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# Solid-phase microextraction for the determination of iodinated trihalomethanes in drinking water

Beatriz Cancho[a], Francesc Ventura[a,*], M[a] Teresa Galceran[b]

[a]*AGBAR, Societat General d'Aigües de Barcelona S.A., Passeig de Sant Joan 39, 08009 Barcelona, Spain*
[b]*Department of Analytical Chemistry, University of Barcelona, Avda Diagonal 647, 08028 Barcelona, Spain*

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**Abstract**

A headspace solid-phase microextraction (HS-SPME) method has been developed for the determination of iodinated trihalomethanes (ITHMs) in treated water samples. Mixed THMs (bromochloroiodo-, bromodiiodo-, chlorodiiodo-, dibromoiodo- and dichloroiodo-) were previously synthesized since commercial standards are not available. HS-SPME has shorter equilibration times than direct SPME, a cleaner background and a longer fiber life. Experimental parameters such as the selection of SPME coatings, sample volume, extraction time and addition of salts were studied. The Carbowax–divinylbenzene fiber appears to be the most suitable for the determination of ITHMs. Analytical parameters such as linearity, limit of detection and precision were also evaluated. HS-SPME was compared to liquid–liquid microextraction for the analyses of spiked treated water samples, obtaining a good agreement. It is concluded that HS-SPME has a great potential for drinking water analysis. 

*Keywords:* Solid-phase microextraction; Extraction methods; Headspace analysis; Water analysis; Trihalomethanes; Halogenated compounds

## 1. Introduction

Iodinated trihalomethanes (ITHMs), identified in drinking water worldwide [1–7], are usually associated with characteristic pharmaceutical or medicinal odors and taste in drinking water. Complaints from consumers related to iodoform have been reported in France [5,8] and also in Australia [6] after chloramination of raw water. This shows that although chlorinated, brominated and mixed chlorobromoderivatives are the main disinfection by-products obtained [9,10] in water treatment plants, ITHMs are also formed when iodide (from natural sources, sea-water intrusion or brines) is present. The low odor and taste threshold concentrations of iodoform (0.02 and 5 μg/l, respectively [6,7]) could explain how ITHMs at concentrations between 0.02–10 μg/l are able to cause medicinal taste and odor problems in drinking water.

The six possible ITHMs have been qualitatively identified using different extraction techniques [5–8,11–13]. However, the lack of ITHM reference standards has hampered their accurate quantitative determination. In a recent study [14], we compared different analytical methods to quantify these compounds, and liquid–liquid microextraction (LLE) with *tert.*-butyl methyl ether (MtBE) was the only

*Corresponding author. Fax: +34-93-342-3666.
*E-mail address:* fventura@agbar.es (F. Ventura)

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extraction technique with recoveries near to 100% at the range of the concentrations studied (0.5 to 10 μg/l).

In recent years solid-phase microextraction (SPME), the extraction technique developed by Pawliszyn and co-workers [15–18] has become popular for the analysis of organic compounds from water samples because it combines sampling and preconcentration in one step. It requires no solvents or complicated apparatus and provides good results over a wide range of analyte concentrations. Analysis of the extracts is performed using gas chromatography (GC); GC–mass spectrometry (MS) or even high-performance liquid chromatography (HPLC) [19–21]. SPME coupled with GC has been applied to the analysis of organic compounds in water such as herbicides [21], volatile organic compounds (VOCs) including chlorinated hydrocarbons [18–24], pesticides [25,26], organometallic compounds [27,28], phenols [29,30], polycyclic aromatic hydrocarbons [31–33], polychlorinated biphenyls [31] and substituted benzene compounds [34,35].

SPME has been applied for the analysis of iodinated by-products generated by using iodine to disinfect recycled water on long-duration manned space missions [36]. Nevertheless only iodo-, chloroiodo- and diiodomethane have been determined. Here, we have studied a headspace (HS) SPME method for the determination of ITHMs in drinking water. Four fibers were considered, and parameters affecting the adsorption of ITHMs onto the fiber (headspace volume, salt addition and sampling time) and the desorption process (time and temperature of GC injector) were evaluated. Once the most appropriate fiber was chosen, linear range, detection limits and precision were examined. HS-SPME was compared with LLE (the best technique to determine ITHMs accurately [14]) in spiked drinking water samples. There was reasonable agreement between results obtained with HS-SPME and LLE. In addition, HS-SPME did not require the use of solvents or concentration steps, and was thus faster than LLE.

## 2. Experimental

### 2.1. Chemicals and materials

Bromochloroiodo- (86%), bromodiodo- (84.5%), chlorodiodo- (94%), dibromoiodo- (92%) and dichloroiodomethane (100%) were synthesized as described elsewhere [14]. Iodoform was purchased from Sigma–Aldrich (USA). The chemical reagent 1,2-dibromopropane used as an internal standard and L-ascorbic acid used as a quenching agent for chlorine were purchased from Sigma–Aldrich. Other reagents used were methanol purge-and-trap grade from Sigma–Aldrich; MtBE Suprasolv grade from Merck (Germany), sodium sulfate ACS-ISO for analysis and sodium chloride ACS-ISO for analysis from Carlo Erba (Italy). Ultrapure water was from a Milli-Q water purification system (Millipore, USA).

For the extraction, water samples were placed in 40-ml EPA vials (Wheaton, USA) equipped with stir bars and sealed with PTFE-faced silicone septa.

### 2.2. Standard solutions

ITHMs decompose in certain organic solvents (i.e., acetone, *n*-pentane). The use of methanol, darkness and freezer storage (at −18 to −20°C) and oxygen elimination was required.

Stock standard solutions were prepared in methanol by weighing approximately 0.1 g of analyte into a 10-ml volumetric flask and diluting to volume. A secondary standard solution was prepared by dilution in methanol of the primary standard to give concentrations of 10 mg/l. When ITHMs were injected directly into the column, the last dilution was made using MtBE as solvent. Ultrapure water solutions were prepared by spiking with different amounts of the secondary standard and used for recovery studies and calibration.

### 2.3. Procedure

#### 2.3.1. HS-SPME

In this study four types of fibers, 7-μm poly(dimethylsiloxane) (7-PDMS), 100-μm poly(dimethylsiloxane) (100-PDMS), 75-μm Carboxen–poly(dimethylsiloxane) (CAR–PDMS) and 65-μm Carbowax–divinylbenzene (CWX–DVB) were used. The commercially available SPME device and fibers were purchased from Supelco (Bellefonte, PA, USA). Fibres were initially conditioned at 320°C for 7-μm PDMS for 5 h; at 250°C for 100-μm PDMS (3 h); at 280°C for 75-μm CAR–PDMS (2 h) and at 250°C for 65-μm CWX–DVB (1 h), according to the

manufacter's instructions in order to remove contaminants and to stabilize the phase. Conditioning was carried out in an extra split/splitless port (split open) with helium carrier gas prior to each extraction. This procedure avoids the passive extraction of analytes from ambient air.

For HS-SPME, water samples (30 ml) were placed in a 40-ml glass sample vial. To each sample, 1,2-dibromopropane as an internal standard (2 μl of a methanolic solution of 30 mg/l) and 7.5 g of sodium chloride was added. The vial was sealed with a PTFE-faced septum cap. The SPME fiber was exposed to the headspace. The sample was agitated with a magnetic stirring bar at 1100 rpm at room temperature (22°C) during the extraction process to allow the equilibration of analytes between the aqueous phase and the headspace and immediately inserted into the GC injector port for thermal desorption of the extracted analytes.

#### 2.3.2. LLE

Water samples (35 ml) were placed in 40-ml EPA glass vials (Wheaton). To each sample, 1,2-dibromopropane as a surrogate standard (5 μl of a methanolic solution of 70 mg/l), 10 g of anhydrous sodium sulfate and 2 ml of glass-double distilled MtBE were added. The vials were then sealed with PTFE septa, shaken for 2 min, placed upright and left to stand for 3 min. Five hundred μl of the organic layer was transferred into a 2-ml vial containing bromochloromethane as an internal standard (5 μl of a methanolic solution of 10 mg/l).

### 2.4. Instruments

#### 2.4.1. HS-SPME

GC was carried out with a Fisons 8130 gas chromatograph equipped with an electron-capture detection (ECD) system. A DB-1 fused-silica column (J&W Scientific) with a 1.0 μm film thickness, 30 m×250 μm I.D. was used. The GC temperature program was 35°C (9 min) to 40°C (3 min) at 1°C/min, then up to 220°C (10 min) at a rate of 6°C/min. Carrier gas was helium (140 kPa) and nitrogen (110 kPa) as make-up. Detector temperature was 300°C.

#### 2.4.2. LLE

Extracts were always analyzed within 24 h in a DB-1 column under the same conditions described above. Peaks were identified by comparison of retention times with the synthesized standards and confirmed by injection of the MtBE extracts in a second column, a DB-624 fused-silica column (J&W Scientific) 1.8 μm film thickness, 30 m×320 μm I.D.

## 3. Results and discussion

### 3.1. Optimization of HS-SPME procedure

In order to develop an HS-SPME method for ITHM analysis, several parameters such as selection of SPME coating, effect of headspace volume, extraction time, desorption conditions and the effect of salt addition were optimized.

#### 3.1.1. Selection of SPME coating – extraction efficiencies

Four SPME fiber coatings were evaluated to select the appropriate coating for the HS-SPME method. The chemical nature of a target analyte (polarity and volatility or molecular mass) determines the type of a coating used. A fortified aqueous sample (30 ml spiked at level of 5 μg/l of each ITHM) was analyzed twice with each fiber. The extraction time was 10 min at room temperature for all the fibers. Desorption times were the following: 60 s (splitless mode) at 220°C for the 7-μm PDMS and at 200 °C for the 100-μm PDMS; and 30 s (split mode, 1/10) at 240°C for the CAR–PDMS and at 200°C for the CWX–DVB. For the two last fibers, split mode was used due to the high amount of analytes adsorbed.

In order to evaluate the extraction efficiency, the ECD areas obtained for each ITHM with the different fibers are shown in Table 1. Previously, areas obtained in split mode were normalized respect to splitless mode to compare all experimental values.

The PDMS fiber (a non-polar phase) is not the best coating due to its low capacity to extract these compounds. Efficiencies obtained with the thin film (7 μm) were 7–8-times lower than thick film (100 μm). Properties of the mixed CAR–PDMS fiber were different from those of PDMS due to the porous carbon adsorbent (Carboxen). This modifies the selectivity toward polar compounds and thus improves the extraction efficiency, although this was

Table 1
Extraction efficiencies of various fiber coatings for sampling ITHMs by HS-SPME

| Compound | ECD peak area counts ($\cdot 10^3$) (mean of 2 determinations) | | | |
|---|---|---|---|---|
| | 7-μm PDMS | 100-μm PDMS | CAR–PDMS[a] | CWX–DVB[a] |
| $CHCl_2I$ | 34 | 271 | 3861 | 3969 |
| CHBrClI | 28 | 242 | 2155 | 3414 |
| $CHBr_2I$ | 57 | 242 | 1529 | 2874 |
| $CHClI_2$ | 93 | 627 | 2645 | 6817 |
| $CHBrI_2$ | 83 | 590 | 1678 | 45 143 |
| $CHI_3$ | 130 | 905 | 1271 | 4422 |

[a] Areas normalized with respect to splitless mode.

lower than the efficiency obtained with the polar CWX–DVB coating. The polar Carbowax coating adsorbed onto a porous polymer (divinylbenzene) was suitable for the extraction of all ITHMs with a relatively high efficiency due to the increase in the surface area of the fiber and the suitable polarity. The CWX–DVB fiber gave better extraction than the CAR–PDMS fiber, especially for the heavier compounds (i.e., $CHClI_2$, $CHBrI_2$ and $CHI_3$).

### *3.1.2. Effect of headspace volume*

In order to optimize the procedure, the effects of the water sample and the headspace volume were studied. The experiment was performed using EPA 40-ml vials and the volume of water was increased from 10 to 30 ml. A fortified aqueous sample (spiked at 5 μg/l of each ITHM) was analyzed twice with the CWX–DVB fiber. The extraction time was 10 min at room temperature and the sample was agitated at 1100 rpm with a magnetic stirrer. The desorption time was 30 s.

SPME theory dictates that for high sensitivity headspace extraction, the volume of the gaseous phase should be minimized [36]. In this study, an increase in the peak area for each ITHM was obtained from 30 to 40% when headspace volume decreased from 30 to 10 ml. The extraction of the analytes is affected by the volume of headspace into which the iodinated compounds diffuse. Further experiments were performed using 30 ml of water sample.

### *3.1.3. Adsorption time profiles*

The CWX–DVB fiber extracts the analytes primarily by adsorption due to the presence of the solid polymer particles (DVB) in the cross-linked structure of the CWX–DVB. The adsorption time profiles of CWX–DVB fiber were obtained by plotting the ECD response versus the extraction time (Fig. 1). Duplicate water samples were analyzed under the experimental conditions described in the HS-SPME procedure.

Acceptable equilibrium times (30 min) were achieved for $CHCl_2I$, CHBrClI and $CHBr_2I$. However, the equilibrium was not reached for the iodinated compounds with higher molecular mass ($CHClI_2$, $CHBrI_2$ and $CHI_3$), indicating that the diffusion of the analytes from the liquid phase into the headspace was important in the equilibration process. It has been shown that an increase in sampling temperature decreases both equilibrium extraction time and recovery [37], so further experiments were performed at higher temperatures but adsorption of water in the fiber was observed, which may damage the column; in addition, a high background was registered.

The extraction time of the three heaviest compounds can also be shortened by working in non-equilibrium conditions. Ai [38,39] has recently proposed a dynamic model of SPME adsorption, indicating that the amount of analyte adsorbed onto the fiber is proportional to the initial concentration in the sample matrix if the agitation and the sampling time are held constant. According to Ai, SPME quantitation is feasible at non-equilibrium conditions.

GC injector temperature and the appropriate desorption time are also important parameters to ensure that analytes are completely desorbed from the fiber

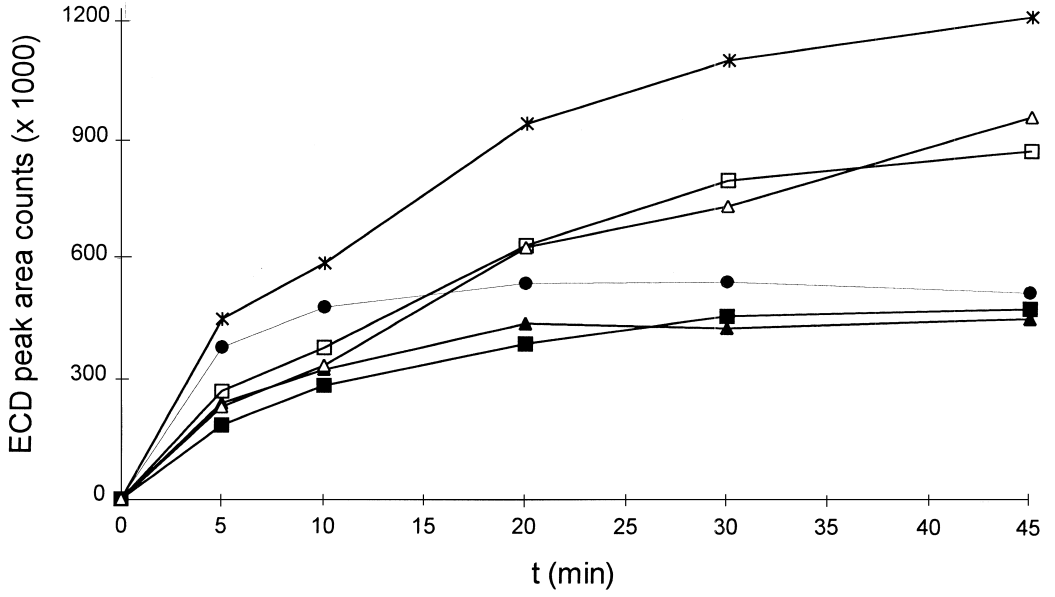


Fig. 1. Adsorption time profiles for ITHMs by HS-SPME using CWX–DVB. Water samples (30 ml) contained ITHMs (5 μg/l of each compound). Key: (●) $CHCl_2I$, (▲) CHBrClI, (♦) $CHBr_2I$, (*) $CHClI_2$, (■) $CHBrI_2$ and (△) $CHI_3$.

in order to reach the highest sensitivity and avoid carryover. For the CWX–DVB fiber, three GC injector temperatures (200, 230 and 260°C) were tested and the most appropriate was 200°C. Desorption profiles (Fig. 2) show that 20 to 30 s is enough to ensure total desorption. The fiber was analyzed again prior to re-exposure. No peaks appeared in the resulting chromatogram, indicating that this time was enough to remove all analytes from the fiber.

### *3.1.4. Effect of the addition of salts*

The effects of the addition of salts on the adsorption were measured. Increasing the ionic strength of the solution favors the diffusion of analytes into the headspace which reduces extraction times. An aqueous sample was spiked at 5 μg/l level of each ITHM and salted at 25% (w/v) with $Na_2SO_4$ or 25% (w/v) NaCl. The extraction time was 10 min at room temperature. For initial evaluation of this effect, non-equilibrium conditions (10 min) were chosen.

Results obtained in this study are presented in Table 2. The addition of 25% $Na_2SO_4$ and 25% NaCl was found to have a significant effect on the extraction of the ITHMs by HS-SPME. With the use of $Na_2SO_4$, the areas of $CHCl_2I$, CHBrClI and $CHBr_2I$ increased 20 to 40%; whereas when NaCl was added, the area increased by up to 50%. No significant differences between these salts were observed for $CHClI_2$ and $CHBrI_2$ (100 and 50%, respectively, from the unsalted extraction). For $CHI_3$, extraction was higher with $Na_2SO_4$ than with NaCl. As a conclusion, addition of salts has an important effect and further experiments were performed using 7.5 g of NaCl.

The adsorption time profiles of the CWX–DVB fiber were obtained for an aqueous sample spiked with ITHMs at 5 μg/l and salted with 25% NaCl. Duplicate water samples were always examined under the experimental conditions described above. No significant differences were observed between the equilibration times with and without salt addition for $CHCl_2I$, CHBrClI or $CHBr_2I$ were observed but an equilibration time of 30 min was obtained for $CHClI_2$, $CHBrI_2$ and $CHI_3$ using these conditions. The increase in sensitivity for all compounds achieved by salting out the sample and the fact that clean blanks were obtained, prompted us to include

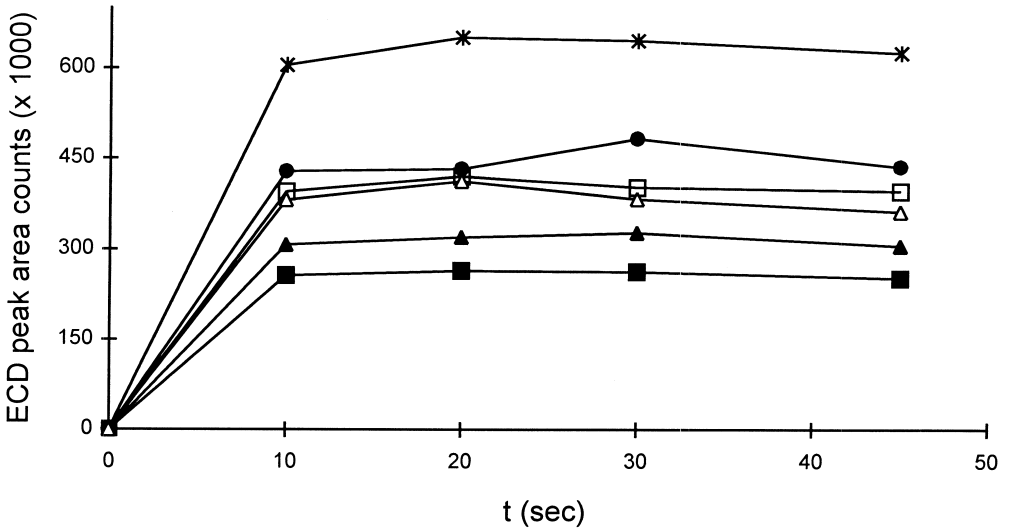


Fig. 2. Desorption profiles for ITHMs by HS-SPME using CWX–DVB. Water samples (30 ml) contained ITHMs (5 μg/l of each compound). Desorption temperature: 200°C. Key: (●) $CHCl_2I$, (▲) CHBrClI, (■) $CHBr_2I$, (*) $CHClI_2$, (□) $CHBrI_2$ and (△) $CHI_3$.

salt addition in the HS-SPME method and to agitate the sample for 30 min.

A chromatogram of an HS-SPME standard solution of ITHM is shown in Fig. 3. Sharp peaks and good chromatographic resolution for all ITHMs were obtained. The chromatogram shows the presence of some THMs and tetrabromomethane as impurities from the synthesis of ITHMs [14] and also trace amounts of chlorinated solvents present in ultrapure water.

### *3.2. Linear range, limits of detection and precision*

Having established the optimum conditions for the HS-SPME–GC–ECD procedure, quality parameters such as linearity, limits of detection and precision were calculated.

The linearity of the HS-SPME method was evaluated by plotting the calibration curves of the area relative to the internal standard 1,2-dibromopropane ($A_i/A_{I.S.}$) versus the concentration of each analyte ($C_i$). Standard calibration curves were plotted for concentrations ranging from 0.1 μg/l to 20 μg/l. The linear ranges and the correlation coefficients ($r^2$) obtained for each compound are given in Table 3. The seven-point calibration curve was found to have good linearity with a correlation coefficient better than 0.995. The loss of linearity observed at high concentrations was probably due to overloading of the fiber capacity.

The sensitivity of the HS-SPME technique was considered in terms of limits of detection (LODs), which depend on the method and the instrument sensitivity. The limits were evaluated on the basis of the signal-to-noise ratio obtained with water samples containing the compounds of interest at low concentrations. The LOD was defined as the concentration of an analyte that produced a signal three-times greater than the baseline noise. The average signal-to-noise of five replicates at low concentrations was used to calculate the LOD. Under the

Table 2
Effect of salt addition on the extraction of ITHMs by HS-SPME using the 65-μm Carbowax–divinylbenzene fiber

| Compound | ECD peak area counts ($\cdot 10^3$) (mean of 2 determinations) | | |
|---|---|---|---|
| | No salt | 25% $Na_2SO_4$ | 25% NaCl |
| $CHCl_2I$ | 428 | 518 | 654 |
| CHBrClI | 307 | 398 | 459 |
| $CHBr_2I$ | 256 | 360 | 382 |
| $CHClI_2$ | 400 | 843 | 899 |
| $CHBrI_2$ | 395 | 614 | 558 |
| $CHI_3$ | 381 | 572 | 446 |

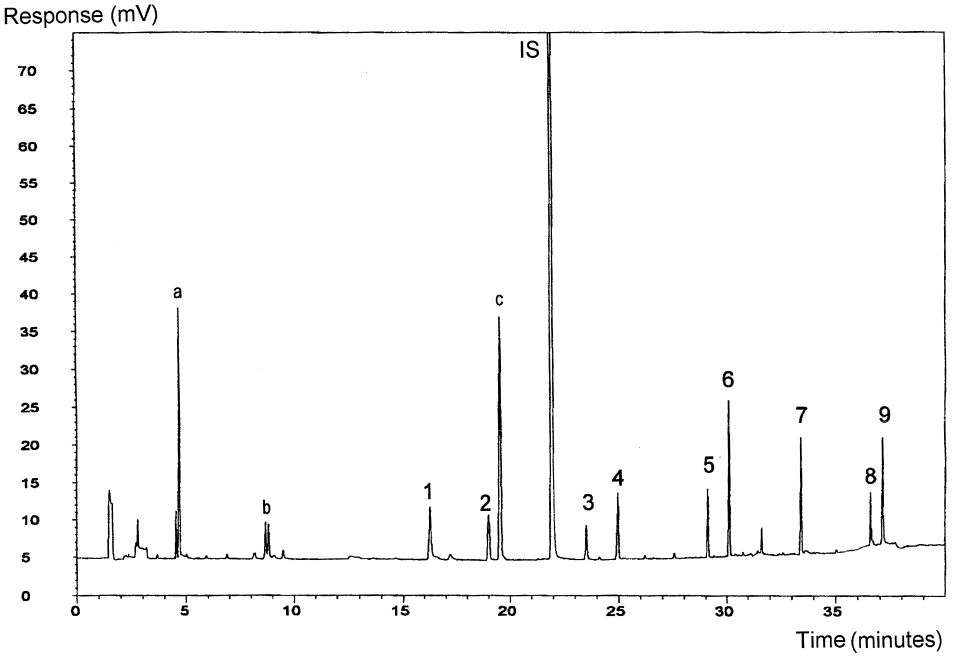


Fig. 3. GC–ECD chromatogram of a water sample (30 ml) spiked with ITHMs at 0.3 μg/l. Extraction was performed by HS-SPME with CWX–DVB fiber under the optimized conditions. Peaks: 1=chlorodibromomethane; 2=$CHCl_2I$; 3=bromoform; 4=CHBrClI; 5=$CHBr_2I$; 6=$CHClI_2$; 7=$CHBrI_2$; 8=tetrabromomethane; 9=iodoform, a=chloroform; b=trichloroethylene; c=tetrachloroethylene and I.S.$_1$: 1,2-dibromopropane. Identified synthesis impurities: 1, 3, 8. Identified analytical artifacts from ambient air: a=chloroform, b=chlorodibromomethane, c=perchloroethylene. (Chromatographic conditions as described in Sections 2.3 and 2.4).

experimental conditions the detection limits (Table 3), were between 2 and 3 ng/l. LODs by HS-SPME were one-tenth of those obtained by LLE method.

The repeatability and reproducibility of HS-SPME were assessed by analyzing five ultrapure water samples on the same day and a total of nine samples at on three different days, respectively. All samples were spiked at a concentration of 5 μg/l of each compound. Results are reported in Table 3. The relative standard deviation (RSD) for repeatability

Table 3
Linear dynamic ranges, correlation coefficients ($r^2$), limits of detection (LODs), repeatability and reproducibility of the optimized HS-SPME method using the 65-μm Carbowax–divinylbenzene fiber

| Compound | Linearity range (μg/l) | Correlation coefficient ($r^2$) | Detection limit[a] (LOD) (ng/l) | Repeatability[a] | | | Reproducibility[b] | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Target | Mean[a] | RSD (%) | Target | Mean[b] | RSD (%) |
| $CHCl_2I$ | 0.3–10.0 | 0.995 | 2.4 | 5.1 | 5.0 | 2.2 | 5.1 | 5.1 | 6.7 |
| CHBrClI | 0.3–7.9 | 0.997 | 2.0 | 5.4 | 5.4 | 1.8 | 5.4 | 5.3 | 6.2 |
| $CHBr_2I$ | 0.3–8.3 | 0.999 | 2.2 | 5.7 | 6.1 | 4.0 | 5.7 | 6.0 | 6.9 |
| $CHClI_2$ | 0.3–14.0 | 0.999 | 1.2 | 5.5 | 5.9 | 4.3 | 5.5 | 5.7 | 7.2 |
| $CHBrI_2$ | 0.3–7.5 | 0.997 | 1.7 | 4.9 | 5.3 | 4.7 | 4.9 | 5.3 | 6.4 |
| $CHI_3$ | 0.3–11.9 | 0.997 | 3.0 | 5.8 | 6.4 | 6.8 | 5.7 | 6.7 | 4.0 |

[a] Mean of five determinations.
[b] Mean of nine determinations.

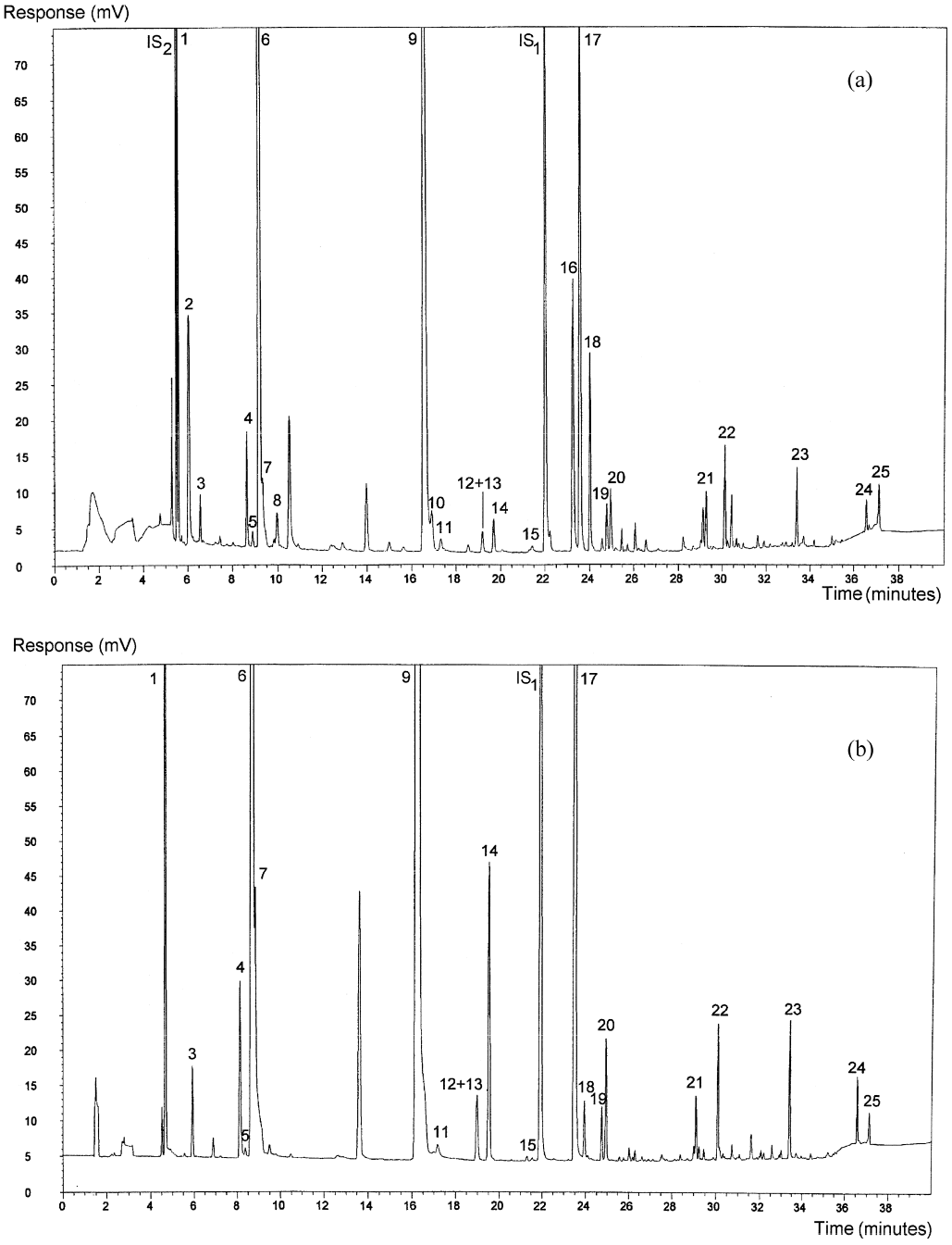


Fig. 4. GC–ECD chromatograms of a chlorinated water spiked with ITHMs. Analyses were performed by the LLE (top) and HS-SPME (bottom) methods. Peaks: 1=chloroform; 2=MtBE impurity; 3=1,1,1-trichloroethane; 4=dibromomethane; 5=dichloroacetonitrile; 6=bromodichloromethane; 7=trichloroethylene; 8=chloral hydrate; 9=chlorodibromomethane; 10=bromochloroacetonitrile; 11=1,2-dibromoethane; 12=$CHCl_2I$; 13=1-bromo-1-chloropropanone; 14=tetrachloroethene; 15=1,1,1-trichloropropanone; 16=MtBE impurity; 17=bromoform; 18=dibromoacetonitrile; 19=1,1-dibromopropanone; 20=CHBrClI; 21=$CHBr_2I$; 22=$CHClI_2$; 23=$CHBrI_2$; 24=tetrabromomethane; 25=$CHI_3$; $I.S._2$: bromochloromethane and $I.S._1$: 1,2-dibromopropane as internal standards. (Chromatographic conditions as described in Sections 2.3 and 2.4).

ranged from 2 to 7%; whereas the RSD for reproducibility ranged from 4 to 7%. These values show that HS-SPME is precise.

### 3.3. Comparison of HS-SPME with LLE

The optimized HS-SPME–GC–ECD method was applied for the determination of ITHMs by spiking samples of ultrapure water and samples of ITHM-free chlorinated water. Triplicate samples of ultrapure and chlorinated water were analyzed, each spiked at two different concentrations (0.3 and 1.0 μg/l). When the chlorinated drinking water analysis was performed, ascorbic acid solution was added prior to analysis in order to eliminate free chlorine. The samples were also analyzed by the conventional LLE–GC–ECD method in order to compare experimental results. Fig. 4 shows the chromatograms obtained by HS-SPME (top) and LLE (bottom) for the analysis of a spiked chlorinated drinking water. Results for both methods are given in Table 4. Quantification in both methods was performed using the calibration curve for each compound relative to the internal standard (1,2-dibromopropane). Both techniques gave the same results. Standard deviations and mean values were compared using the *F* Fischer test (95% probability) and the Student *t*-test (95% probability and two sides), respectively [40]. No significant differences were found between the results given by these two techniques. Analysis of solutions of known concentration shows that HS-SPME provides precision comparable to LLE, with the added advantages of requiring no solvent and being more rapid. Analysis of ITHMs in spiked chlorinated drinking water showed that this method can be applied to real samples, avoiding the problems of the complex matrix. Coelution of $CHCl_2I$ with 1-bromo-1-chloropropanone was observed; so, the DB-624 column was used for confirmatory purposes.

## 4. Conclusions

The present study has shown that the optimized HS-SPME–GC–ECD method is suitable for monitoring ITHMs in drinking water samples. The 65-μm Carbowax–divinylbenzene fiber is proposed for extracting ITHMs, which allows the quantitative analysis of this group of disinfection by-products in water samples. Equilibration without an increase in sample temperature was achieved and sensitivity was improved by addition of salt. The method has good linearity in the range of concentrations of interest

Table 4
Estimated concentrations and standard deviations of ITHMs in ultrapure spiked water and chlorinated drinking spiked water (italics) determined by HS-SPME (65-μm Carbowax–divinylbenzene fiber) and LLE methods

| Compound | HS-SPME–GC–ECD | | | | LLE–GC–ECD | | | |
|---|---|---|---|---|---|---|---|---|
| | 0.3 μg/l | | 1.0 μg/l | | 0.3 μg/l | | 1.0 μg/l | |
| | Mean (μg/l) | ±SD | Mean (μg/l) | ±SD | Mean (μg/l) | ±SD | Mean (μg/l) | ±SD |
| $CHCl_2I$ | 0.30 | 0.017 | 1.02 | 0.041 | 0.30 | 0.009 | 1.02 | 0.091 |
| | *0.31* | *0.020* | *0.92* | *0.018* | *0.30* | *0.021* | *1.02* | *0.037* |
| CHBrClI | 0.30 | 0.013 | 1.02 | 0.033 | 0.30 | 0.013 | 1.02 | 0.165 |
| | *0.27* | *0.010* | *0.91* | *0.054* | *0.30* | *0.010* | *1.02* | *0.057* |
| $CHBr_2I$ | 0.30 | 0.029 | 1.18 | 0.009 | 0.30 | 0.062 | 1.02 | 0.004 |
| | *0.33* | *0.025* | *1.09* | *0.070* | *0.30* | *0.006* | *1.04* | *0.422* |
| $CHClI_2$ | 0.30 | 0.019 | 1.02 | 0.027 | 0.30 | 0.102 | 1.00 | 0.009 |
| | *0.34* | *0.017* | *0.93* | *0.016* | *0.22* | *0.005* | *0.98* | *0.042* |
| $CHBrI_2$ | 0.30 | 0.009 | 1.02 | 0.083 | 0.30 | 0.041 | 1.02 | 0.022 |
| | *0.34* | *0.018* | *1.10* | *0.037* | *0.28* | *0.037* | *0.96* | *0.059* |
| $CHI_3$ | 0.31 | 0.074 | 1.04 | 0.080 | 0.31 | 0.022 | 1.04 | 0.066 |
| | *0.35* | *0.020* | *1.49* | *0.138* | *0.30* | *0.030* | *1.04* | *0.302* |

with good precision between 2 to 7% and it is sufficiently sensitive with limits of detection in the ng/l range.

The HS-SPME method can be considered a good alternative to LLE extraction with the advantage that solvents are not needed. It is thus faster because eliminates the intensive manual labor of the liquid–liquid extraction and finally, it is more sensitive. Analysis of spiked chlorinated drinking water demonstrates that the method is applicable to real water samples.

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