Stir Bar Sorptive Extraction: A New Way to Extract Off-Flavor Compounds in the Aquatic Environment

Application

Food and Flavors

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Abstract

The objective of this study was to analyze organic off-flavors in water by gas chromatography/mass spectrometry (GC/MS) using Stir Bar Sorptive Extraction (SBSE). Six compounds were quantitatively determined using Selected Ion Monitoring (SIM): 2-methylisoborneol (MIB), geosmin, 2,4,6-trichloroanisole, 2,3,6-trichloroanisole, 2,3,4-trichloroanisole and 2,4,6-tribromoanisole. The Limit of Quantification (LOQ) was found to be from 0.1 ng/L to 0.2 ng/L for haloanisoles, 0.5 ng/L for geosmin and 1 ng/L for MIB. Relative standard deviation at the quantification limit ranges from 7% to 14.6%. Recovery was evaluated by spiking real water samples. It ranged from 80% to 120% depending on the compound. GC/MS detection in the scanning mode combined with olfactometry were used for qualitative analysis in order to characterize new odorous compounds. Using this technique, it was possible to extract and analyze more than 20 samples a day.

Introduction

Complaints received by water companies are most often due to bad taste and odors in drinking water. Furthermore, the presence of these unpleasant tasting but otherwise harmless compounds can be taken as unsafe water by the consumer. In most cases, complaints concern chlorine and earthy/musty smelling compounds. A better understanding of the chemical causes of taste and odors in drinking water supplies would help in the control of taste and odor problems.

For 30 years, it was commonly accepted that earthy/musty aromas in drinking water were associated with the presence of geosmin, MIB and/or haloanisoles [1, 2, 3]. MIB and geosmin have strong odors, which are detectable at extremely low thresholds. MIB has a woody or camphor odor, detectable at a threshold ranging from 5 to 10 ng/L, while geosmin has a characteristic earthy odor detectable in water at a threshold ranging from 1 to 10 ng/L [4, 5]. The presence of these compounds in water was previously associated with the presence of actinomycetes or their metabolic products [6, 7, 8] in raw water, as well as cyanobacteria and fungi [9, 10, 11]. Haloanisoles have a

musty odor at a low threshold. For instance, the threshold odor of 2,4,6-trichloroanisole ranges from 0.05 to 4 ng/L. Their formation is probably caused by microbiological methylation of halophenols during water treatment or during transport through the distribution system [12, 13, 14]. Halophenols are formed during chlorine disinfection of drinking water and some of them have been identified as natural halogenation products [15].

For a long time, the identification of these compounds in water has been a real analytical problem because they are odorous at very low concentrations. The main analytical method used to identify odorous compounds in water is Closed Loop Stripping Analysis (CLSA). With this method [16, 17], organic substances are released from the water sample in a hermetically sealed, closed circuit system, which uses air or inert gas at 40 °C to strip away the volatiles. These liberated substances are transferred to a very small amount of charcoal localized in the closed circuit. Finally, the organic substances are eluted from the charcoal with solvent and are analyzed by GC. "Purge and Trap" analysis is based on the same principles as CLSA, but it exhibits lower sensitivity and, therefore, is very useful for concentration levels above 100 ng/L. Nevertheless, these "stripping" techniques were not efficient enough for less volatile and/or more polar compounds. Some authors have used solid phase micro extraction (SPME) [18]. From a chromatographic point of view, GC linked with MS is the only detection method, which combines high powers of separation, identification, and quantitation.

Today, a novel extraction technique that is sensitive, simple, and fast is an alternative choice to conventional stripping methods. This SBSE technique is based on sorption instead of adsorption. The principle includes a magnetic stirring bar incorporated into a glass jacket coated with a 0.5-mm layer of polydimethylsiloxane (PDMS). Extraction is performed by placing a suitable sample amount in a vial, adding a stir bar, and stirring for 30 to 120 min. After extraction, the stir bar is introduced into a glass desorption tube and placed in a thermal desorption unit where it is desorbed at 200–300 °C. Compounds are detected using GC/MS.

The aim of the present study was to analyze six odorous organic compounds in water with the SBSE technique. These compounds (Table 1) must be quantified at the subnanogram/L level, under or close to their odor threshold.

Table 1. Analyzed Odorous Compounds

Name	Abbreviation	Taste	Odor threshold, ng/L	CAS number
2-methylisoborneol	MIB	Earthy	5–10	N/A
2,4,6-trichloroanisole	2,4,6-TCA	Musty	0.1–2	6130-75-2
2,3,6-trichloroanisole	2,3,6-TCA	Musty	0.1–2	50375-10-5
Geosmin	Geosmin	Camphor	1–10	19700-21-1
2,3,4-trichloroanisole	2,3,4-TCA	Musty	0.2–2	54135-80-7
2,4,6-tribromoanisole	2,4,6-TBA	Musty	0.15–10	607-99-8

Principles of SBSE

The analysis of odorous organic compounds in aqueous environmental samples must be performed after extraction and enrichment of the solutes from the matrix. Some 10 years ago, a new method was developed called SPME. With this extraction based on sorption, a relatively thin layer of PDMS (7–100 µm) coated on the outside of a needle device was used as the extraction medium. Sorptive enrichment offers several advantages over adsorption processes. These advantages include:

- Predictable sorption thanks to calculated or experimental $K_{O/W}$ [19]
- Absence of displacement effect (no breakthrough volume)
- Faster and milder desorption

In contrast to stripping techniques, SPME and SBSE are equilibrium techniques by nature, based on the partitioning of the solutes between the PDMS phase and the aqueous (or gas) matrix. In fact, the principle of these techniques is the same as liquid-liquid extraction (LLE), but with a very low quantity of solvent (0.5 µL of PDMS for SPME and 24 to 100 µL of PDMS for SBSE).

The theory of SBSE is straightforward and similar to SPME. With the approximation that the partitioning coefficient between PDMS and water ($K_{PDMS/W}$) is proportional [19] to the octanol-water partitioning coefficient ($K_{O/W}$), it can be shown that equilibrium is based on Equation 1. Recovery (R) is based on Equation 2 where m_{PDMS} is the quantity absorbed in the PDMS phase, m_W is the quantity of non-extracted analyte, β is the ratio of the volume of water/the volume of PDMS, and m_0 is the initial quantity.

$$1.\quad K_{o/w} \approx K_{PDMS/W} = \frac{C_{PDMS}}{C_W} = \frac{m_{PDMS}}{m_W} \times \frac{m_{PDMS}}{m_W} = \frac{m_{PDMS}}{m_W} \times \beta$$

$$2.\quad R = \frac{m_{PDMS}}{m_0} = \frac{\left(\frac{K_{O/W}}{\beta}\right)}{1 + \left(\frac{K_{O/W}}{\beta}\right)}$$

The only parameter governing the recovery of an analyte from the sample is the ratio of distribution coefficient and the phase ratio between the PDMS coated on the stir bar and the water sample.

Figure 1 illustrates the extraction recovery of a compound as a function of $K_{O/W}/\beta$ ratio. At a $K_{O/W}/\beta$=1, the recovery is 50%. At low $K_{O/W}/\beta$ values, the recovery is closely proportional to $K_{O/W}/\beta$ and extraction is minimal.

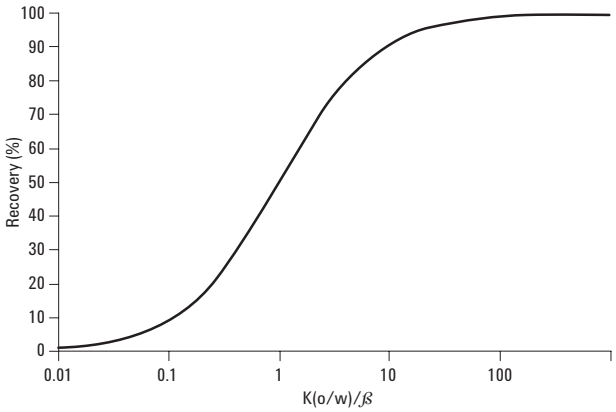

Figure 1. Recovery as a function of octanol-water partitioning constant and phase ratio.

In SPME, the maximum volume of PDMS coated on the fiber is 0.5 µL. For a typical sample volume of 10 mL, the phase ratio equals 2×10^4. This implies that quantitative extraction is only obtained for compounds with a $K_{O/W}$ in excess of 10^5. Only a very limited number of components exhibit such high $K_{O/W}$ values and, moreover, it was recently shown [20] that this type of apolar solute strongly adsorbs onto the stir bar and glass vial, as used in SPME. In SBSE, on the other hand, the situation is more favorable. A stir bar coated with 100 µL of PDMS can easily be used to extract 10 mL of water leading to a β factor of 100, which implies that solutes with $K_{O/W}$ in excess of 500 are quantitatively extracted into the PDMS coated stir bar. This not only renders quantification straightforward but also ensures a significant sensitivity for those compounds with $K_{O/W}$ below 10^5.

In Figure 2, the theoretical extraction recovery of analytes from a 10-mL water sample is shown for SPME and SBSE. It is clear that quantitative extraction is obtained at much lower $K_{O/W}$ in SBSE compared to SPME. This is due solely to the much lower phase ratio in SBSE. In case of incomplete extraction with SBSE, calibration is still possible using water samples with known concentrations of the target solutes.

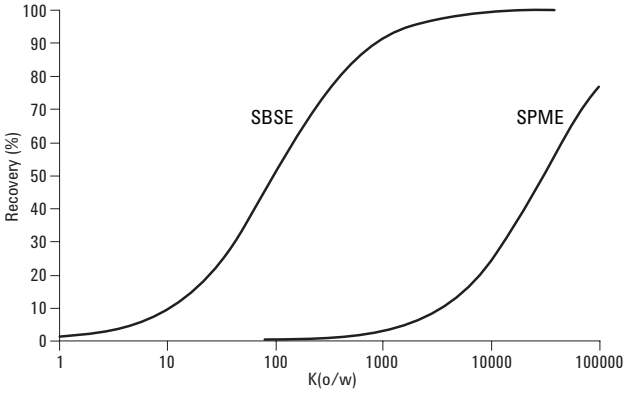

Figure 2 . Theoretical recovery as a function of octanol-water partitioning constant and typical phase ratio for SBSE and SPME (that is, the volume of PDMS on the SPME fiber = 0.5 µL, the volume of PDMS on the SBSE stir bar = 100 µL, and the volume of extracted water = 10.0 mL).

So far, the discussion has been limited to the equilibrium conditions of SBSE. However, considering the thickness of the coating (0.5 or 1 mm), the speed of extraction (required equilibration time) is also an important factor to consider. Due to the thickness of the coating, it is assumed that all resistance to mass transfer is in the coating and that the sample is perfectly stirred. For this situation it is possible to apply Equation 3 [21]

$$3.\quad t_{95\%} = \frac{d^2_{PDMS}}{2D_{PDMS}}$$

where $t_{95\%}$ is the time required to reach 95% extraction, d_{PDMS} is the thickness of the PDMS layer used (in meter), and D_{PDMS} is the diffusion coefficient of the analyte under investigation in PDMS, in m^2/s. For instance, for benzene (D_{PDMS}=2.5*10^{-10} m^2/s) the equilibration time is 30 minutes.

Experimental

Equipment

The gas chromatograph used was an Agilent 6890 - Agilent 5973 MSD (Agilent Technologies, Palo Alto, CA, USA)-olfactometric detector combination (GERSTEL® GmbH, Mülheim a/d Rhur, Germany). This chromatograph was equipped with a thermal desorption unit (TDSA) and a PTV inlet (CIS-4) from GERSTEL GmbH, Mülheim a/d Rhur, Germany.

Samples were extracted with 20-mm long stir bars (also called GERSTEL-Twister®) having a 0.5-mm layer of PDMS. The stir bar was thermally desorbed in the splitless mode using the following desorption temperature program: 30 °C (0.8 min), 60 °C/min to 280 °C (5 min). The desorbed solutes were cryofocused in the CIS-4 at -100 °C. After the stir bar desorption, the PTV inlet was programmed to 300 °C at 10 °C/s and held for 2 min. Injection was done in solvent vent mode. The compounds were separated on a 30 m × 0.25 mm id × 0.25 µm HP5-MS capillary column using helium carrier gas at 1.5 mL/min (constant flow). The oven was programmed from 50 °C (2 min) to 200 °C at 10 °C/min then to 300 °C at 25 °C/min (2 min). Detection was achieved in SIM mode for quantitative analysis and in scan mode for qualitative analysis. The olfactometer transfer line was heated at 250 °C. One-third of the effluent was directed to the mass spectrometer and two-thirds to the olfactometer.

Chemical Standards and Reagents

- Methanol (pesticide grade) obtained from Merck (Darmstad, Germany)
- Spring water to prepare blanks and standards
- The standard compounds 2-methylisoborneol; 2,4,6-trichloroanisole; 2,3,6-trichloroanisole; 2,3,4-trichloroanisole; 2,4,6-tribromoanisole; geosmin; and 2,4,6-trichloroanisole-d_5 obtained from Promochem (France).
- A stock solution containing MIB, geosmin, and the haloanisoles at 1 µg/L was prepared in spring water. Storage conditions for this stock solution: 4 °C for 1 month.
- An internal standard solution of 2,4,6-TCA-d_5 prepared in spring water at 20 µg/L. Storage conditions for this solution: 4 °C for 1 month.

Extraction Procedure

Extractions were performed in duplicate by placing a Twister (20-mm long, 0.5 mm of PDMS) into a 125-mL vial with 100 mL of the water sample and 5 mL of methanol. Each vial was spiked with 40 µL of the 2,4,6-TCA-d_5 internal standard solution. After stirring both samples for 2 hours at room temperature, the Twisters were removed from the duplicate samples and dried with a clean wipe. In order to increase sensitivity, both Twisters were introduced into a single glass desorption tube and desorbed using the conditions noted above.

Results and Discussion

Tuning the Mass Selective Detector (MSD)

To enhance sensitivity even further, the MSD was tuned manually in order to increase transmission of desired ions. Perfluoro-5,8-dimethyl-3,6,9-

trioxadodecane (PFDTD) was used as the calibrant. Conventional Autotunes are performed for optimum monitoring of the 69, 219, and 502 PFTBA ion ratios. The 219/69 and 502/69 ratios are usually about 60% and 3%, respectively, although this can vary considerably. Since the target compounds have masses ranging from 112 to 344, manual tuning was used to adjust the 219/69 ratio to 110% and the 414/69 ratio to 10%. The 414 ion was used instead of 502 because it is closer in mass to the target ions of the analytes. These ratios could be obtained using one of two procedures. The first approach was to ramp the repeller for ions 69, 219, and 414 and to choose the optimum response for 219. The second way was to perform a Target Tune by specifying the desired abundances and ion ratios for selected ions in the Agilent ChemStation.

This manual tune was used only for quantitative applications because structural information was not required. When using this manual tune, the Probability Based Matching System gave no satisfactory matching between an unknown and a reference spectrum from the NIST or Wiley libraries.

Mass Spectra of MIB, Geosmin and Haloanisoles

Figure 3 shows the experimental mass spectra for the target compounds listed in Table 1. For monitoring ions in the SIM mode, 95, 108, 110 were chosen for MIB, 112 and 125 for geosmin, 210 and 212 for the three chloroanisoles, 346 and 344 for the 2,4,6-tribromoanisole. The internal standard, 2,4,6-trichloroanisole-d_5, was monitored at *m/z* 217.

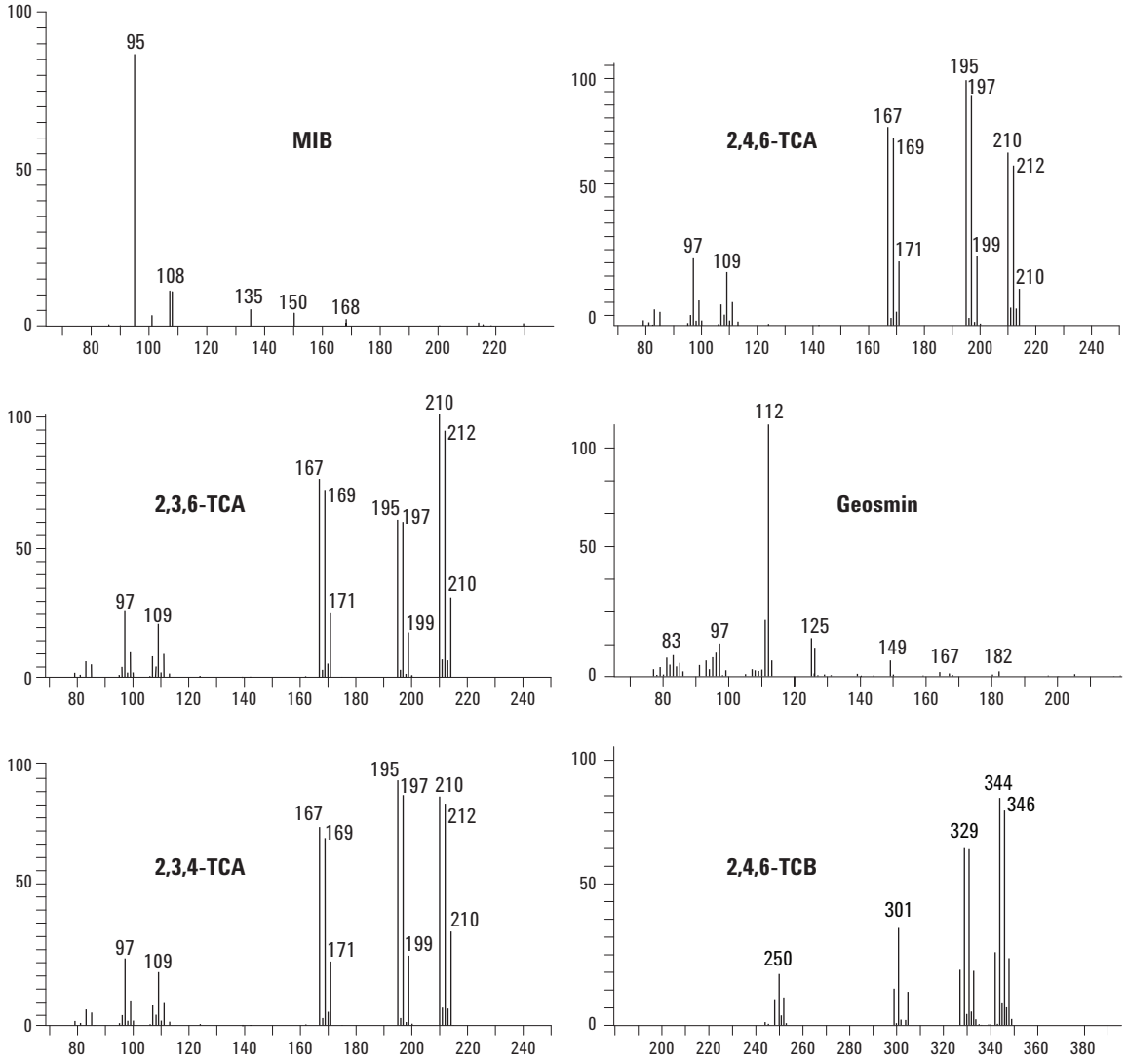

Figure 3. Experimental mass spectra of target compounds.

Figure 4 shows a SIM chromatogram of spring water spiked with 2 ng/L of each target compound.

Influence of Extraction Time

This experiment measured the sorption rates of compounds into PDMS. Spring water spiked with 2 ng/L of each compound was analyzed after extraction times ranging from 15 min to 300 min. Figure 5 shows the relationship between the extraction time and the response obtained for target compounds.

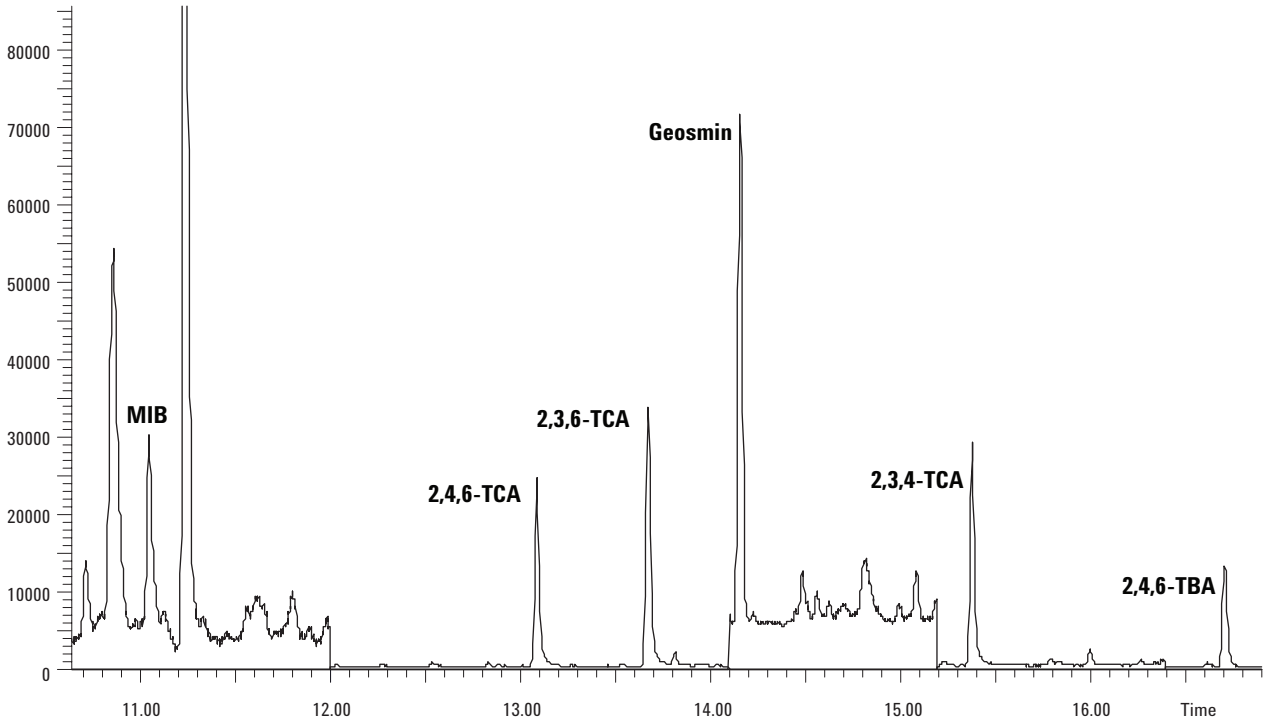

Figure 4. SIM chromatogram of target compounds.

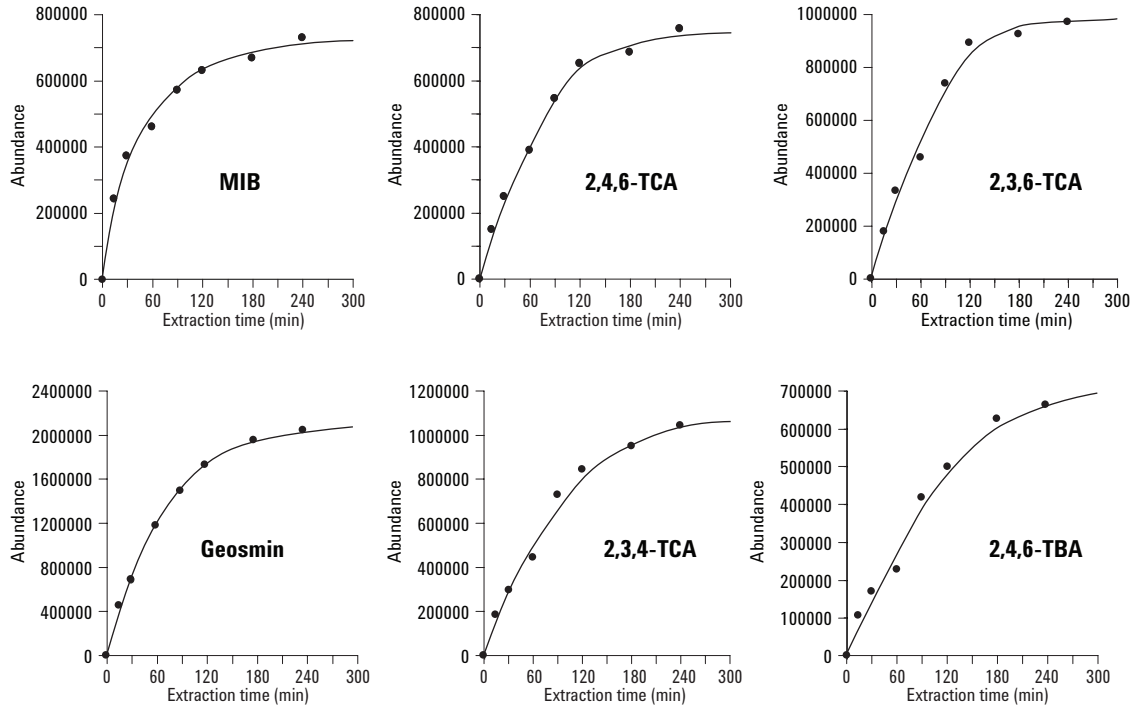

Figure 5. Influence of extraction time upon quantity extracted on PDMS.

For all compounds, the sorption rate is fast for the first 120 minutes and then slows without reaching a plateau. For routine analysis with high sample throughput, an extraction time of 120 minutes was empirically chosen.

Influence of Sample Volume

According to Equation 2, maximum recovery can be estimated with the octanol/water distribution coefficient ($K_{O/W}$). Log $K_{O/W}$ values for the target compounds were experimentally determinated and calculated using KnowWin software [19].

Table 2. Octanol/Water Distribution Coefficients ($K_{O/W}$) of Investigated Compounds

Name	Experimental log $K_{O/W}$	Calculated log $K_{O/W}$
2-methylisoborneol	3.31	2.85
2,4,6-trichloroanisole	3.85	4.01
2,3,6-trichloroanisole	3.64	4.01
Geosmin	n/a	3.57
2,3,4-trichloroanisole	3.74	4.01
2,4,6-tribromoanisole	4.48	4.75

For this experiment, different sample volumes of spring water from 10 to 200 mL were spiked with 1 ng of each compound. Extraction was done for 2 hours with a 2-cm long Twister (47 µL PDMS). Figure 6 shows experimental recoveries (A) compared to theoretical recoveries estimated using calculated $K_{O/W}$ (B) and experimental $K_{O/W}$ (C) values.

Experimental results were in accordance with theory (the more sample volume increases, the more the recovery decreases), but were inferior to expected values. This experiment proved that equilibrium was not reached after 2 hours of stirring. The difference between experimental and expected values increased when the sample volume increased and it was dependant on the compound.

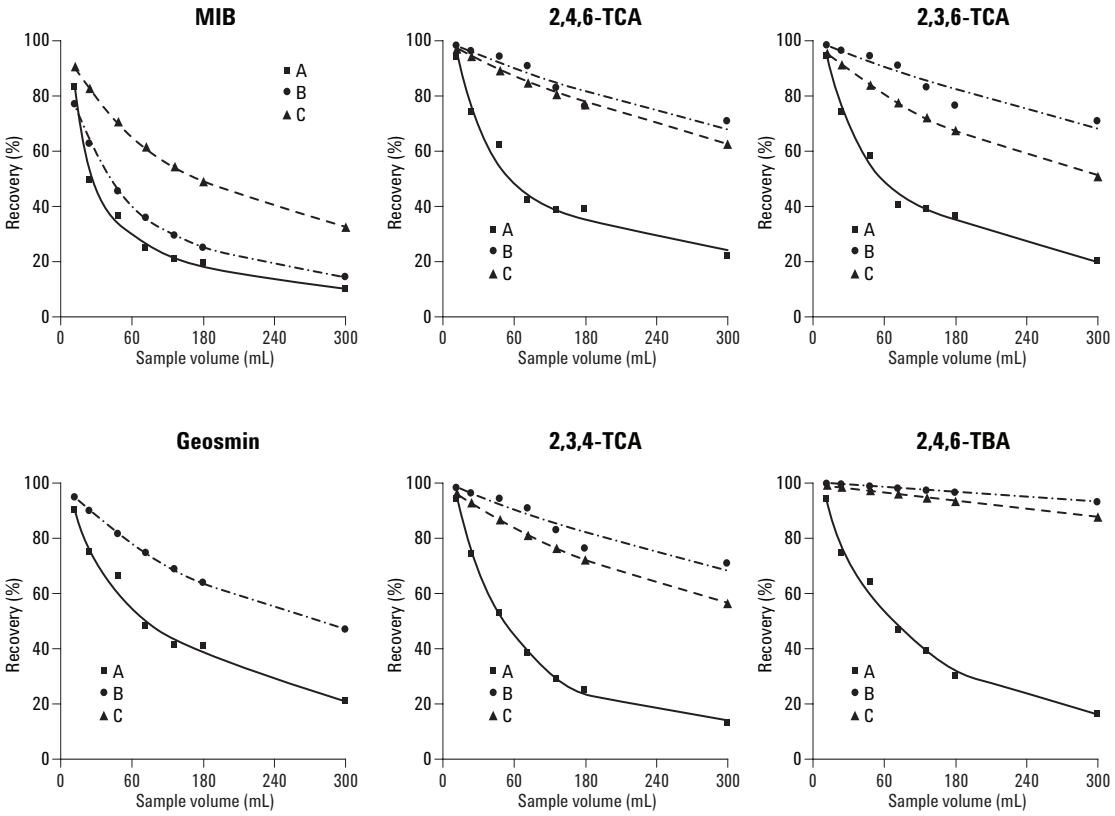

Figure 6. Influence of sample volume on recovery. A: Experimental results, B: Theoretical results (calculated $K_{O/W}$), C: Theoretical results (experimental $K_{O/W}$).

However, the enrichment on the PDMS media increases with the sample volume as shown in Figure 7. For most of the compounds, the extracted amount increases up to 100 mL of the sample and a volume of 200 mL does not lead to a significant gain in response. In order to achieve concentrations close to the odor threshold, it was necessary to use two 100-mL aliquots of each sample and two Twisters, which were desorbed together.

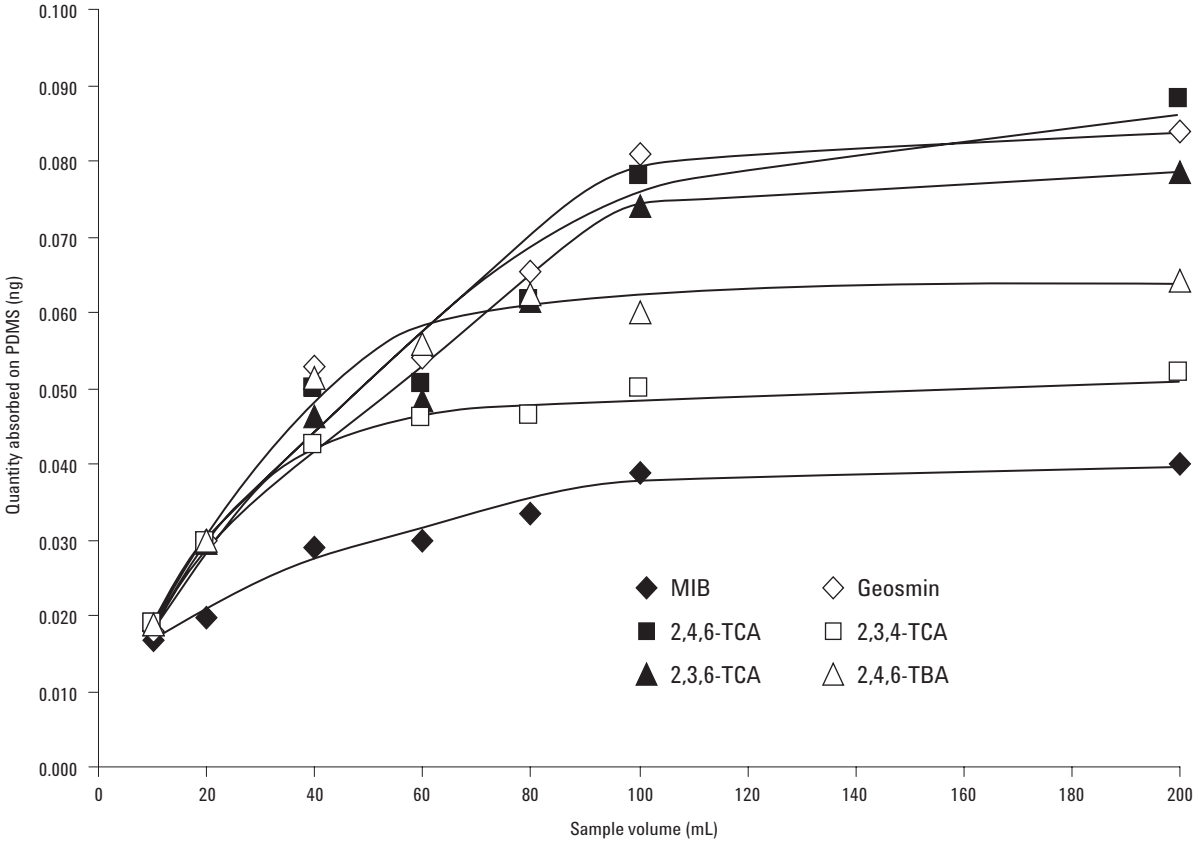

Figure 7. Influence of sample volume on quantity extracted.

Influence of Storage After Extraction

Extraction of a spring water sample spiked with 2 ng/L of each compound was replicated six times; each 100-mL sample was extracted by one Twister for 2 hours. One Twister was analyzed immediately and the others were stored at 4 °C in closed vials for later analysis. Figure 8 shows the influence of storage time on the response for all compounds.

These results show that no compound loss occurs during 1 week of storage and imply that:

- It is possible to store the Twister after extraction instead of storing water samples when the chromatographic analysis cannot be done immediately.
- Instead of sending bad tasting or odorous water samples to the laboratory, it would be possible to extract off-flavor compounds directly at the consumer's home.

Method Validation

This method was validated according to the AFNOR regulation XP T 90-210. This validation determines the following:

- The scope of linearity: linearity was studied over seven concentration levels, from 0.1 to 10 ng/L, replicated five times. Calibration was done in internal standard mode with 2,4,6-TCA-d_5. Linearity is achieved when the correlation coefficient (R) is better than 0.999.
- The LOQ is validated when the relative standard deviation (RSD) of 10 replicate samples, spiked with supposed LOQ, is under 20%.
- The repeatability is expressed as %RSD and is calculated on the basis of three replicates of eight different water samples. It must be under 20%.
- The trueness is expressed as the percent recovery of spiked real water samples and must be between 80% and 120%.
- The reproducibility is expressed as a %RSD of a check calibration standard (2 ng/L). It must be under 20%.

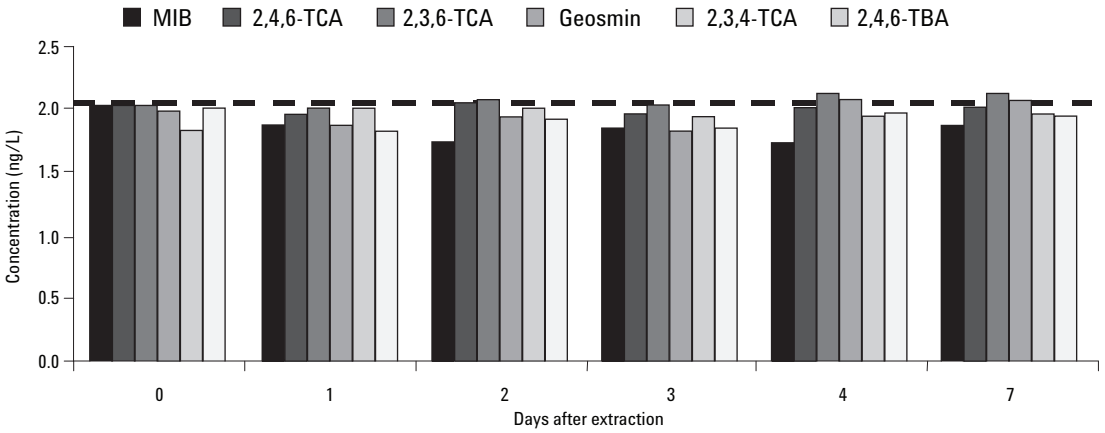

Figure 8. Influence of Twister storage time after extraction.

The results of this validation are summarized in Table 3 and in the calibration curves shown in Figure 9.

Table 3. Validation Results for Target Compounds

	R	LOQ, ng/L	Repeatability %	Trueness %	Reproducibility %
MIB	0.9987	1	4–10	89–110	13
2,4,6-TCA	0.9998	0.1	1–5	97–110	4
2,3,6-TCA	0.9998	0.1	4–11	97–117	5
Geosmin	0.9991	0.5	2–10	83–101	9
2,3,4-TCA	0.9998	0.2	7–15	87–110	13
2,4,6-TBA	1.0000	0.2	2–9	91–104	15

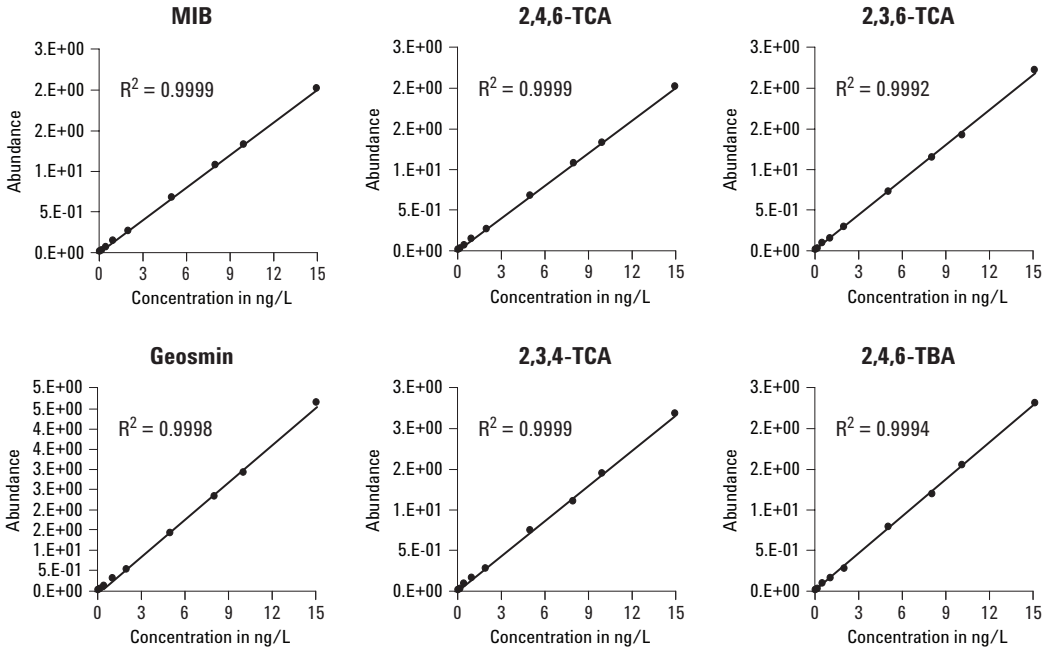

Figure 9. Calibration curves for investigated compounds.

The validation criteria were achieved for all target compounds.

Application to Real Water Samples

Different water samples were analyzed following complaints about taste and odor problems.

Case 1

Two samples (A and B) were collected at the consumer's home. Sample A gave a very pronounced musty odor and sample B gave a soft musty odor and a pronounced metallic odor. Samples A and B were treated by SBSE and analyzed in SIM mode in order to detect MIB, geosmin, and the haloanisoles. Quantitative results and chromatograms for each sample appear in Table 4 and in Figure 10.

Table 4. Concentration of Target Compounds in Sample A and B

	Sample A [C] (ng/L)	Sample B [C] (ng/L)
2-methylisoborneol	<1	<1
2,4,6-trichloroanisole	**8.9**	**0.2**
2,3,6-trichloroanisole	<0.1	<0.1
Geosmin	**5.2**	<0.5
2,3,4-trichloroanisole	<0.2	<0.2
2,4,6-tribromoanisole	**0.4**	**1.3**

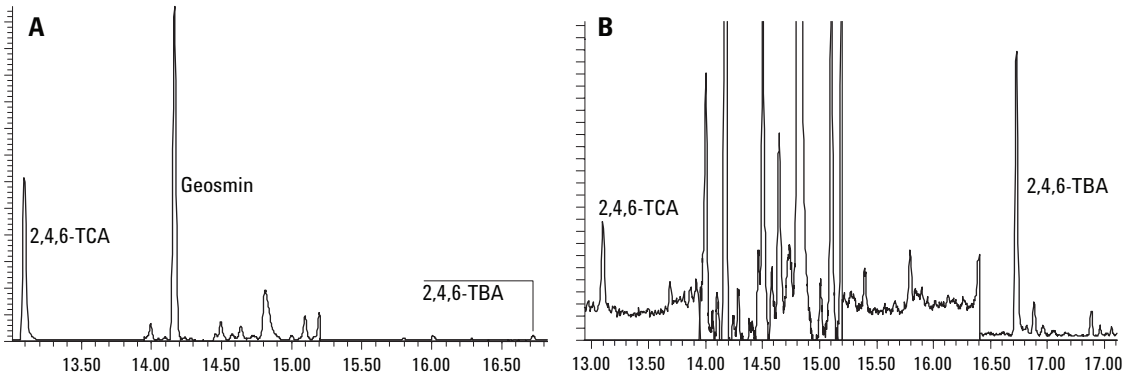

Figure 10. SIM chromatograms for samples A and B.

The concentration levels found in both samples can certainly explain the musty odor. In order to identify the other odorous compounds, the water samples were treated another time by SBSE without internal standard, and the GC/MS was run in the scan mode.

For sample A, the olfactometric detection showed a pronounced musty odor at the retention times of 2,4,6-TCA and geosmin, but also a medicinal one at 8 minutes and a solvent-like one at 14 minutes. For sample B, the olfactometric detection gave a mild musty odor at the retention time of 2,4,6-TBA and also a medicinal one around 8 minutes.

Interpretation of isotope ratios in the spectra for sample A showed two halogenated compounds - a brominated one (8.4 min) and a chlorinated one (13.9 min). The medicinal odor was associated with dibromoiodomethane, which is a chlorination byproduct. The solvent odor was associated with tetrachlorobenzene as shown in Figure 11. For sample B, dibromoiodomethane was also detected.

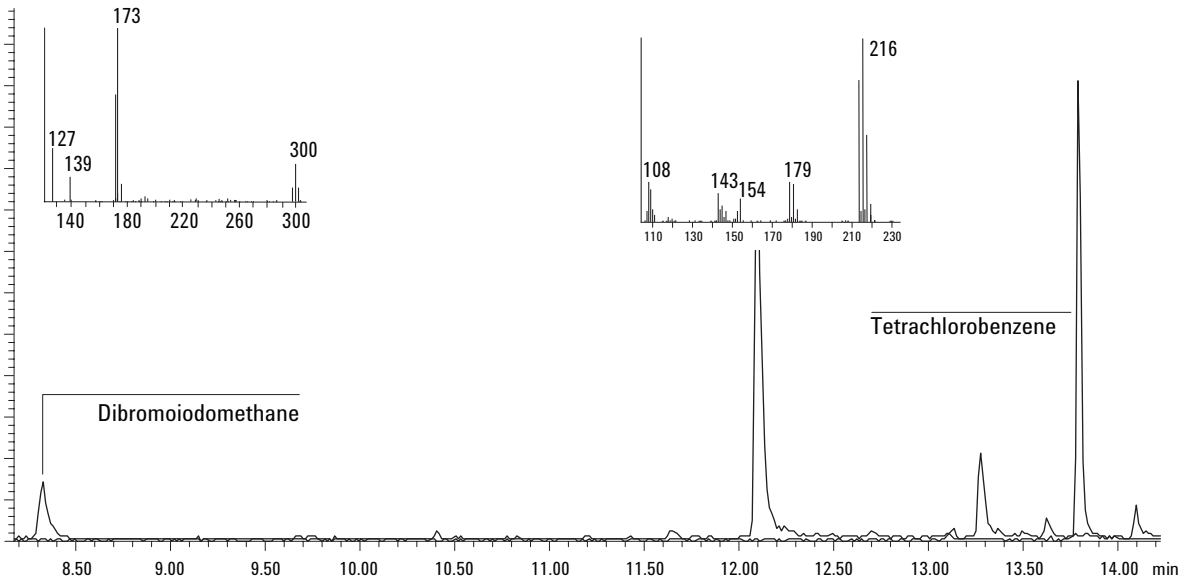

Figure 11. Sample A Scan chromatogram.

Case 2

In this case, an off-flavor episode occurred in a tank located near Paris. Degradation of the water's organoleptic quality was observed soon after some cracks appeared on the tank's coating and important living organisms were found on the interrior surface. Following complaints, several flavor analyses were performed on water originating from the tank. Results indicated that the chlorinous taste of the treated water was masked by an intense musty taste (Threshold Test Number: 5).

Drinking water stored in this tank is produced from ground water which undergoes a two-step treatment process: the water first undergoes aeration and sand filtration for iron removal and then the water is chlorinated just prior to entering the tank. The tank's coating, which must provide an impermeable seal to the water during storage, is a synthetic coating prepared by mixing a gray elastic cement and a white synthetic resin in aqueous solution. The theoretical mechanical and physical properties of this coating ensure high elasticity and no release of organic compounds. Filtered and chlorinated waters were treated by SBSE for quantitative analysis in order to search for the target odorous compounds.

Quantitative results and chromatograms of each sample appear in the Table 5 and in Figure 12.

Table 5. Concentration of Target Compounds in Filtered and Chlorinated Waters

	Filtered water [C] (ng/L)	Chlorinated water [C] (ng/L)
2-methylisoborneol	<1	<1
2,4,6-trichloroanisole	<0.1	<0.1
2,3,6-trichloroanisole	<0.1	<0.1
Geosmin	<0.5	<0.5
2,3,4-trichloroanisole	<0.2	<0.2
2,4,6-tribromoanisole	< 0.2	**5.6**

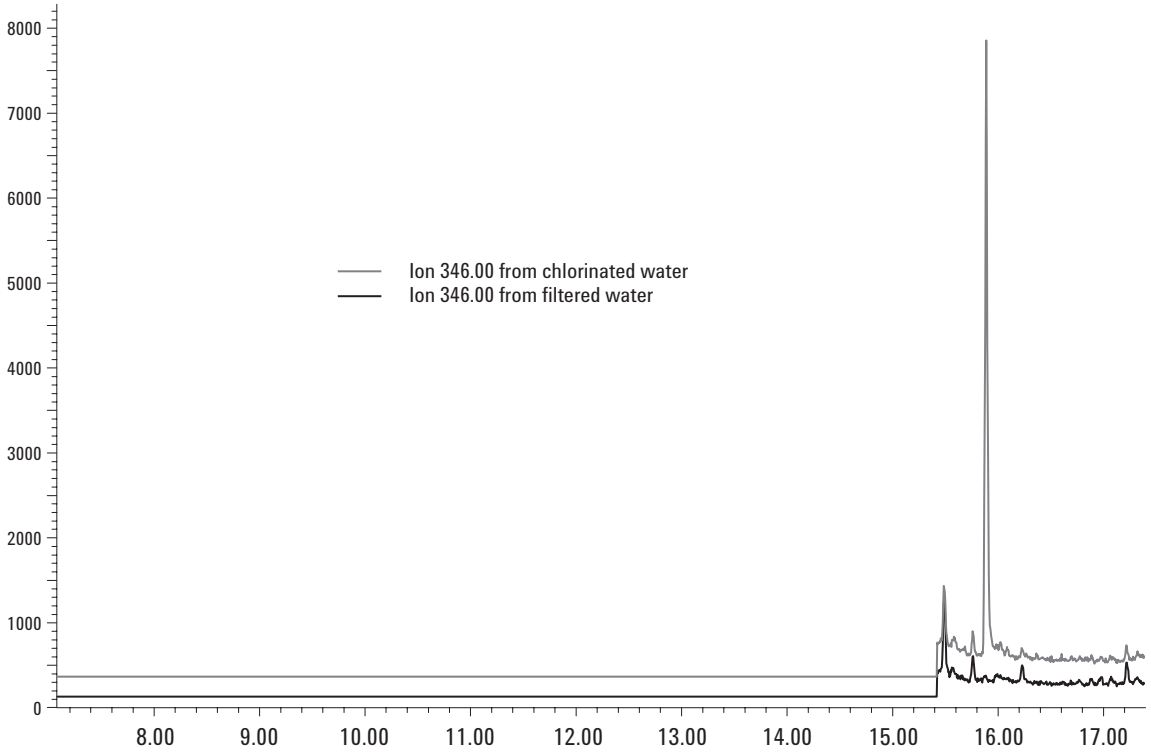

Figure 12. EIC (*m/z:* 346) of chlorinated and filtered water.

The only compound found among the six targets was 2,4,6-tribromoanisole at a concentration of 5.6 ng/L. The presence of 2,4,6-TBA can easily explain the significant musty taste imparted to the water. None of the target compounds was found in the filtered water.

GC with olfactometric detection of filtered water did not exhibit any of the characteristic odors. However, for chlorinated water, it gave a significant musty odor at the retention time of 2,4,6-TBA in addition to different phenolic odors at around 8, 14, and 17 minutes. In order to make phenolic compounds more amenable to GC, they were derivatized with 1 g of K_2CO_3 and 500 µL of acetic anhydride for 100 mL of water sample. Detection was achieved in scan mode for qualitative analysis. Results obtained for both sniffing and MS detection appear in Table 6 and in the scan chromatogram in Figure 13.

Table 6. Odors Generated During the Chromatographic Run Time for Sample B

Tr (min)	Odor	Intensity	Qualification (acetate derivative)
8.5	Phenolic	++++	Phenol
13.7	Phenolic	++	2,4,6-trichlorophenol
15.9	Musty		2,4,6-tribromoanisole
16.8	Phenolic	+++	2,4,6-tribromophenol

According to these results, the hypothesis was that the tank's coating released phenol, which was halogenated to 2,4,6-TCP and 2,4,6-TBP because of the residual chlorine. 2,4,6-TBA was then synthesized by living organisms present at the surface of the coating. The authors cannot yet explain why only 2,4,6-TBA was formed by living organisms despite the presence of both 2,4,6-TCP and 2,4,6-TBP.

Case 3

This case consisted in studying deterioration in organoleptic quality of water along the network distribution system. The complaints came only from consumers who were located far from the treatment plant. Two samples were taken - the first one at the outlet of the treatment plant (sample A) and the second one at the consumer's home at the end of the network (sample B). Sample A gave only a chlorine odor whereas sample B gave musty, swampy, earthy odors (Threshold Test Number: >10).

The two samples were treated by SBSE in order to monitor MIB, geosmin, and haloanisols. The results showed that sample A was free of these compounds. In sample B, 2,4,6-TCA and 2,3,4-TCA were found at 0.1 ng/L and 0.2 ng/L, respectively. However, these concentrations cannot explain the significant taste and odor impairment. Fresh water samples were treated another time by SBSE without internal standard. These were analyzed by TDS/GC/MS in the scan mode and by olfactometry.

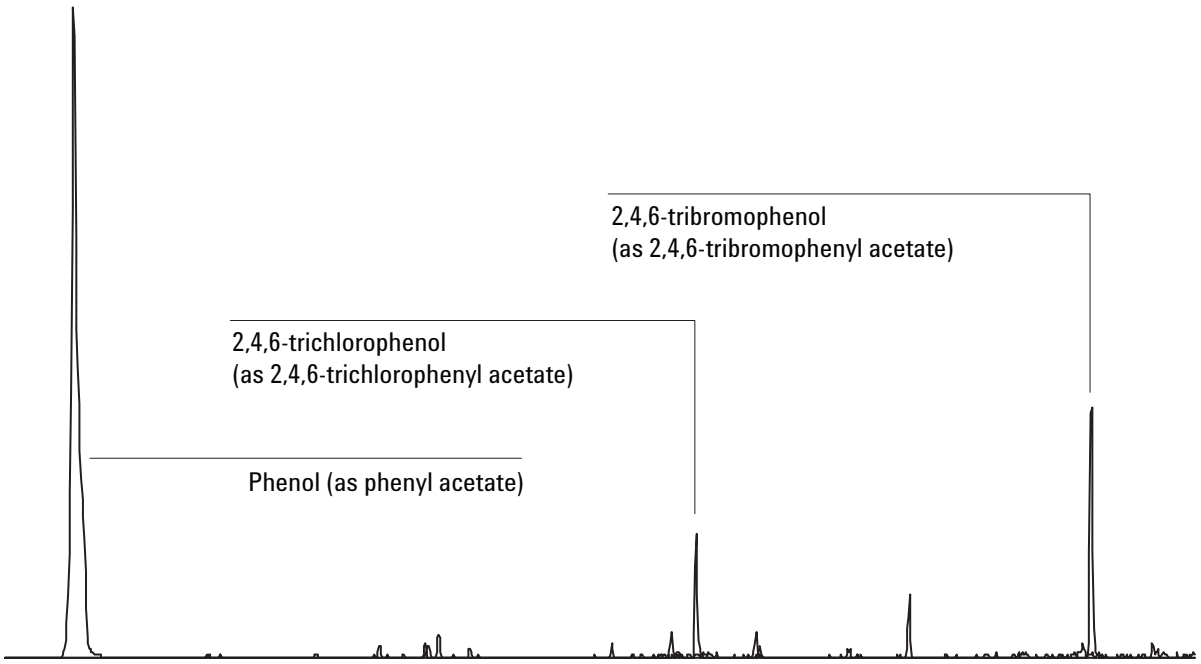

Figure 13. TIC of water sample after insitu-derivatization.

Olfactometry allowed the detection of various odors along the chromatographic run time for sample B, whereas nothing was smelled in sample A. The results for sample B for both sniffing and MS detection are listed in Table 7.

Table 7. Odors Generated During the Chromatographic Run Time for Sample B

Tr (min)	Odor	Qualification
7	Sweaty	Phenylacetaldehyde
7.8	Swampy	Dimethyltrisulfide
10.7	Citrus	Decanal
12	Flower	Undecanal
12.8	Sweaty	Not qualified
12.9 to 15.2	Musty	Alkylbromobenzene isomers
16.07	Rancid	Isopropyldodecanoate
16.8 to 17.4	Tar	Diisopropylnaphthalene
20.15	Tar	Dodecahydrophenanthrene

Seven different odors were detected by sniffing detection and some of them were in good agreement with the flavor profile analysis, as for instance, the swampy smell associated with dimethyl trisulfide. A musty odor was smelled from 13 to 15 minutes and was matched to different alkylbromobenzene isomers, of which the major component was 2-methyl-4-isopropylbromobenzene. Rancid and tar odors corresponded with isopropyldodecanoate and dodecahydrophenanthrene, respectivly. Pleasant odors like sweet and fruity (aldehyde compounds) were not detected by tasters.

Figure 14 shows the comparison of total ion chromatograms (TIC) of each compound that could be smelled in samples A and B.

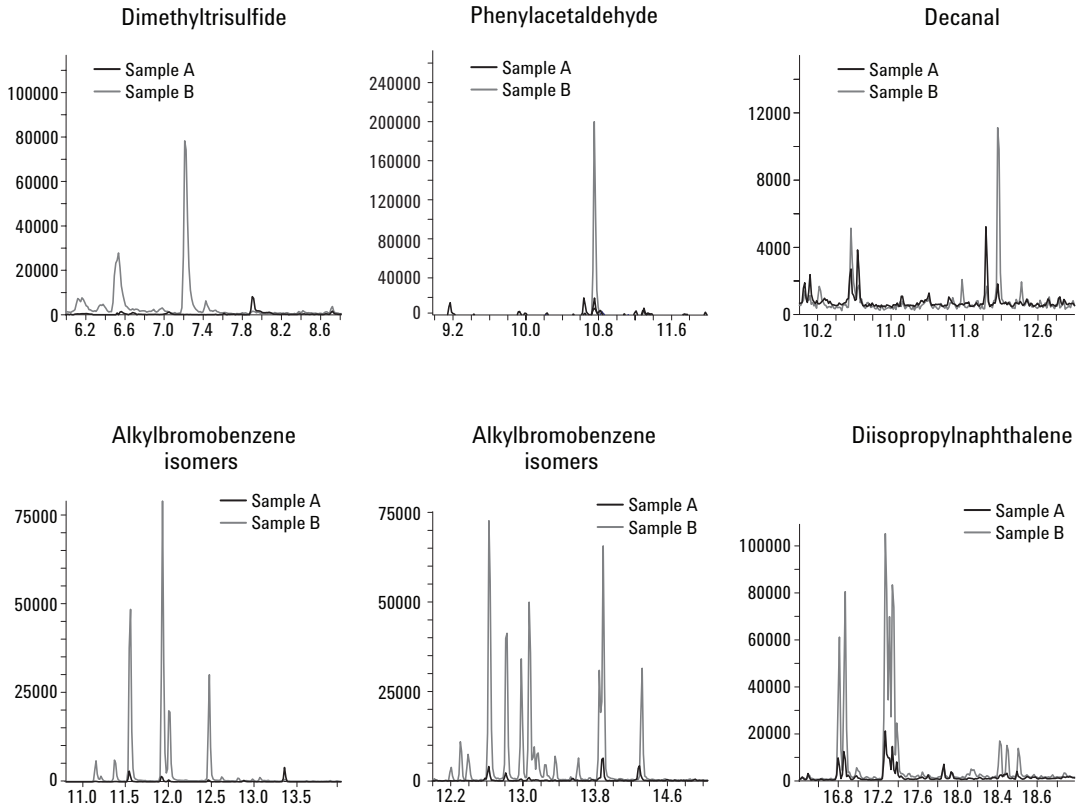

Figure 14. EIC of samples A and B for dimethyltrisulfide, phenylacetaldehyde, decanal, alkylbromobenzene isomers, and diisopropylnaphthalene.

Conclusions

- Most often, taste and odor problems in drinking water are due to very low traces of compounds present in a complex mixture. That is why GC/MS is the best separation and detection choice to quantify odorous compounds.
- A rapid SBSE-TD-GC/MS-Olfactometry method for the determination of MIB, geosmin, and haloanisol compounds in water samples was developed. The combination of TD-GC/MS and the SBSE made it possible to quantify all of the odorous components at levels close to or under their odor threshold limit.
- The influence of extraction time, sample volume, and storage time were studied in order to optimize the method's sensitivity. The final method was validated according to the AFNOR regulation. Linearity was checked with the correlation coefficient (R) ranging from 0.9987 to 1.0000. The repeatability and reproducibility values were under 15%. Recoveries were all between 87% and 117%, depending upon the compound.
- Storage time for Twisters is for at least 7 days after extraction without loss of the extracted compounds.
- When applied to real odorous water samples, SBSE showed a good correlation between flavor profile analysis, MS analysis, and olfactometric detection. In addition to the target compounds, it was possible to identify unknown odorous compounds at very low levels far more rapidly than possible using conventional techniques.

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