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# Simultaneous determination of "earthy-musty" odorous haloanisoles and their corresponding halophenols in water samples using solid-phase microextraction coupled to gas chromatography with electron-capture detection

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**Abstract**

Certain haloanisoles present at trace levels cause a large part of earthy-musty off-flavor problems in drinking water. These potent odorous chemicals come mainly through biomethylation of their corresponding halophenols. To enable the investigation of both families of compounds, a method involving solid-phase microextraction (SPME) was developed and the main parameters governing SPME were optimized. This method allows the simultaneous quantification of haloanisoles and halophenols at levels ranging from 1 to 100 or 250 ng/l, with detection limits of about 0.5 ng/l and could be applied to potable as well as raw surface waters.
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*Keywords:* Water analysis; Solid-phase microextraction; Haloanisoles; Halophenols; Anisoles; Phenols

## 1. Introduction

Off-flavor problems are significant for water suppliers, first because tastes and odors are regulated by guidelines for potable water and, secondly, because consumers judge water by what they first perceive. Tastes and odors account for the largest single class of consumer complaints submitted to water utilities [1]. Among the eight odor groups described in the water flavor wheel, the earthy-musty odors are specially troublesome because they are particularly unpleasant and often encountered in water [2].

Recently, beside the well-known earthy-musty algae metabolites (e.g. geosmin and 2-methylisoborneol), attention was drawn to certain haloanisoles [3,4], such as 2,4,6-trichloroanisole or 2,4,6-tribromoanisole, which impart an intense musty odor to water when present at about 30 pg/l [5]. The relative importance of haloanisoles in earthy-musty off-flavors cases was pointed out [5] and the presence of these chemicals at levels of about 0.04–7 ng/l were proved to be the cause of the odor in 62% of the examined cases [6]. To improve the organoleptic quality of water, studies of these potent odorous compounds as well as their biological precursors, the corresponding halophenols [3,7], must be deepened in order to assess treatment process efficiencies and kinetics of bioformation in the distribution system.

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This requires a relatively inexpensive and high throughput method for the routine analysis of these compounds and their halophenolic precursors.

For the analysis of haloanisoles in water, closed-loop stripping analysis (CLSA) [8], purge and trap technique [9], steam distillation extraction [10], liquid/liquid extraction or micro-extraction [11,12] were applied. CLSA, the most widely used method, has low detection limits, but is time consuming, labor intensive and does not allow analysis of halophenols. For these later analytes, liquid–liquid extraction [13,14] and solid-phase extraction were employed [15,16]. Liquid–liquid extraction was tested for the simultaneous determination of haloanisoles and halophenols, but it did not provide satisfactory results in terms of linearity and sensitivity [17].

Developed by Pawliszyn and co-workers in the early 1990s [18,19], solid-phase microextraction (SPME) has become very popular for water and environmental analysis, because of its rapidity, simplicity and ease of automation. SPME was successfully applied to the analysis of certain ‘‘earthy-musty’’ odorous compounds in water [20,21], for the quantification of 2,4,6-trichloroanisole in wine [22] and for the determination of phenols in water [23–25].

The aim of this study was to evaluate if a method involving SPME would make it possible to analyze simultaneously four ‘‘earthy-musty’’ off-flavor haloanisoles and their four respective halophenolic precursors at concentration levels expected in water samples (e.g. at the ng/l level for haloanisoles and tens of ng/l for halophenols). For the analysis, gas chromatography with electron-capture detection (ECD) was selected, because ECD is selective to organics substituted with halogens (thus limiting potential matrix interference problems) and provides great sensitivity for molecules with three to four chlorine or bromine atoms, such as the studied molecules.

Three commercially available SPME fibers were tested in headspace and direct modes. Main parameters which affect the sorption and desorption processes were studied for the most appropriate one. Once the SPME procedure was optimized, quality parameters such as linearity, repeatability and limits of detection were determined and the method was applied to potable and raw surface water to test for matrix effects.

## 2. Experimental

### *2.1. Standards and reagents*

The standards of the eight target analytes were purchased from the following sources: 2,4,6-trichloroanisole (2,4,6-triCA), 2,3,4,6-tetrachloroanisole (2,3,4,6-tetraCA), 2,4,6-tribromoanisole (2,4,6-triBA), 2,3,6-trichlorophenol (2,3,6-triCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-tetraCP), 2,4,6-tribromophenol (2,4,6-triBP) from Sigma–Aldrich (Milwaukee, WI, USA), 2,3,6-trichloroanisole (2,3,6-triCA) from K&K/ICN Pharmaceuticals (Orsay, France), 2,4,6-trichlorophenol (2,4,6-triCP) from Fluka (Buchs, Switzerland).

Individual stock standard solutions (1 g/l) of each analyte were prepared by weight in acetone. Standard stock solutions of the four halophenols and the four haloanisoles (10 mg/l) were prepared from the individual standard solutions by dilution with acetone. A water standard solution containing 10 μg/l of each analyte was prepared by adding 100 μl of both 10 mg/l stock solutions to 100 ml of Milli-Q (Millipore, Bedford, MA, USA) water. Reference water used for the SPME procedure optimization and for quality control experiments was purchased from Evian (Evian, France). Sodium chloride, sodium dihydrogenphosphate and hydrochloric acid were supplied by VWR International (Fontenay sous Bois, France).

### *2.2. Instrumentation and chromatographic conditions*

Analyses were carried out with a Varian 3800 CX system connected to a Varian 8200 CX AutoSampler for SPME (Varian, Les Ulis, France). The gas chromatograph (GC) was equipped with a 1078 split/splitless injector, an ECD system, and a fused-silica capillary column, 30 m×0.32 mm I.D., 0.25-μm film thickness (DB-5; J&W Scientific, Folsom, CA, USA). The carrier gas was helium, its flow-rate was 1 ml/min. The oven temperature program was as follows: hold at 80 °C for 1 min, ramp to 220 °C at 4 °C/min, ramp to 280 °C at 40 °C/min, hold at 280 °C for 10 min. The injector temperature was fixed at the desorption temperature. Injection was performed in the splitless mode for 1 min, then a split ratio of 40 was applied. The detector was set at

300 °C, with a nitrogen make-up gas flow of 40 ml/min.

### 2.3. SPME procedure

Three SPME fiber coatings were evaluated: 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB), 65 μm Carbowax–divinylbenzene (CW–DVB) and 50/30 μm divinylbenzene–Carboxen–polydimethylsiloxane (DVB–CAR–PDMS). The commercially available SPME device and the fibers were purchased from Supelco (Bellefonte, PA, USA). Fibers were initially conditioned according to the manufacturer's instructions in order to remove contaminants and to stabilize the solid-phase.

For SPME optimization, aqueous solutions at 100 ng/l were prepared by diluting the 10 μg/l water standard solution with the appropriate volume of reference water. Aqueous samples of 13 and 9 ml, for direct and headspace SPME, respectively, were introduced into 13.5-ml vials capped with PTFE-lined silicone septum.

The effect of low pH and salt on the SPME technique was examined. A pH 2.6 buffer was prepared by adding 6 g of $NaH_2PO_4$ to 500 ml of water and adjusting the pH to 2.6 with HCl (6 *M*). Saturated salt solutions were prepared with NaCl (116 g in 500 ml of water).

## 3. Results and discussion

### 3.1. Selection of the fiber coating and the extraction mode

The extraction efficiencies of halophenols and haloanisoles were evaluated using SPME with different stationary phases. Among the fibers commercially available for GC use, those incorporating one polymer were not tested. Previous studies demonstrated that the polyacrylate (PA) fiber was appropriate for halophenols [23] but not for semi-volatile odorous compounds [26] and that polydimethylsiloxane (PDMS) fiber was suitable for haloanisoles [21] but not for halophenols [23]. Three fibers, constituted by two or three different polymers, were tested: 65 μm PDMS–DVB, 65 μm CW–DVB and 50/30 μm DVB–CAR–PDMS. These coatings were chosen because they all incorporate DVB, which favors the extraction of aromatic compounds by π-interactions.

Because semi-volatile (haloanisoles) and polar (halophenols) compounds have to be determined simultaneously and also because the method will be applied for the analysis of clean matrices (water samples), both direct and headspace sampling were investigated with each of the tested fibers. Direct extraction consists of plunging the fiber directly into water. In headspace mode, the fiber is placed in the gaseous volume above water. The initial conditions were: pH 2.6, saturation with NaCl, agitation by needle vibration, extraction time and temperature 30 min and 60 °C, respectively, and desorption during 3 min including 1 min splitless at temperatures of 250 °C for the CW–DVB fiber and of 260 °C for the PDMS–DVB and the DVB–CAR–PDMS fibers.

The responses obtained for the eight analytes using the three fibers and both extraction modes are shown in Fig. 1.

For both families of compounds, sampling in the direct mode (Fig. 1b) provided a better extraction efficiency than sampling in the headspace mode (Fig. 1a), independently of the nature of the fiber. For a given fiber, the differences observed between the extraction modes were less significant for the haloanisoles than for the halophenols. This could be justified by the greater volatility of haloanisoles (Henry's law constant of 2,4,6-triCA is $28.8\cdot10^{-5}$ atm $m^3$/mol; 1 atm = 101 325 Pa) compared to halophenols (Henry's law constants of halophenols are lower than $10^{-5}$ atm $m^3$/mol).

Concerning the fiber coatings, irrespectively of the mode of extraction, better performances were obtained with the non-polar DVB–CAR–PDMS fiber for haloanisoles and with the polar CW–DVB fiber for halophenols.

The haloanisoles, having low odor threshold concentrations (about tens pg/l), are generally present in water at concentration levels much lower than halophenols (about hundreds ng/l). Consequently, better sensitivity is needed for haloanisoles than for halophenols. Therefore, direct mode extraction with the DVB–CAR–PDMS fiber was selected yielding chromatograms with ''balanced'' peak areas when all eight analytes were present at the same concentration level.

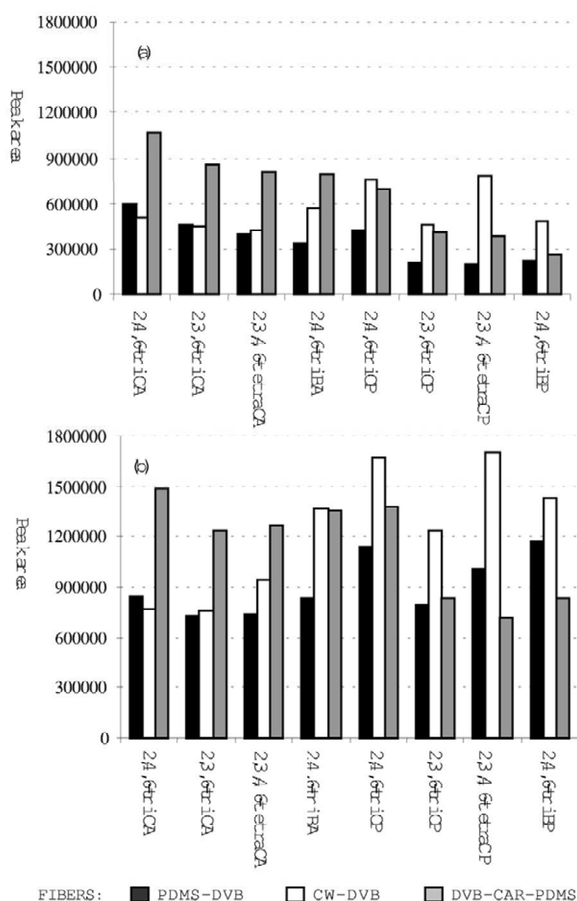


Fig. 1. Extraction efficiency of the SPME fibers (a) in headspace mode and (b) in direct mode. Reference water containing 100 ng/l of each analyte; pH 2.6; NaCl, 4 mol/l; extraction time, 30 min; extraction temperature, 60 °C; desorption 3 min including 1 min splitless at temperatures of 250 °C for the CW–DVB fiber and of 260 °C for the PDMS–DVB and the DVB–CAR–PDMS fibers.

### 3.2. Optimization of the extraction parameters

In order to optimize the SPME procedure, several parameters governing the extraction efficiency [27,28], such as pH and ionic strength, agitation of the sample, extraction temperature and time, were optimized.

#### 3.2.1. Effect of pH and ionic strength

The addition of acid and salt, singularly and in combination, was investigated as a means of enhancing the extraction efficiency. The relative responses (normalized to peak areas obtained for a control sample at neutral pH, with no salt added) are reported in Table 1. For halophenols, which have p$K$ values of about 5–6, the decrease in pH produced a 9- to 20-fold increase in response. At neutral pH, these analytes are still largely in their ionic form. When the pH is lowered, their acid–base equilibrium shift significantly toward the neutral form, which has a greater affinity for the fiber, thereby increasing the amount extracted. The addition of salt also enhanced, but much less, the extraction efficiencies of halophenols (2–3-fold increase). The increased ionic strength (salt addition) decreases the solubility of neutral molecules in the water and forces more of theses analytes into the fiber. The combination of acid and salt addition gave results quite similar to those obtained with acid addition alone. Increased ionic strength (either by salt or acid addition) had a slightly negative effect on the extraction of haloanisoles. It was thought that for these semi-volatile analytes, ‘‘salting out’’ forced their partition into the headspace instead of the fiber. As a compromise, all subsequent extractions were performed at pH 2.6.

#### 3.2.2. Agitation of the sample

Agitation of the sample during extraction facilitates analytes transport towards the fiber coating, decreases the thickness of the static layer around fiber, and reduces the required extraction time. Peak areas obtained with and without stirring by fiber vibration indicated that stirring resulted in a 3–5-fold increase of the extraction efficiencies for all compounds. Consequently, all samples were agitated by fiber vibration during extraction in the remaining experiments.

#### 3.2.3. Influence of the extraction temperature

The influence of sample temperature on SPME was examined at 25 °C and from 40 to 70 °C in 10 °C increments (Fig. 2). By increasing the temperature from 25 to 60 °C, extraction efficiencies were significantly enhanced for all compounds. At 70 °C, losses of haloanisoles were observed. Thus, 60 °C was selected as optimum temperature.

#### 3.2.4. Extraction–time profiles

The extraction–time profiles were obtained by

Table 1
Effect of sample pH and ionic strength on SPME extraction efficiencies of haloanisoles and halophenols[a]

| Compound | $pK_a$ [b] | Response relative to pH 7 and no salt addition | | |
|---|---|---|---|---|
| | | pH 2.6 | NaCl (4 mol/l) | pH 2.6 and NaCl (4 mol/l) |
| 2,4,6-TriCA | NA | 0.9 | 0.5 | 0.7 |
| 2,3,6-TriCA | NA | 0.8 | 0.5 | 0.7 |
| 2,3,4,6-TetraCA | NA | 0.9 | 0.5 | 0.6 |
| 2,4,6-TriBA | NA | 0.8 | 0.6 | 0.7 |
| 2,4,6-TriCP | 6.00 | 14.4 | 3.1 | 16.3 |
| 2,3,6-TriCP | 5.80 | 14.1 | 1.9 | 17.3 |
| 2,3,4,6-TetraCP | 5.22 | 22.8 | 3.3 | 21.3 |
| 2,4,6-TriBP | <6.35 | 8.7 | 2.8 | 8.3 |

NA, not applicable.
[a] Concentration, 100 ng/l; extraction in direct mode with the DVB–CAR–PDMS fiber; extraction time, 30 min; extraction temperature, 60 °C; agitation by fiber vibration; desorption 3 min including 1 min splitless at 260 °C.
[b] Refs. [31,32].

plotting the ECD response versus the extraction time, as can be seen in Fig. 3. The quantity of analytes extracted was roughly doubled when the extraction time was increased from 5 to 10 min, than again doubled from 30 (extraction time fixed for the previous experiments) to 60 min. The increase was small above 120 min, though 240 min was still not enough to reach equilibrium.

The analysis took approximately 55 min (47.5 min for the chromatographic separation plus 5–8 min to cool down the chromatographic oven). The dedicated SPME autosampler used for this study allowed us to

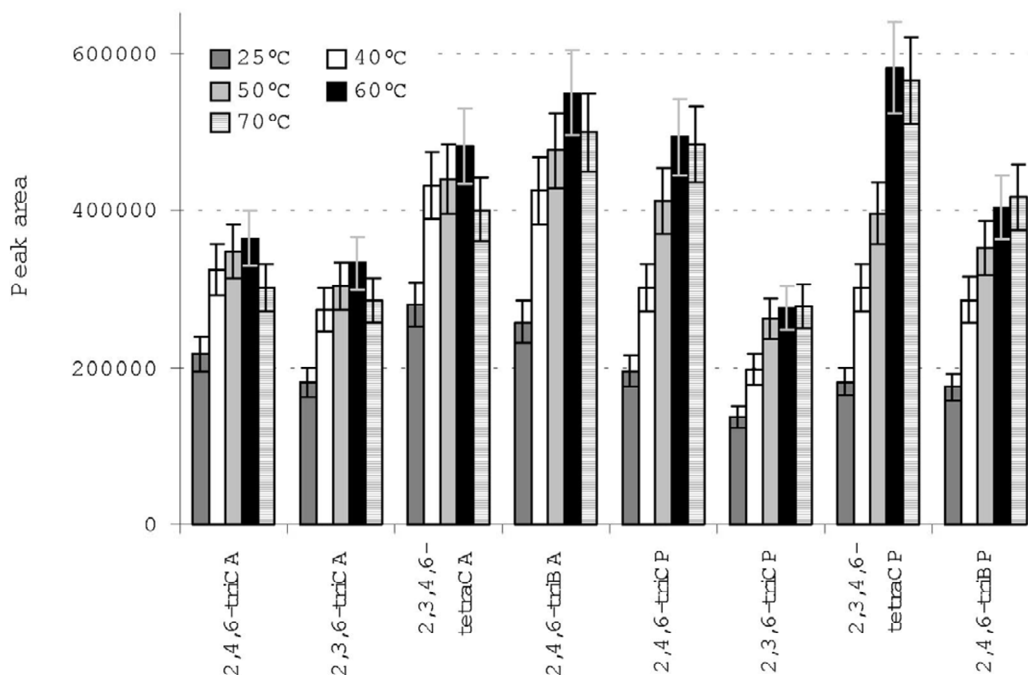


Fig. 2. Influence of the extraction temperature. Reference water containing 100 ng/l of each analyte; extraction in direct mode with the DVB–CAR–PDMS fiber; pH 2.6; extraction time, 30 min; agitation by fiber vibration; desorption 3 min including 1 min splitless at 260 °C.

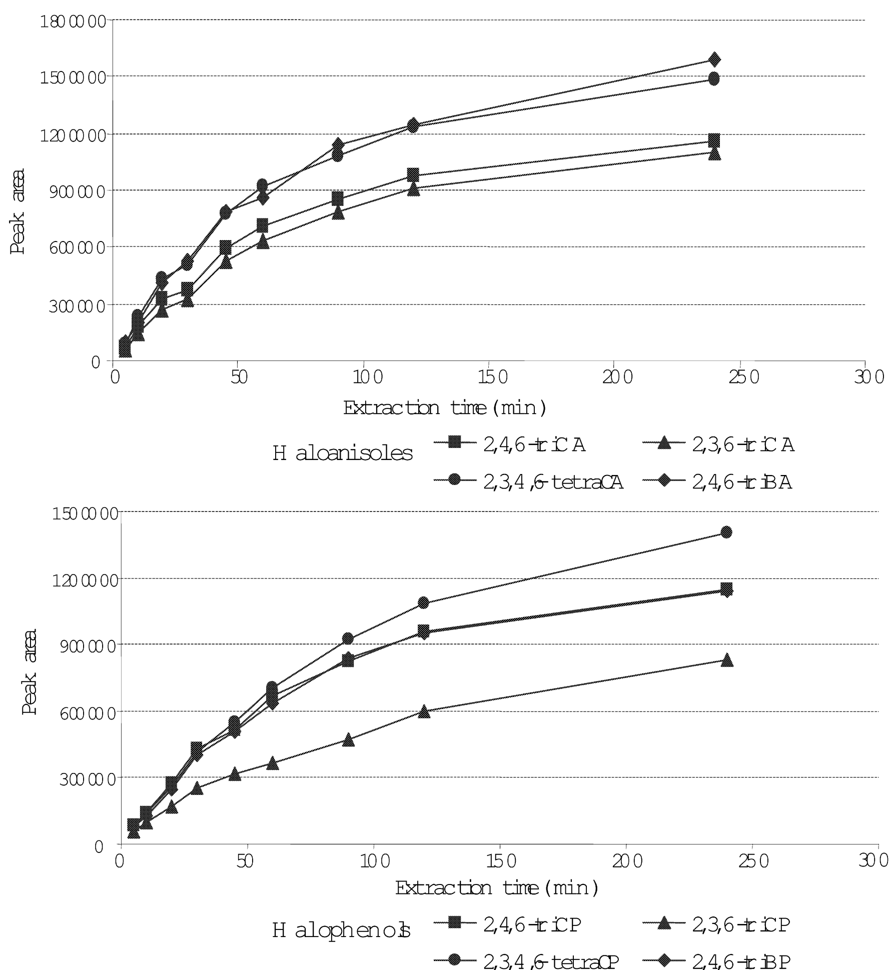


Fig. 3. Extraction–time profiles. Reference water containing 100 ng/l of each analyte; extraction in direct mode with the DVB–CAR–PDMS fiber; pH 2.6; extraction temperature, 60 °C; agitation by fiber vibration; desorption 3 min including 1 min splitless at 260 °C.

extract the next sample while the compounds extracted from the previous sample were analyzed. Thus, for an extraction time lower or equal to the analysis time, the global analysis time (extraction and analysis of compounds) remained unchanged. An extraction period of 60 min was chosen for the subsequent experiments as a compromise between performance and throughput. Although this extraction time corresponded to a non-equilibrium situation, this did not cause any problem as several papers [29,30] had demonstrated that SPME quantification before reaching equilibrium was feasible, as long as the extraction conditions were held constant.

### *3.3. Optimization of the desorption parameters*

After optimization of the sorption conditions, the desorption parameters, i.e. the GC injector temperature and the appropriate desorption time, were optimized.

The DVB–CAR–PDMS fiber can be used with desorption temperatures of 230–270 °C. Therefore, five desorption temperatures ranging from 230 to 270 °C in 10 °C increments were tested. For the eight analytes, the desorption temperature had little effect. Therefore, to protect the fiber coating from thermal degradation, the desorption temperature was fixed at

240 °C, instead of 260 °C set for the previous experiments.

In order to optimize the time necessary to ensure total analyte desorption, the fiber was successively desorbed five times for 1 min each in the splitless mode. After each desorption step, throughout the ensuing chromatographic analysis, a septum was placed at the needle's tip to avoid losses of analytes sorbed on the fiber [19]. As shown in Table 2, 92–96% of halophenols and 96–98% of haloanisoles were desorbed during the first minute. During the second and third desorption steps, an additional 1.5–5 and 0.5–3%, respectively, were desorbed. No analyte was detected in the chromatograms corresponding to the fourth and fifth desorption steps. However, to obtain a chromatogram with a low background level, the fifth desorption step was required. Thus, to ensure complete desorption and to avoid fiber carryover, the desorption time was lengthened from 3 to 5 min, including 2 min in the splitless mode instead of 1 min.

### 3.4. Summary of the set up conditions

The optimum conditions established for the method were as follows: direct extraction with the CAR–DVB–PDMS fiber; pH 2.6; agitation by fiber vibration; extraction temperature, 60 °C; extraction time, 60 min; desorption temperature, 240 °C; desorption time, 5 min including 2 min in splitless mode enabling simultaneous analysis of haloanisoles and halophenols. The analysis is relatively fast (60 min) and totally automated by the use of a dedicated SPME autosampler. The chromatogram obtained by analyzing a reference water sample spiked at 10 ng/l with each analyte of interest is presented in Fig. 4, demonstrating that all the compounds are easily detected at this concentration level.

Table 2
Quantity of analytes desorbed (%) by five successive desorption steps of 1 min each

| Compound | Successive desorption step of 1 min each at 240 °C | | | | |
|---|---|---|---|---|---|
| | Step 1 | Step 2 | Step 3 | Step 4 | Step 5 |
| 2,4,6-TriCA | 97.8[a] | 1.4 | 0.8 | ND[b] | ND |
| 2,3,6-TriCA | 96.9 | 2.0 | 1.1 | ND | ND |
| 2,3,4,6-TetraCA | 95.9 | 2.8 | 1.3 | ND | ND |
| 2,4,6-TriBA | 96.0 | 2.9 | 1.1 | ND | ND |
| 2,4,6-TriCP | 96.3 | 2.6 | 1.1 | ND | ND |
| 2,3,6-TriCP | 91.8 | 5.3 | 2.9 | ND | ND |
| 2,3,4,6-TetraCP | 93.0 | 5.1 | 1.9 | ND | ND |
| 2,4,6-TriBP | 92.6 | 5.3 | 2.1 | ND | ND |

Reference water containing 100 ng/l of each analyte; extraction in direct mode with the DVB–CAR–PDMS fiber; pH 2.6; extraction temperature, 60 °C; extraction time, 60 min; agitation by fiber vibration; desorption at 240 °C. ND, not detected.

[a] A value of 100% corresponds to the total quantity of analyte desorbed in five steps.

### 3.5. Quality control experiments

Quality parameters such as linearity, limits of detection and repeatability (Table 3) were estimated by applying the optimum conditions established for the analysis of halophenols and haloanisoles by SPME–GC–ECD. Standard calibration curves were obtained using reference water with concentrations ranging from 1 to 500 ng/l. All compounds showed good linearity with correlation coefficients greater than 0.98. The linear ranges were between 1 and 100 ng/l for the four haloanisoles and between 1 and 250 ng/l for the four halophenols. The similarity of the slope values confirmed that balanced chromatograms were acquired when the eight analytes were spiked at the same concentration levels. Detection and quantification limits, expressed as ng/l and based on signal-to-noise ratios of 3:1 and 10:1, respectively, were determined experimentally in reference water spiked at 0.5 ng/l with each compound (Table 3). Detection limits as low as 0.1–0.3 ng/l were achieved and proved the good agreement between the performance of the method and the previously mentioned sensitivity requirements. The repeatability of the method was also evaluated at concentration levels of 1, 10 and 100 ng/l with five replicates. Results reported in Table 3 showed a satisfactory repeatability of the method with relative standard deviations (RSDs) ranging from 4 to 8% at concentrations levels of 10 and 100 ng/l. At 1 ng/l, the RSDs were about 10–20%, which are still satisfactory for such a low level of concentration.

Further experiments were carried out to test for matrix effects and to examine the feasibility of quantification by SPME with external calibration performed in reference water (natural mineral water proper for human consumption with a total organic

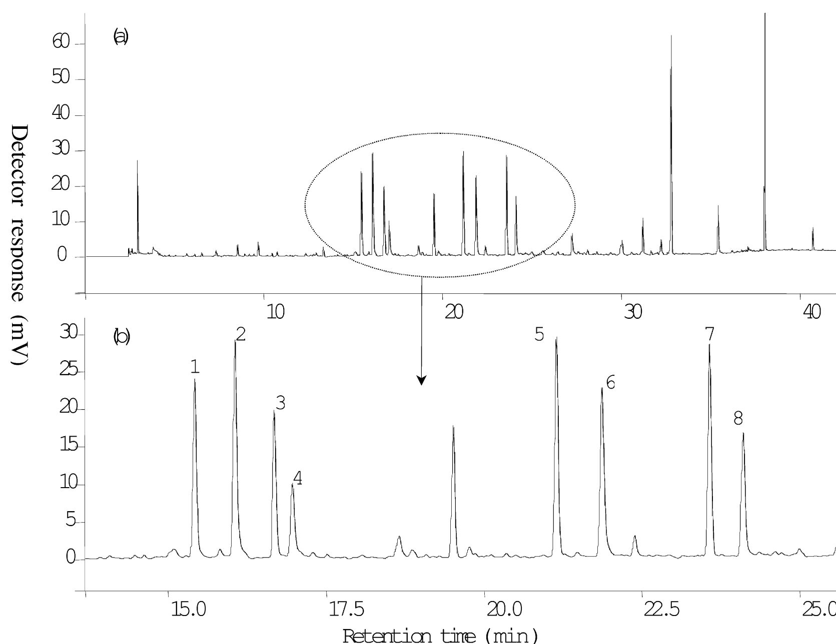


Fig. 4. Chromatogram of Evian reference water spiked at 10 ng/l with each compound analyzed by the proposed procedure using SPME–GC–ECD; (a) total retention time scale, (b) enlarged retention time window where the compounds studied are eluted. 1=2,4,6-TriCA, 2=2,4,6-TriCP, 3=2,3,6-TriCA, 4=2,3,6-TriCP, 5=2,3,4,6-TetraCA, 6=2,3,4,6-TetraCP, 7=2,4,6-TriBA, 8=2,4,6-TriBP.

carbon (TOC) of 0.2 mg/l). Quantification by external calibration is generally applicable for SPME analysis of slightly polluted liquid samples, such as potable water (water for domestic use or for human consumption being treated to meet the potability criteria) or raw waters (untreated ground or surface waters), because problems related to matrix effects are not expected in this case [19]. Two aqueous matrices, one tap water (treated drinking water meeting the potability criteria and proper for human consumption with a typical TOC ranging from 0.5 to 1 mg/l) and one raw surface water (untreated natural surface water such as river water having a typical TOC of about 10 mg/l), spiked at 5 ng/l with haloanisoles and at 100 ng/l with halophenols were analyzed in duplicate. The chromatograms are shown

Table 3
Linear dynamic ranges, correlation coefficients ($r^2$), slope, limits of detection (LODs) and quantification (LOQs), and repeatability of the optimized direct SPME–GC–ECD method using the CAR–PDMS–DVB fiber

| Compound | Linearity | | | Limits (ng/l) | | Repeatability | | |
|---|---|---|---|---|---|---|---|---|
| | Linear range (ng/l) | Slope | $r^2$ | LOD | LOQ | RSD (%) at 1 ng/l | RSD (%) at 10 ng/l | RSD (%) at 100 ng/l |
| 2,4,6-TriCA | 1–100 | 6799 | 0.9760 | 0.1 | 0.4 | 20 | 6 | 5 |
| 2,3,6-TriCA | 1–100 | 6468 | 0.9831 | 0.1 | 0.5 | 16 | 8 | 6 |
| 2,3,4,6-TetraCA | 1–100 | 8658 | 0.9757 | 0.1 | 0.4 | 19 | 4 | 5 |
| 2,4,6-TriBA | 1–100 | 9433 | 0.9820 | 0.2 | 0.5 | 11 | 5 | 7 |
| 2,4,6-TriCP | 1–250 | 7245 | 0.9789 | <0.1 | 0.1 | 10 | 4 | 6 |
| 2,3,6-TriCP | 1–250 | 5599 | 0.9996 | 0.3 | 0.8 | 17 | 8 | 6 |
| 2,3,4,6-TetraCP | 1–250 | 8260 | 0.9902 | <0.1 | 0.1 | 12 | 6 | 6 |
| 2,4,6-TriBP | 1–250 | 6677 | 0.9958 | 0.1 | 0.5 | 13 | 8 | 8 |

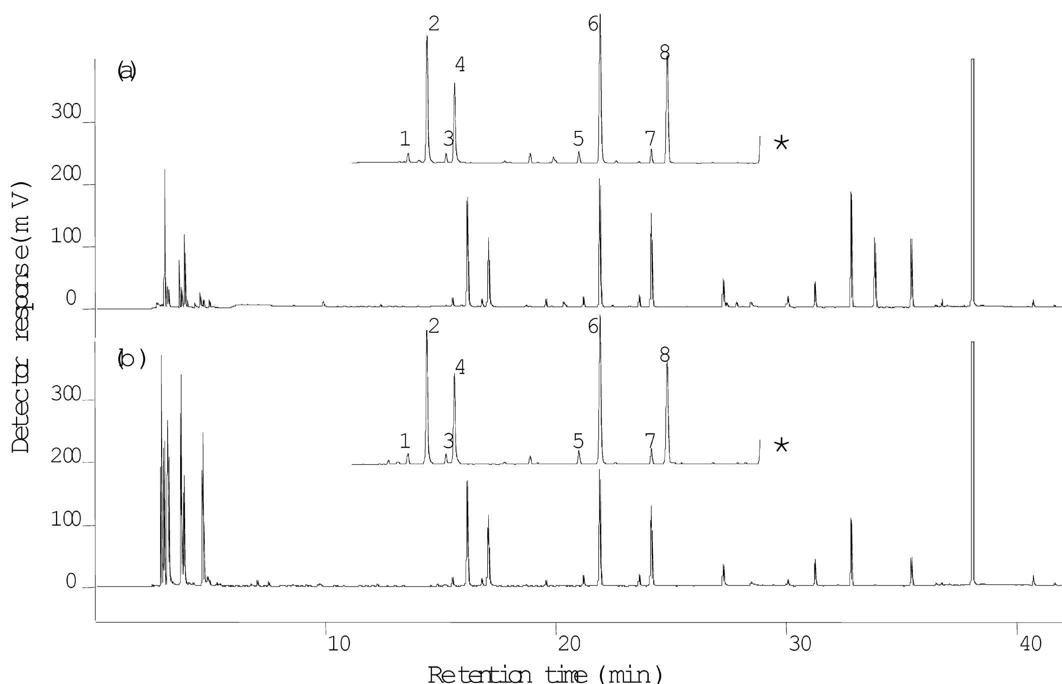


Fig. 5. Chromatogram of (a) tap water and (b) raw surface water spiked at 5 ng/l with each haloanisole and 100 ng/l with each halophenol analyzed by the proposed procedure using SPME–GC–ECD. 1=2,4,6-TriCA, 2=2,4,6-TriCP, 3=2,3,6-TriCA, 4=2,3,6-TriCP, 5=2,3,4,6-TetraCA, 6=2,3,4,6-TetraCP, 7=2,4,6-TriBA, 8=2,4,6-TriBP. * Enlarged retention time window where the compounds studied are eluted.

in Fig. 5. The amounts extracted from these matrices were compared to those obtained from a reference water sample spiked at the same concentration levels. As can be seen in Table 4, recoveries ranged from 80 to 120%, indicating the absence of significant matrix effects even in a relatively complex matrix, such as raw surface water. Limits of detection based on a signal-to-noise ratio of 3:1 were determined in the aqueous matrices spiked at 1 ng/l. Although these limits were slightly higher than those

Table 4
Recoveries and limits of detection measured in two aqueous matrices[a]

| Compound | Matrix recovery (%)[b] | | Limits of detection (ng/l)[c] | |
|---|---|---|---|---|
| | Drinking water | Raw surface water | Drinking water | Raw surface water |
| 2,4,6-TriCA | 97 | 86 | 0.7 | 0.7 |
| 2,3,6-TriCA | 114 | 108 | 0.5 | 0.6 |
| 2,3,4,6-TetraCA | 125 | 113 | 0.7 | 0.7 |
| 2,4,6-TriBA | 115 | 117 | 0.2 | 0.8 |
| 2,4,6-TriCP | 87 | 91 | 0.1 | 0.1 |
| 2,3,6-TriCP | 92 | 83 | 0.4 | 0.4 |
| 2,3,4,6-TetraCP | 88 | 98 | 0.2 | 0.1 |
| 2,4,6-TriBP | 86 | 96 | 0.2 | 0.4 |

[a] Total organic carbon concentrations are 0.2, 1.2 and 3.3 mg/l for the reference water, the tap water and the raw surface water, respectively.

[b] 100% recovery represents the amount recovered from a reference water spiked at the same levels as the aqueous matrices (5 ng/l for haloanisoles, 100 ng/l for halophenols). Mean of two values, RSDs ranged from 5 to 10%.

measured in reference water, they ranged from 0.5 to 0.8 ng/l, which still remained in good agreement with the required sensitivity.

## 4. Conclusions

The feasibility of SPME–GC–ECD for the simultaneous analysis of halophenols and haloanisoles was demonstrated. The method is suitable for high throughput routine analysis, because it is relatively rapid (analysis time of 60 min) and it is automated. The method is linear over two orders of magnitude and has satisfactory repeatability even at trace levels (RSDs of about 10–20% at 1 ng/l). Linear ranges and limits of detection of about 0.3 ng/l indicated that the method would be suitable to quantify halophenols and haloanisoles at realistic concentration levels in environmental samples. Preliminary tests in water samples proved that the method has sufficient selectivity for being applied in different aqueous matrices even if relatively complex, and quantification by external calibration performed in reference water would be feasible.

It has to be noted that, owing to the odor threshold concentrations of some haloanisoles, the proposed method could not be employed to diagnose the cause of off-flavors problems in waters. However, as required in this work, due to its speed and ease of automation, it enables the simultaneous determination of anisoles and phenols at realistic levels. Thus, it represents a valuable analytical tool to be used for laboratory or pilot-scale studies to assess treatment processes efficiencies or bio-transformation kinetics.

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