headspace conversely to direct immersion, since the volatilization of highly volatile compounds from water is a rather critical step in headspace analysis, more dependent on the adsorption from the gaseous phase [17].

3.2 *Method validation in agreement with the international norm ISO/IEC 17025:2005*

According to the ISO/IEC 17025:2005 standard [20], the method validation should include the confirmation through examination and objective evidence that the method is fit for the intended purpose. The validation parameters depend on the analytical task and the scope of the method. An adequate schedule and plan of revalidation should be established to check the stability of method performance once first validated. The validation process should include the legal requirements and the determination of the critical characteristics of the method, which have a notable impact on the quality of results. Therefore, the validation process is always a compromise between costs, risks, and available technical facilities [20].

3.2.1 Linearity and working range. For quantitative application of the SPME methodology, calibration curves in the range of 0.25–5 $\mu g\,L^{-1}$ were constructed based on seven concentration levels (0.25, 0.50, 0.75, 1.0, 1.5, 2.5, and 5.0 $\mu g\,L^{-1}$). Each point of the curve can be tested on its linearity, calculating their individual response/concentration ratios, also known as the normalized heights test. This ratio for each calibration point should not differ by more than ±25% from the average of all points response/concentration ratio. Only one of the six calibration points may not satisfy this criterion [21]. All calibrations have complied with the above requisites. Furthermore, we also present in table 2 the obtained determination coefficients (r^2) for all compounds. However, it should be kept in mind that the interpretation of the latter must be cautious, since it is well known that the correlation coefficient is not necessarily a good indicator of linearity. Alternatively, the ISO 8466/1 [22] recommends a linearity check based on a comparative test between the linear calibration function (ISO 8466/1) and the non-linear calibration function (ISO 8466/2) [23] for the same raw data. The residual standard deviations from both functions (S_{y1} and S_{y2}) are compared using the following equation to give a measure of the difference of variances (DS^2):

$$\mathrm{DS}^2 = (N-2) \times S_{y1}^2 - (N-3) \times S_{y2}^2.$$

The value of PG is then calculated and compared with the F value from the Snedecor/Fisher distribution for a given confidence level (95% was used):

$$\mathrm{PG} = \frac{DS^2}{S_{y2}^2}.$$

Comparing these two values, it is possible to make conclusions about the calibration linearity. As can be seen in table 2, the PG value for all compounds was below the critical F value, and so all calibrations follow a linear regression estimated through the least-squares method. All the tests performed indicate that the calibration linearity was acceptable in all cases, and so the working range has been established between the lower and upper standards used for calibration (0.25–5.0 $\mu g\,L^{-1}$). It should be noted that concentrations above 5.0 $\mu g\,L^{-1}$, namely for THMs, are quantified in treated water samples using a separate calibration in the range of 5.0–100 $\mu g\,L^{-1}$.

Table 2. Analytical figures of merit obtained with the proposed methodology SPME-GC-MS for the analysis of VOCs in water: detection limits, precision, and linearity.

	Theoretical value (μg L^{-1}), $n=7$		Experimental value (μg L^{-1}), $n=7$		Intermediate precision	Linearity		
Compound	LOD	LOQ	LOQ	RSD	RSD (%)	PG	*F*-critical	r^2
Vinyl chloride	0.11	0.32	0.25	11.3	9.92	0.02	10.13	0.999
Dichloromethane	0.10	0.29	0.25	9.1	11.61	0.12	10.13	0.998
MTBE	0.14	0.41	0.50	5.1	10.20	1.2	10.13	1.000
1,2-(*E*)-Dichloroethylene	0.13	0.40	0.50	13.2	12.35	0.002	10.13	0.997
1,1-Dichloroethene	0.14	0.42	0.50	11.6	10.60	0.001	10.13	0.997
1,2-(*Z*)-Dichloroethylene	0.15	0.45	0.50	10.1	11.58	0.01	10.13	0.998
Bromochloromethane	0.15	0.45	0.50	6.9	10.87	0.01	10.13	0.997
Chloroform	0.17	0.51	0.50	6.5	13.06	0.6	10.13	0.999
Benzene	0.06	0.19	0.25	8.6	11.16	10.6	10.13	1.000
1,2-Dichloroethane	0.07	0.20	0.25	5.9	10.43	0.13	10.13	1.000
Trichloroethylene	0.12	0.36	0.50	10.3	12.61	0.25	10.13	0.997
1,2-Dichloropropane	0.12	0.36	0.50	8.4	10.50	0.13	10.13	0.999
Bromodichloromethane	0.13	0.38	0.50	9.8	9.41	0.34	10.13	0.999
Epichlorhydrine	0.07	0.21	0.25	20.7	15.30	1.2	10.13	0.999
Toluene	0.14	0.42	0.50	8.6	11.26	4.91	10.13	0.995
Tetrachloroethylene	0.16	0.48	0.50	7.6	16.33	0.8	10.13	0.999
Dibromochloromethane	0.15	0.44	0.50	4.5	8.59	2.66	10.13	0.998
1,2-Dibromomethane	0.13	0.39	0.50	10.6	9.88	3.04	10.13	0.998
Chlorobenzene	0.14	0.42	0.50	9.6	9.12	0.01	10.13	0.998
Ethylbenzene	0.07	0.22	0.25	10.8	14.6	0.25	10.13	0.995
o-Xylene	0.09	0.26	0.25	5.6	8.9	0.33	10.13	0.994
$m+p$-Xylene	0.17	0.52	0.50	12.2	9.2	0.13	10.13	0.993
Bromoform	0.15	0.44	0.50	5.1	8.6	0.62	10.13	0.998

3.2.2 Limits of detection and limits of quantification.

The limits of detection (LODs) were calculated according to the following equation [24]:

$$\mathrm{LOD} = \frac{K \times \sigma_{y/x}}{b}$$

Considering X_o as Gaussian (normal distribution of the errors), the value of K is 3.3 for a confidence level of 99.74%. $\sigma_{y/x}$ is the residual standard deviation of the calibration curve and b the slope of the regression line. The limits of quantification (LOQs) were calculated using the following equation [24]:

$$\mathrm{LOQ} = \frac{10 \times \sigma_{y/x}}{b}.$$

The estimated limits based on the calibration parameters ($n=7$) are given in table 2. The experimental verification of the LOQ took into consideration that the International Union of Pure and Applied Chemistry definition [25] additionally suggests a precision <10% RSD, and so aqueous solutions of two approximate LOQ concentrations (0.25 or 0.50 μg L^{-1}) were analysed in order to verify such a criterion. The calibration parameters indeed allowed a good estimation of the detection capabilities, since the true LOQs are actually very close to the estimated value, eventually a little higher in a few cases. Furthermore, these limits allow the quantification of the selected VOCs at the required levels, for those which maximum threshold levels have been established in the Drinking-Water Directive. Only in the case of epichlorhydrine is the analysis somehow critical, but the required LOD is achieved. In the great majority of cases, the relative standard deviation (RSD) at the LOQ level is below 10%, which is in accordance with a good estimation of the LOQ.

3.2.3 Repeatability and intermediate precision. The intermediate precision and repeatability were calculated at a spiking level of $1.0\,\mu g\,L^{-1}$ for all compounds. The intermediate precision (intra-laboratory reproducibility) was calculated using a single injection of the standard in different days and different matrices during six months, whereas the repeatability was calculated using 10 different injections in the same day, also for different matrices. The intermediate precision is reported in table 2 as the relative standard deviation of the respective peak areas and includes the entire procedure of SPME–GC–MS. The precision of the proposed methodology ranges from 8.6 (bromoform) to 16.3% (tetrachloroethylene) with an average RSD of 11.1%.

3.2.4 Matrix effect/accuracy. Three different matrices (drinking-water, surface water, and industrial effluent) were used for the determination of the matrix effect. All matrices were spiked with $1.0\,\mu g\,L^{-1}$ of all VOCs and compared with the results obtained with a standard in Milli-Q water at the same concentration level. The recovery values for all compounds were between 85 and 125% in the three matrices, except tetrachloroethylene in drinking-water. On average, the recoveries were of 106% in drinking-water, 100% in industrial effluent, and 106% in surface water, which demonstrates that the method affords a high accuracy, being slightly influenced by the sample matrix. The accuracy of the proposed method was further evaluated analysing proficiency test samples supplied by Aquacheck: distributions 294, 304, and 314. As can be seen in table 3, the method produces accurate results. All z scores are satisfactory ($|z \text{ score}| < 2$) except in the case of chloroform and trichloroethylene, which scored a dubious result ($2 < |z \text{ score}| < 3$), and benzene, which scored an unsatisfactory result ($|z \text{ score}| < 3$). Each of these situations was limited to one event.

3.2.5 Overall uncertainties. The overall uncertainties for this method were calculated following the recommendations of the Eurachem/CITAC guide [26]. For the calculation of the expanded uncertainty associated with the final results, it is mandatory to previously identify and measure the sources of the individual standard uncertainties. We have considered the following major contributions: standard uncertainty associated with the interpolation of the sample reading in the calibration curve, standard uncertainty associated with the preparation of the working standards, and standard uncertainty associated with the variability/precision of the method in routine use (intermediate precision).

The standard uncertainty associated with the calculation of the sample concentration from the calibration curve is given by the following equation:

$$u(\text{calibration\_curve}) = \frac{S_y}{b} \times \sqrt{\left[\frac{1}{N} + \frac{1}{n} + \frac{(y_{\text{read}} - \bar{y})^2}{b^2 \times \sum_{i=1}^{N} (x_i - \bar{x})^2}\right]},$$

Table 3. Influence of sample matrix on extraction recoveries (matrix effect) and accuracy results obtained in three Aquacheck distributions.

	Matrix effect (% recovery) ($n = 10$)			Aquacheck interlaboratory assays					
				Dist. 294		Dist. 304		Dist. 314	
Compound	Dinking water	Industrial effluent	Surface water	Ref. value[a]	*z*-Score	Ref. value	*z*-Score	Ref. value	*z*-Score
Vinyl chloride	99.8	95	96.1						
Dichloromethane	108.8	87.6	95.4						
MTBE	101.2	101	120.2						
1,2-(*E*)-Dichloroethylene	123	95.2	110.3						
1,1-Dichloroethene	111.8	99.8	95.4						
1,2-(*Z*)-Dichloroethylene	106.9	119.2	98.2						
Bromochloromethane	89.5	90.7	106.2						
Chloroform	100.5	98.1	101.3	119	−2.8	116	1.21	36.5	−0.47
Benzene	116.5	86.3	121.2	0.68	0.59	0.77	4.21	0.37	0.13
1,2-Dichloroethane	101.3	93.9	96.2	3.03	0.89	1.02	0.84	1.2	−0.68
Trichloroethylene	126	112	120.1	11	−2.18	9.41	−0.33	3.02	0.16
1,2-Dichloropropane	100.5	96.5	118.1						
Bromodichloromethane	100.8	90.4	96.3	85.6	−0.81	91.3	−0.69	88.5	0.68
Epichlorhydrine	99.2	95.4	112.1						
Toluene	106	98	125						
Tetrachloroethylene	145.5	121.3	99.2	6.52	−1.56	9.55	−0.68	4.29	1.22
Dibromochloromethane	100.6	94.3	89.4	71.3	0.81	98.9	−0.39	91.1	0.59
1,2-Dibromomethane	109	96.7	91.2						
Chlorobenzene	110	111	111.2						
Ethylbenzene	89	96	109.4						
o-Xylene	85	118	125.2						
m+*p*-Xylene	105	115	112.4						
Bromoform	106.9	98.3	99.4	37.3	1.14	58.6	−0.47	85.3	1.16

[a] Reference values are given in $\mu g\,L^{-1}$.

where S_y is the residual standard deviation, N indicates the number of standards used in the calibration curve, n is the number of replicates, b is the slope of calibration curve $(y_{\mathrm{read}} - \bar{y})$ corresponding to the difference between the obtained signal and the average signal of all calibration standards, and finally $\sum_{i=1}^{N} (x_i - \bar{x})^2$ is the sum of the obtained concentration (given by the calibration curve) minus the average concentration ($\bar{x}$) of the standards used in the calibration curve.

The standard uncertainty associated with the preparation of the calibration standards (u(standards)) was calculated according to the following equation:

$$u(\mathrm{standards}) = \sqrt{\left[(u(C_1))^2 + (u(C_2))^2 + (u(C_3))^2 + \cdots + (u(C_i))^2\right]},$$

in which $u(C_1)$, $u(C_2)$, and $u(C_i)$ are the uncertainties associated with the individual standards used in the calibration curve. For the estimation of the standard uncertainty associated with the preparation of each calibration standard ($u(C_1)$), we have considered the following contributors: uncertainty associated with the pippeted volume of stock solution ($u(V_{\mathrm{pip}})$, uncertainty in the measured volume in the volumetric flask ($u(V_{\text{volumetric-flask}})$), and uncertainty of the stock solution ($u(C_{\text{stock\_solution}})$);

$$u(C_i) = C_i \times \sqrt{\left[\left(\frac{u(C_{\text{stock\_solution}})}{C_{\text{stock\_solution}}}\right)^2 + \left(\frac{u(V_{\text{pip}})}{V_{\text{pip}}}\right)^2 + \left(\frac{u(V_{\text{volumetric-flask}})}{V_{\text{volumetric-flask}}}\right)^2\right]}.$$

The method's intermediate precision (intra-laboratory reproducibility) was estimated using the results of an external control standard (middle range concentration value in the calibration curve, $1.0\,\mu\text{g L}^{-1}$) quantified each day the method was run. The control standard was prepared from a different stock standard solution than the calibration one, thus giving an independent measurement. The method's precision (u(Precision)) was given by the standard deviation of all control standards quantified in routine during 8 months, as follows:

$$u(\text{precision}) = \frac{S_n}{\sqrt{n}}.$$

The combined uncertainty ($u_c(C)$) was calculated in the following manner:

$$u_c(C) = \sqrt{\left[(u(\text{calibration\_curve}))^2 + (u(\text{precision}))^2 + (u(\text{standards}))^2\right]},$$

whereas the Expanded uncertainty for a confidence level of 95.45% ($K = 2$) is obtained by:

$$U(C) = K \times u_c(C).$$

The estimated values of the uncertainties ($\mu\text{g L}^{-1}$) together with the respective concentration levels (around $1.0\,\mu\text{g L}^{-1}$) at which the calculations were performed are displayed in table 4. In general, the expanded uncertainties ranged from 28 to 45%, with an average value of 37%, which are typical values found in trace-level analysis of environmental micropollutants at the 95% confidence level. Exceptions were found for 1,2-(*E*)-dichloroethylene and 1,1-dicloroethene which have a higher associated uncertainty perhaps due to the calibration fit rather than the method's precision.

The developed method has been useful for the evaluation of different pollution events in day-to-day water monitoring as well as the analysis of THMs in drinking-water. Figure 4 presents an SPME–GC–MS extracted ion chromatogram of a contaminated surface water sample.

4. Conclusions

After proper optimization, the performance of the entire analytical procedure was demonstrated to be suitable for the intended purpose, in terms of sensitivity, precision, and accuracy. Moreover, the method presented allows the analysis of all VOCs listed in the Drinking-Water Directive plus other halogenated volatile substances and the

Table 4. Estimation of the global uncertainty associated with the analysis of VOCs in water at a typical concentration around 1.0 µg L^{-1}.

Compound	Uncertainties		
	Concentration (µg L^{-1})	Combined uncertainties (µg L^{-1})	Expanded uncertainties (µg L^{-1})
Vinyl chloride	0.92	0.16	0.33
Dichloromethane	0.75	0.16	0.33
MTBE	1.03	0.17	0.34
1,2-(*E*)-Dichloroethylene	0.79	0.24	0.48
1,1-Dichloroethene	0.75	0.19	0.38
1,2-(*Z*)-Dichloroethylene	1.05	0.19	0.38
Bromochloromethane	0.96	0.20	0.40
Chloroform	1.01	0.22	0.43
Benzene	1.02	0.19	0.39
1,2-Dichloroethane	0.99	0.16	0.32
Trichloroethylene	1.08	0.19	0.38
1,2-Dichloropropane	0.99	0.19	0.39
Bromodichloromethane	1.10	0.17	0.33
Epichlorhydrine	0.89	0.20	0.40
Toluene	1.15	0.23	0.46
Tetrachloroethylene	1.21	0.17	0.34
Dibromochloromethane	1.09	0.16	0.32
1,2-Dibromomethane	1.21	0.17	0.34
Chlorobenzene	1.09	0.19	0.38
Ethylbenzene	0.95	0.17	0.34
o-Xylene	1.10	0.17	0.34
m+*p*-Xylene	0.99	0.15	0.30
Bromoform	1.02	0.18	0.36

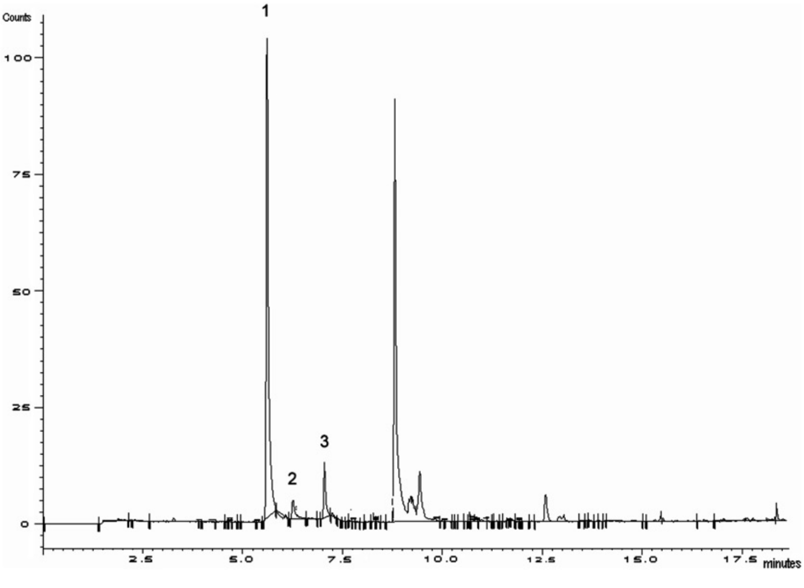

Figure 4. Extracted ion chromatogram (*m*/*z* 78, 83, and 130) representing the analysis of a contaminated surface water sample containing the following concentrations: (1) 3.0 µg L^{-1} of chloroform, (2) 0.25 µg L^{-1} of benzene, and (3) 0.62 µg L^{-1} of trichloroethylene.

BTEX group in a single run. The new Carboxen-PDMS fibre was responsible for the improved performance of the SPME technique when analysing volatile compounds in the headspace mode. The equilibration time was faster, and the amount of analyte adsorbed was higher, which allowed the analysis of typically difficult substances, such as vinyl chloride, epichlorhydrine, and MTBE. SPME is a non-polluting technique, so it does not contribute to the number of solvents found in the environment, which in fact are some of the analytes to be monitored. GC–MS improved the multiresidue features of the developed method allowing the analysis and confirmation of several chemical groups in a time-effective manner. Automated operation of the SPME–GC–MS system should be highlighted. Furthermore, the method is currently implemented in routine quality-control analysis of drinking-water according to the ISO/IEC 17025 standard to accomplish the Water Framework Directive. The results obtained in proficiency assays are highly satisfactory and demonstrate a good accuracy.

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