Headspace solid-phase microextraction for the determination of trace levels of taste and odor compounds in water samples

The Analyst

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The use of the headspace solid-phase microextraction (SPME) technique, combined with gas chromatography-ion-trap detection mass spectrometry (GC-ITDMS), for the determination of 34 taste- and odor-causing organic compounds in water is presented. The compounds studied include aliphatic hydrocarbons, aldehydes, ketones and alcohols. The factors affecting the headspace SPME process, such as fiber type, salt addition, stirring, headspace volume and sampling time, were examined. The polydimethylsiloxane-divinylbenzene-coated fiber was found to be effective for the extraction of the compounds studied. The precision of the method was evaluated with spiked bidistilled water and river water samples. The RSDs obtained were similar for both water samples and in the range 4.3–17.1%. Using the standard addition calibration method, the problem of matrix effects observed for river water samples can be reduced. The method showed good linearity over two orders of magnitude of concentration in river water. With 40 ml of water sample, the detection limits were lower than 1 ng l^{-1} for 2-methylisoborneol and geosmin, and 0.8–50 ng l^{-1} for the other compounds.

Introduction

The control of taste and odor problems in drinking water is of great importance to water utilities because the taste and odor of the drinking water are the primary criteria that consumers use for judging the quality and acceptability of their water supply. Numerous surveys of customer attitudes and opinions about the quality of drinking water, both in Europe and in the USA, have shown that the public generally is more concerned about how their water tastes and smells than about other issues regarding their water supply, and taste and odor complaints from consumers are frequently the major problems received by the drinking water suppliers.[1]

Worldwide, most of the taste and odor problems in drinking water supplies appear to be caused by the presence of certain metabolites, such as aliphatic hydrocarbons, aldehydes, ketones, alicyclic alcohols and sulfur-containing compounds, produced by algae and microbiological processes in raw water or in finished water storage facilities and piping.[2–4] For example, most of the earthy–musty odor problems have been reported to be caused by two biogenic alicyclic alcohols: 2-methylisoborneol (MIB) and geosmin.[3] Because of the varying characteristics of the organic compounds present in raw water over a range of concentrations, the control and treatment of the taste and odor problem are difficult if the specific causes of a particular off-flavor are unknown. The analytical methods used for the detection and quantification of taste- and odor-causing compounds in water samples include sensory and instrumental analysis. Sensory analysis is based on the use of trained human noses (panelists), common descriptive terms and reference standards. Results obtained with sensory analysis, such as the flavor-profile analysis (FPA) method,[5] include the description of each flavor and its respective intensity. However, sensory analysis is not always reliable since there can be marked differences in the response, not only between individuals to specific compounds,[6] but also of individuals from day to day.[7]

Because a variety of organic compounds are present in water, and many known taste- and odor-causing compounds, such as geosmin and MIB, can cause off-flavor problems at concentrations as low as a few ng l^{-1}, the instrumental analytical methods require very low detection limits and a high discriminatory capability. The most suitable method for the determination of taste- and odor-causing compounds at trace levels present in water involves a preconcentration step in combination with capillary gas chromatography (GC) followed by mass spectrometry (MS) for compound identification. A variety of methods, including closed-loop stripping analysis (CLSA),[8,9] open stripping analysis (OSA),[10] liquid–liquid extraction (LLE),[11] solid-phase extraction (SPE) with different adsorbents,[12,13] hollow fiber stripping analysis (HFSA)[14] and liquid–liquid microextraction (LLME),[15] have been reported to date for the preconcentration of taste- and odor-causing compounds from water samples. CLSA, OSA and HFSA in combination with GC–MS can detect low ng l^{-1} concentrations of taste- and odor-causing compounds, such as MIB and geosmin, in water, but these methods are time consuming and expensive because of the specialized equipment. SPE and LLME are rapid and inexpensive, but to achieve the required limits of detection, a concentration step (solvent evaporation) is required, which increases the sample preparation step and may also cause the loss of volatile analytes during the evaporation.

Recently, solid-phase microextraction (SPME), developed by Pawliszyn and co-workers,[16,17] has become popular in environmental analysis. SPME is a convenient and solvent-free extraction method that involves the use of a thin polymer-coated silica fiber to adsorb analytes of interest from a sample matrix. This method combines extraction, concentration and sample introduction in one step, and has been shown to be efficient for the extraction of organic compounds with different volatility and polarity from different environmental samples, such as water,[18–23] air[24,25] and soil,[26,27] flavors in beverages and food,[28–31] and drugs in biological matrices, such as human blood and urine.[32,33]

The purpose of this paper was to develop and optimize an SPME procedure for the determination of trace levels of taste- and odor-causing compounds belonging to different classes in

water. The method is based on the extraction of the analytes of interest from the headspace over the water sample with SPME followed by gas chromatography-ion-trap detection mass spectrometry (GC-ITDMS) analysis. Factors affecting the SPME process, such as the extraction mode, fiber type, effects of salt addition and stirring, headspace volume over the water sample, precision, linear range and detection limits, were examined.

Experimental

Reagents

Table 1 lists the 34 taste- and odor-causing compounds studied. The compounds selected represent four groups: aliphatic hydrocarbons (α-pinene, β-pinene, camphene, 2-carene, 3-carene, α-terpinene, γ-terpinene, limonene, 2,6-dimethyl-2,4,6-octatriene), aldehydes (C_6–C_{10} linear aldehydes, benzaldehyde, citronella, β-cyclocitral, citral, 2,4-decadienal), ketones (2-methyl-3-heptanone, 6-methyl-5-hepten-2-one, fenchone, camphor, pulegone, geranylacetone, β-ionone) and alcohols (dihydromyrcenol, linalool, borneol, menthol, MIB, α-terpineol, geosmin). The standards of all these compounds were purchased from Aldrich (Milwaukee, WI, USA) with the exception of MIB (99.9%) and geosmin (>98%) which were obtained from Wako Pure Chemicals, Ltd. (Osaka, Japan). Stock standard solutions of each compound at 1 mg ml^{-1} were prepared with pure analyte dissolved in methanol, and then diluted with methanol to prepare mixed working standard solutions. Stock standard solutions were kept at −20 °C. Sodium chloride (NaCl) of analytical grade (Merck, Darmstadt, Germany) was previously heated at 550 °C for 8 h.

Apparatus

The SPME holder for manual sampling and SPME fibers were obtained from Supelco (Bellefonte, PA, USA). Four commercially available SPME fibers differing in sorbent phase coating [100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane-divinylbenzene (PDMS-DVB), 65 μm carbowax-polydimethylsiloxane (CW-DVB) and 75 μm carboxen-polydimethylsiloxane (CX-PDMS)] were tested and compared in this study. The fibers were conditioned in the GC injector port according to the manufacturer's instructions. A magnetic stirrer from VELP Scientifica (Milan, Italy) was used for stirring the water samples during the SPME procedure.

Analyses were carried out in a Varian (Walnut Creek, CA, USA) 3400 GC system coupled to a Finnigan (San Jose, CA, USA) Mat 800 ion-trap detection mass spectrometer. A 30 m × 0.25 mm id (0.25 μm film thickness) DB-5 coating fused-silica capillary column (J & W Scientific, Folson, CA, USA) was used. The GC oven was held at 40 °C for 1 min, increased to 130 °C at 4 °C min^{-1} and then from 130 to 280 °C at 10 °C min^{-1}. The carrier gas was helium at 9.65 × 10^4 Pa. The injection port was kept at 240 °C for PDMS, PDMS-DVB and CW-DVB fibers, and at 280 °C for the CX-PDMS fiber. Injections (fiber desorption) were carried out in the splitless mode and the split valve was closed for 3 min. Preliminary experiments showed that complete desorption was achieved for all the extracted analytes after 3 min of desorption at a temperature of 240 °C for PDMS, PDMS-DVB and CW-DVB

Table 1 Nomenclature of taste- and odor-causing compounds investigated in this study

Common name	IUPAC name	M_r[a]	CAS NR[b]
Hexanal	Hexaldehyde	100.2	66-25-1
Heptanal	Heptaldehyde	114.2	111-71-7
α-Pinene	2,6,6-Trimethylbicyclo(3.1.1)hept-2-ene	136.2	80-56-8
2-Methyl-3-heptanone	Butyl isopropyl ketone	128.2	13019-20-0
(+)-Camphene	2,2-Dimethyl-3-methylene-[1*r*]-bicyclo(2.2.1)heptane	136.2	5794-03-6
Benzaldehyde	Benzaldehyde	106.1	100-52-7
β-Pinene	6,6-Dimethyl-2-methylenebicyclo(3,1,1)heptane	136.2	18172-67-3
6-Methyl-5-hepten-2-one	6-Methyl-5-hepten-2-one	126.2	110-93-0
2-Carene	3,7,7-Trimethylbicyclo(4.1.0)hept-2-ene	136.2	554-61-0
Octanal	Octylaldehyde	128.2	124-13-0
3-Carene	3,7,7-Trimethylbicyclo(4.1.0)hept-3-ene	136.2	13466-78-9
α-Terpinene	1-Isopropyl-4-methyl-1,3-cyclohexadiene	136.2	99-86-5
(+)-Limonene	(*R*)-4-Isopropenyl-1-methyl-1-cyclohexene	136.2	5989-27-5
γ-Terpinene	1-Isopropyl-4-methyl-1,4-cyclohexadiene	136.2	99-85-4
Dihydromyrcenol	2,6-Dimethyl-7-octen-2-ol	156.3	18479-58-8
(−)-Fenchone	(−)-1,3,3-Trimethyl-2-norbornanone	152.2	7787-20-4
(±)-Linalool	*dl*-3,7-Dimethyl-3-hydroxy-1,6-octadiene	154.3	78-70-6
Nonanal	Nonylaldehyde	142.4	124-19-6
2,6-Dimethyl-2,4,6-octatriene	2,6-Dimethyl-2,4,6-octatriene	136.2	673-84-7
(+)-Camphor	1,7,7-Trimethylbicyclo(2.2.1)heptan-2-one	152.2	464-49-3
(*R*)-(+)-Citronella	3,7-Dimethyl-6-octenal	154.3	2385-77-5
(−)-Borneol	(1*s*)-*endo*-1,7,7-Trimethylbicyclo(2.2.1)heptan-ol	154.3	464-45-9
(-)-Menthol	5-Methyl-2-(1-methylethyl)cyclohexanol	156.3	2216-51-5
2-Methylisoborneol (MIB)	1,2,7,7-Tetramethyl-*exo*-bicyclo(2.2.1)heptan-2-ol	168.3	237-42-8
α-Terpineol	(*s*)-2,2,4-Trimethyl-3-cyclohexene-1-methanol	154.3	10482-56-1
Decanal	Decylaldehyde	156.3	112-31-2
β-Cyclocitral	2,6,6-Trimethyl-1-cyclohexene-1-carboxaldehyde	152.2	432-25-7
(+)-Pulegone	(*R*)-5-Methyl-2-(1-methylethylidene)-cyclohexanone	152.2	89-82-7
(±)-Citral	3,7-Dimethyl-2,6-octadienal	152.2	5392-40-5
(−)-Bornyl acetate	[1*s*]-1,7,7-Trimethylbicyclo(2.2.1)heptan-ol, acetate	196.3	5655-61-8
2,4-Decadienal	*trans*,*trans*-2,4-Decadienal	152.2	25152-84-57
Geosmin	*trans*-1,10-Dimethyl-*trans*-9-decalol	182.3	19700-21-1
Geranylacetone	*trans*-6,10-Dimethyl-5,9-undecadien-2-one	194.3	3796-70-1
β-Ionone	4-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-3-buten-2-one	192.3	79-77-6

[a] M_r, relative molecular mass. [b] CAS RN, Chemical Abstracts Service Registry Numbers.

fibers, and at a temperature of 280 °C for the CX-PDMS fiber. The transfer line was maintained at 240 °C. The mass spectrometer scanned from 35 to 399 u in 1.0 s. Mass spectra were collected in the full-scan acquisition mode, while quantification and calibration of the analytes of interest were based on the selected-ion monitoring mode, with the exception of C_6–C_{10} linear aldehydes (see Table 3).

SPME procedure

During the preliminary experiments, sampling from the liquid (liquid SPME) and from the headspace (headspace SPME) above the liquid was compared. For liquid SPME, 40 ml of aqueous sample was placed in a 47 ml glass vial (6.5 × 3 cm). After the addition of a 1.5 × 0.6 cm stir bar, the vial was closed with a PTFE-lined septum. The SPME fiber was immersed into the water for a fixed time. For headspace SPME, 40 ml of aqueous sample was placed in a 62 ml glass vial (8 × 3.5 cm), to which a 3 × 0.6 cm stir bar was added. The vial was closed with a PTFE-lined septum and stirred for 10 min to allow for the equilibration of analytes between the aqueous phase and the headspace. The SPME fiber was then exposed in the headspace over the water for a fixed time at room temperature. The aqueous samples were agitated rapidly and consistently during the liquid and headspace SPME experiments. After sampling, the SPME fiber was withdrawn into the needle, removed from the vial and inserted into the GC injection port for thermal desorption.

Because of the poor extractive behaviour of the liquid SPME method for the compounds studied (detailed results will be discussed below), only the headspace SPME procedure was optimized. The factors affecting the extraction efficiency of the headspace SPME technique, including the fiber coatings, salt addition, stirring, headspace volume, sample vial size and extraction time, were studied. Spiked samples of bidistilled Milli-Q (Millipore, Bedford, MA, USA) water (50 ng l^{-1} for MIB and geosmin, 100 ng l^{-1} for β-ionone and 500 ng l^{-1} for the other compounds) were used for all these experiments, and each analysis was carried out in duplicate or triplicate. The precision of the headspace SPME procedure was evaluated by the analysis of bidistilled water and river water (River Arno, Florence, Italy) samples spiked at different concentration levels. To evaluate the linearity of the proposed method, a standard addition calibration study was performed by analyzing a series of spiked river water samples. Additionally, a comparative study using the headspace SPME technique and the LLME method was also performed by analyzing a river water sample which contained certain compounds of interest. The LLME method was that reported by Bao *et al.*[15] Briefly, a 1 l water sample was spiked with 500 ng of 1-chlorooctane as internal standard. After the addition of 100 g of NaCl, the sample was extracted with 2 × 3 ml of hexane. The hexane extract was dried with anhydrous sodium sulfate and then concentrated to 0.1 ml with a gentle stream of N_2 at room temperature; 1 μl of the concentrated extract was injected into the GC-ITDMS apparatus for analysis.

Results and discussion

Selection of extraction mode

Due to the different polarity of the taste- and odor-causing compounds studied, the extraction modes (sampling from the liquid phase and from the headspace over the liquid) were firstly examined. Fig. 1 shows the responses obtained by both SPME methods with the PDMS-DVB-coated fiber. As shown in Fig. 1, for the studied aliphatic hydrocarbons, which are non-polar and highly volatile, the extraction efficiency achieved with headspace SPME was generally an order of magnitude higher than that obtained with liquid SPME. For the polar compounds studied, including aldehydes, ketones and alcohols, with no salt addition, both sampling methods gave a similar, poor extraction efficiency. With 20% (w/v) of salt addition, the responses obtained by liquid SPME did not change appreciably, while, in this case, the responses obtained by headspace SPME were 5–44 times higher than those obtained with no salt addition. Detailed results on the effects of salt addition on the headspace SPME process will be discussed later. The same results were also observed using other SPME fibers. Because of the poor extractive behavior of the liquid SPME method for the taste- and odor-causing compounds studied, all subsequent experiments were performed with the headspace SPME method.

Selection of SPME fiber

The results of the fiber comparison study are shown in Fig. 2. The data in Fig. 2 show that the CW-DVB fiber was not suitable for all of the analytes studied. In addition, the PDMS fiber was inefficient for most of the compounds studied.The CX-PDMS fiber was efficient for the extraction of most of the analytes studied, with the exception of citral, 2,4-decadienal, geranylacetone and β-ionone, which showed relatively low extraction efficiency. The major problem encountered with the CX-PDMS fiber was that significant peak tailing occurred for most of the compounds studied, and both the peak shape and the resolution were difficult to optimize by changing the oven temperature program and fiber desorption temperature. As shown in Fig. 2, the most suitable fiber for the extraction of the compounds studied was the PDMS-DVB-coated fiber which extracted all of the analytes with good efficiency. Thus, the

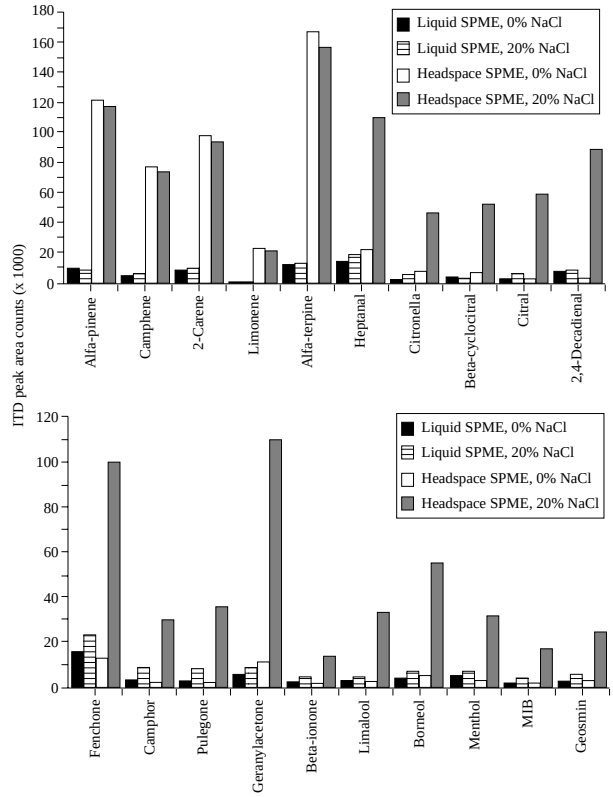

Fig. 1 Comparison of the extraction efficiency of taste- and odor-causing compounds in water by liquid SPME and headspace SPME with PDMS-DVB fiber. The SPME sampling time was 30 min.

PDMS-DVB-coated fiber was chosen for further optimization.

Effects of salt addition and stirring

Fig. 3 shows the effects of salt (NaCl) addition and stirring of the solution on the extraction efficiency of the compounds studied by headspace SPME. The data in Fig. 3 show that the effects of salt addition and stirring depend on the polarity of the compounds studied. The addition of salt (0–30%) and stirring were found to have no significant effect on the extractability of the studied aliphatic hydrocarbons. On the other hand, the polar compounds studied showed a significant increase in extraction efficiency with the addition of salt and stirring; salt addition of 30%, compared to no salt added, offers an improvement in the extraction efficiency of about one order of magnitude for polar compounds, and the stirring of the solution produces a factor of 2–5 improvement in the extraction efficiency compared to no stirring.

The suitability of the headspace SPME technique for the extraction of compounds in water depends on the transfer of analyte from the aqueous phase to the gaseous phase.[34] The aliphatic hydrocarbons studied are highly volatile and can easily be transferred into the gaseous phase. For these compounds, the controlling step in the headspace SPME process is the diffusion of the analyte in the SPME fiber. On the other hand, for compounds such as aldehydes, ketones and alcohols, which are less volatile and have a high water solubility, the mass transfer from the liquid to the gaseous phase may be the rate-controlling step in the headspace SPME process. Salt addition could significantly decrease their solubility in water, resulting in a higher concentration of these compounds in the headspace, and stirring may also speed up the mass transfer of these compounds from the liquid to the gaseous phase.

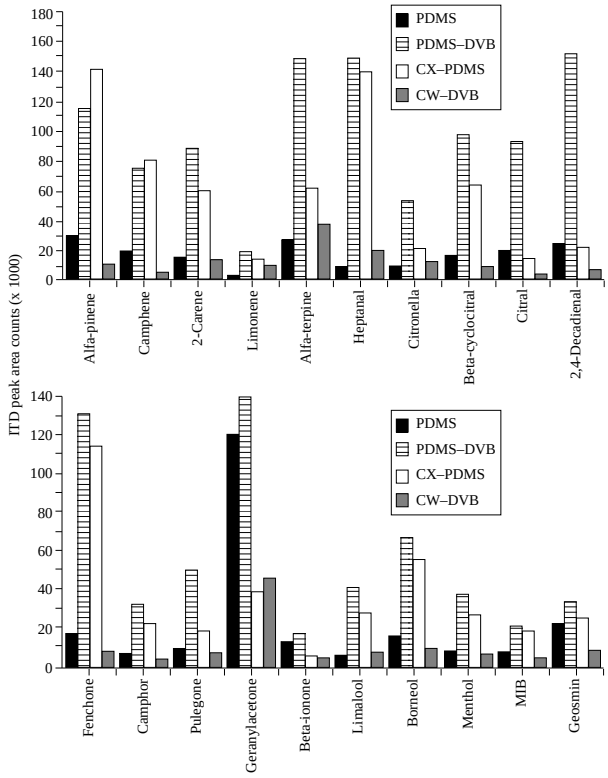

Fig. 2 Comparison of the extraction efficiency of taste- and odor-causing compounds in water by headspace SPME with various fibers. The sample volume was 40 ml of spiked bidistilled water containing 30% of NaCl. The SPME sampling time was 30 min.

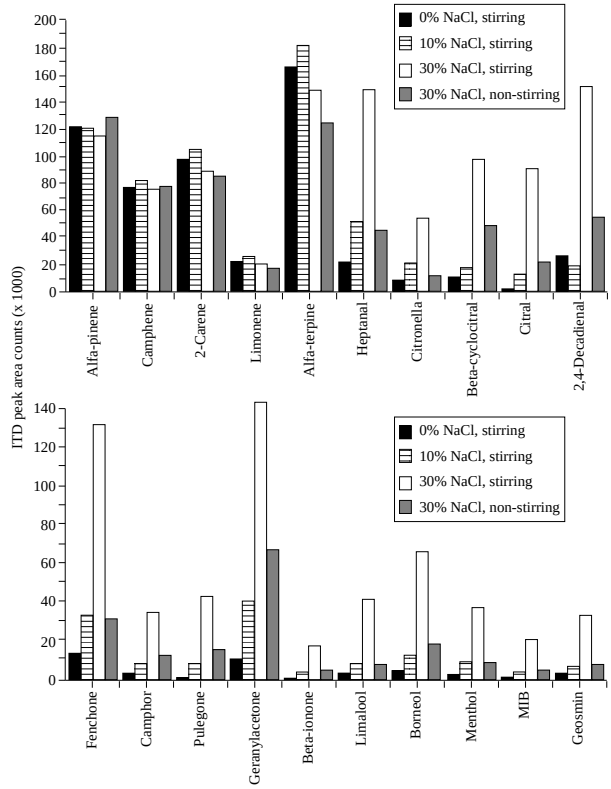

Fig. 3 Effect of salt (NaCl) addition and stirring on the extraction efficiency of taste- and odor-causing compounds in water by headspace SPME using a PDMS-DVB fiber. The SPME sampling time was 30 min.

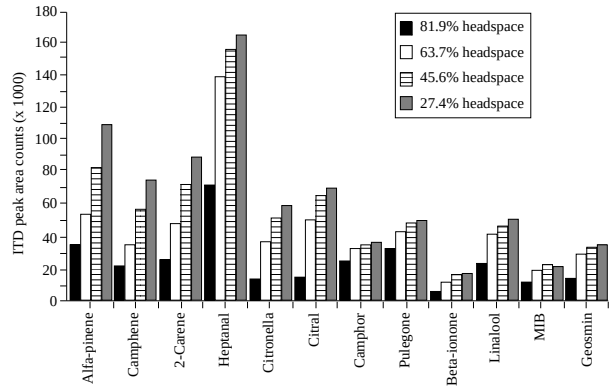

Fig. 4 Effect of the headspace volume on the response obtained by headspace SPME using a constant vial (62 ml). The SPME fiber was PDMS-DVB. The SPME sampling time was 30 min.

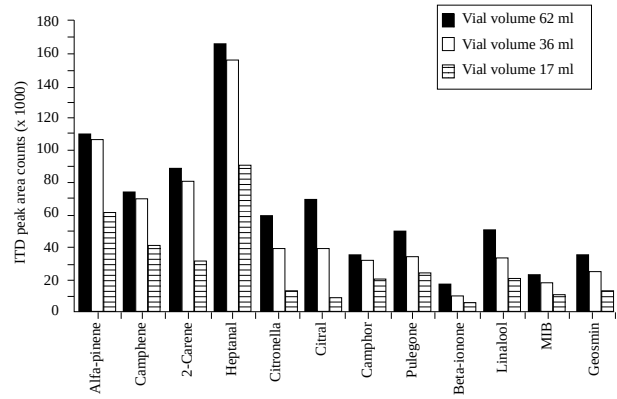

Fig. 5 Effect of the sample vial size on the response obtained by headspace SPME with constant percentage headspace (27.4%). The SPME fiber was PDMS-DVB. The SPME sampling time was 30 min.

Finally, 30% of NaCl was added to all samples in further experiments and sampling was performed with magnetic stirring.

Effects of headspace volume

The effects of the headspace volume on the extraction of the compounds studied by headspace SPME were investigated as follows. One set of experiments was performed using a constant vial (62 ml), but with different water volumes (10, 20, 30 and 40 ml). In this case, the percentage headspace decreased from 81.9 to 27.4% when the water volume was increased from 10 to 40 ml. Typical results are shown in Fig. 4. For non-polar compounds, such as α-pinene, camphene and 2-carene, a nearly linear increase in response was observed when the percentage headspace decreased from 81.9 to 27.4. These results indicate again that the rate-controlling step in the headspace SPME process for compounds with high volatility is the diffusion of the analyte into the SPME fiber, since the analytes diffuse quickly to the fiber coating when the headspace volume is smaller. For the polar compounds studied, the response significantly increases when the percentage headspace decreases from 81.9 to 63.7; a decrease in the percentage headspace from 63.7 to 27.4 only produces a slight increase in the response, especially for compounds such as pulegone, MIB, geosmin and β-ionone. As mentioned before, the mass transfer of analytes from the liquid phase to the headspace is often the limiting factor in the headspace SPME process for polar compounds. Thus, when the water volume increases, the polar analytes will take more time to transfer from the liquid to the headspace phase.

Another set of experiments was performed using a constant percentage headspace (27.4%), but with different vials: 62 ml vial, 36 ml vial (6.5 × 2.7 cm) and 17 ml vial (5.5 × 2.0 cm). In this case, the water volume was 40, 26 and 11 ml, respectively. Fig. 5 shows the typical results. For the non-polar compounds studied, the responses obtained with the 62 ml and 36 ml vials were similar, but significantly higher than that obtained with the 17 ml vial. On the other hand, the response obtained for the polar compounds studied decreased with the decrease in vial size from 62 ml to 17 ml. Additionally, triplicate determinations showed that the relative standard deviations (RSDs) obtained decreased as the vial size increased; the mean RSD value for the 34 compounds studied was 6.8% with 62 ml vials, 8.2% with 36 ml vials and 11.7% with 17 ml vials. As a

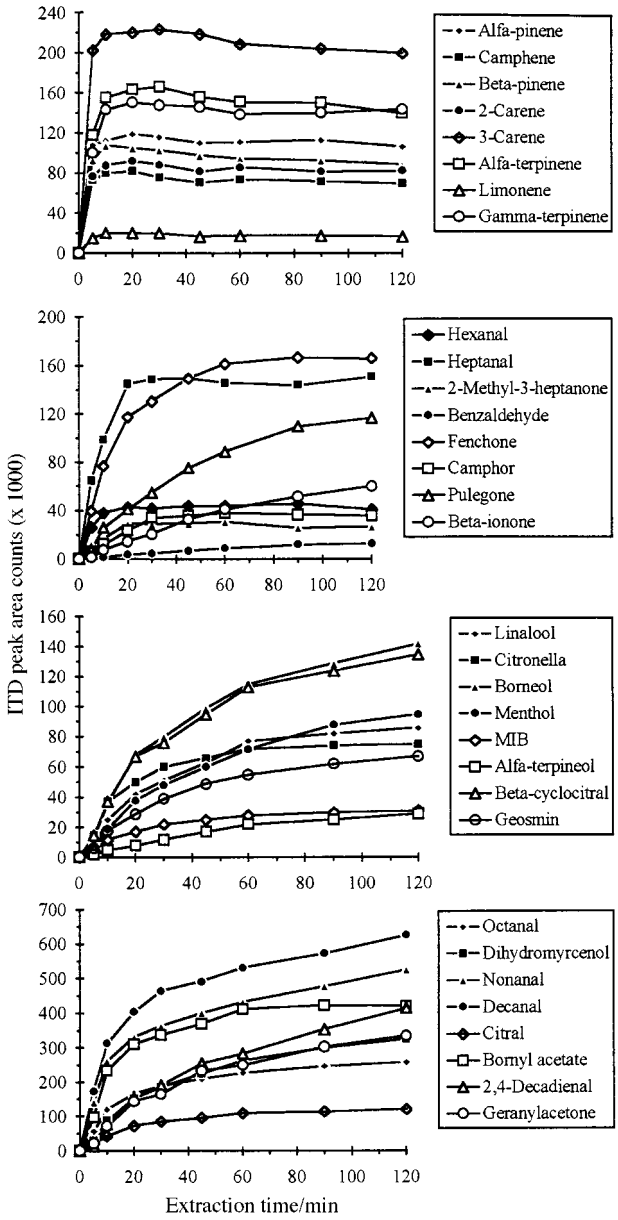

Fig. 6 Extraction–time profiles for the taste- and odor-causing compounds studied in water by headspace SPME using the PDMS-DVB fiber.

Table 2 Precision (RSD) of the proposed headspace SPME-GC-ITDMS method for taste- and odor-causing compounds spiked in different water matrices[a]

		Bidistilled water	River water	
Compound	Spiking level/ng l^{-1}	RSD (%)	Relative recovery[b] (%)	RSD (%)
Hexanal	50, 200, 500	14.1	67.0	17.2
Heptanal	50, 200, 500	8.2	79.3	7.9
α-Pinene	50, 200, 500	6.8	67.9	6.9
2-Methyl-3-heptanone	50, 200, 500	5.9	82.0	4.5
(+)-Camphene	50, 200, 500	5.5	74.5	5.9
Benzaldehyde	50, 200, 500	14.8	89.0	15.9
β-Pinene	50, 200, 500	4.8	73.7	4.5
6-Methyl-5-hepten-2-one	50, 200, 500	7.9	76.8	9.6
2-Carene	50, 200, 500	5.1	66.2	6.4
Octanal	50, 200, 500	6.7	65.6	9.2
3-Carene	50, 200, 500	4.6	64.0	5.7
α-Terpinene	50, 200, 500	5.9	65.2	6.3
(+)-Limonene	50, 200, 500	7.1	65.9	7.9
γ-Terpinene	50, 200, 500	4.6	64.6	4.9
Dihydromyrcenol	50, 200, 500	7.1	65.9	5.7
(−)-Fenchone	50, 200, 500	4.5	79.0	4.7
(±)-Linalool	50, 200, 500	8.6	61.1	8.1
Nonanal	50, 200, 500	5.8	61.6	10.1
2,6-Dimethyl-2,4,6-octatriene	50, 200, 500	4.7	60.3	4.3
(+)-Camphor	50, 200, 500	7.1	82.5	7.6
(*R*)-(+)-Citronella	50, 200, 500	6.0	71.4	5.6
(−)-Borneol	50, 200, 500	6.1	64.3	7.9
(−)-Menthol	50, 200, 500	6.1	65.4	5.6
MIB	5, 20, 50	6.4	78.8	6.8
α-Terpineol	50, 200, 500	5.8	61.5	5.3
Decanal	50, 200, 500	9.6	62.0	12.3
β-Cyclocitral	50, 200, 500	5.9	76.4	4.3
(+)-Pulegone	50, 200, 500	7.1	68.8	7.9
(±)-Citral	50, 200, 500	10.9	61.2	10.2
(−)-Bornyl acetate	50, 200, 500	5.4	76.8	9.9
2,4-Decadienal	50, 200, 500	11.5	62.1	14.3
Geosmin	5, 20, 50	6.2	73.5	5.3
Geranylacetone	50, 200, 500	5.7	69.6	8.7
β-Ionone	10, 40, 100	7.1	74.1	7.1

[a] Water sample volume was 40 ml, containing 30% of NaCl; sample vial volume was 62 ml; sampling time was 40 min with stirring; four determinations were performed for each spiking level. [b] Relative recoveries for spiked river water were calculated relative to the spiked bidistilled water after blank correction.

result of these data, the sample volume selected for further experiments was 40 ml in a 62 ml vial.

Extraction–time profile

We studied the extraction–time profile between 5 and 120 min. Fig. 6 shows the results obtained. It is evident that the time needed to reach equilibrium depends on the polarity and the relative molecular mass of the analyte. For the non-polar compounds studied, extraction equilibrium was reached in 10 min, while for the polar compounds studied, the equilibration times ranged from 10 min to more than 120 min, and generally increased with increasing relative molecular mass of the analyte. For example, hexanal and heptanal reached extraction equilibrium in 10 and 20 min, respectively, while for nonanal and decanal, equilibrium was not reached even after 120 min.

Based on the curves shown in Fig. 6, an extraction time of 40 min was selected for further experiments, because this provides sufficient extraction (most analytes reaching more than 80% of their final equilibrium value by 40 min) and allows the headspace SPME procedure to be performed approximately in the same time as that required for GC analysis.

Precision, linearity and detection limits

The precision of the proposed headspace SPME method in optimized conditions was assessed by analyzing spiked samples of bidistilled Milli-Q water and river water. The spiked levels were 5, 20 and 50 ng l^{-1} for MIB and geosmin, 10, 40 and 100 ng l^{-1} for β-ionone and 50, 200 and 500 ng l^{-1} for the other compounds studied. For each level and each type of aqueous sample, four extractions were performed. The results are reported in Table 2. A comparison of the data shows that the RSD values obtained from spiked river water samples were similar to those obtained from spiked bidistilled water samples and ranged from 4.3 to 17.2%.

The data on the relative recovery (%) listed in Table 2 from spiked river water samples were calculated by normalizing to the results obtained from spiked bidistilled water samples after correcting for the data obtained from non-spiked river water samples. The relative recoveries from spiked river water samples were between 58.1 and 89.0%. Based on these data, the water matrix seems to have an appreciable effect on the headspace SPME procedure for the compounds studied. Thus, the method of external standard calibration would lead to an inaccurate quantification in this case. The problem of matrix effects on the reliability of headspace SPME quantification can be reduced by using a standard addition calibration method or isotopically labeled internal standards. In this study, the method of standard addition calibration was used to evaluate the linearity of the proposed headspace SPME method and to quantify the real sample. A series of river water samples spiked with seven different concentrations of the analytes studied was analyzed by the headspace SPME procedure described above. The spiking levels were in the range 2–300 ng l^{-1} for MIB and geosmin, 4–600 ng l^{-1} for β-ionone and 20–3000 ng l^{-1} for the other compounds studied. For each level, three or four replicates were performed. Table 3 shows the linear ranges, slopes,

Table 3 Linearity range, slopes, correlation coefficients (R^2), quantification ions and limits of detection (LODs) for the analysis of taste- and odor-causing compounds in river water with headspace SPME-GC-ITDMS[a]

No.	Compound	Linear range/ng l^{-1}	Slope area/ counts ng 1^{-1}	R^2	Quantification ions[b]	LOD/ ng l^{-1}
1	Hexanal	50–3000	55.22	0.989	T	50
2	Heptanal	20–3000	204.2	0.975	T	18
3	α–Pinene	20–3000	134.4	0.973	93	1.0
4	2–Methyl–3–heptanone	20–3000	43.58	0.997	128	3.0
5	(+)–Camphene	20–3000	88.86	0.964	93	1.3
6	Benzaldehyde	50–3000	11.07	0.985	77	50
7	β–Pinene	20–3000	120.6	0.981	93	0.9
8	6–Methyl–5–hepten–2–one	20–3000	40.66	0.991	108	3.5
9	2–Carene	20–3000	99.26	0.985	121	2.5
10	Octanal	20–3000	713.6	0.992	T	20
11	3–Carene	20–3000	286.6	0.985	93	1.5
12	α–Terpinene	20–3000	243.1	0.999	121	1.4
13	(+)–Limonene	20–3000	25.86	0.991	67	9
14	γ–Terpinene	20–3000	220.2	0.998	93	0.9
15	Dihydromyrcenol	20–3000	268.9	0.997	59	1.2
16	(−)–Fenchone	20–3000	186.9	0.991	81	1.0
17	(±)–Linalool	20–3000	74.69	0.997	71	4.0
18	Nonanal	20–3000	1086	0.991	T	8.0
19	2,6–Dimethyl–2,4,6–octatriene	20–3000	210.7	0.998	121	1.5
20	(+)–Camphor	20–3000	49.14	0.990	95	4.5
21	(*R*)–(+)–Citronella	20–3000	85.64	0.997	95	13
22	(−)–Borneol	20–3000	115.7	0.999	95	3.2
23	(−)–Menthol	20–3000	71.16	1.000	81	3.0
24	MIB	2–300	299.2	0.995	95	0.7
25	α–Terpineol	20–3000	23.06	0.999	59	8
26	Decanal	20–3000	1288	0.987	T	8
27	β–Cyclocitral	20–3000	121.6	0.997	137	2.0
28	(+)–Pulegone	20–3000	97.36	1.000	81	6.0
29	(±)–Citral	50–3000	145.3	0.995	69	25
30	(−)–Bornyl acetate	20–3000	452.1	0.995	95	0.8
31	2,4–Decadienal	50–3000	264.8	0.997	81	20
32	Geosmin	2–300	487.9	0.999	112	0.5
33	Geranylacetone	20–3000	261.9	0.997	69	1.4
34	β–Ionone	4–600	192.9	0.999	177	1.5

[a] Water sample volume was 40 ml, containing 30% of NaCl; sample vial volume was 62 ml; sampling time was 40 min with stirring; seven plots with different concentrations (2–300 ng l^{-1} for MIB and geosmin, 4–600 ng l^{-1} for β–ionone and 20–3000 ng l^{-1} for the other compounds) were used. [b] T, total ion used for quantification.

correlation coefficients (R^2) and limits of detection (LODs). For most of the compounds studied, the resulting calibration curves, obtained by plotting the GC–ITDMS response (area counts) *vs.* analyte concentration, were found to have good linearity in the tested concentration range, with R^2 values ranging between 0.983 and 1.000. The LODs were calculated by comparing the signal-to-noise ratio (S/N) obtained by extraction of a river water sample with the lowest spiking level (2 ng l^{-1} for MIB and geosmin, 4 ng l^{-1} for β-ionone and 20 ng l^{-1} for the other compounds) to S/N = 5. The LODs for MIB and geosmin were 0.7 and 0.5 ng l^{-1}, respectively. For the other compounds studied, the LODs were between 0.8 and 50 ng l^{-1}. These LODs were achieved using only 40 ml of water sample with 40 min of extraction time and are comparable to those obtained by methods such as CLSA-GC-MS (2 l of water sample and 2 h of extraction time),[9] HFSA-GC-MS (3.8 l of water sample and 2 h

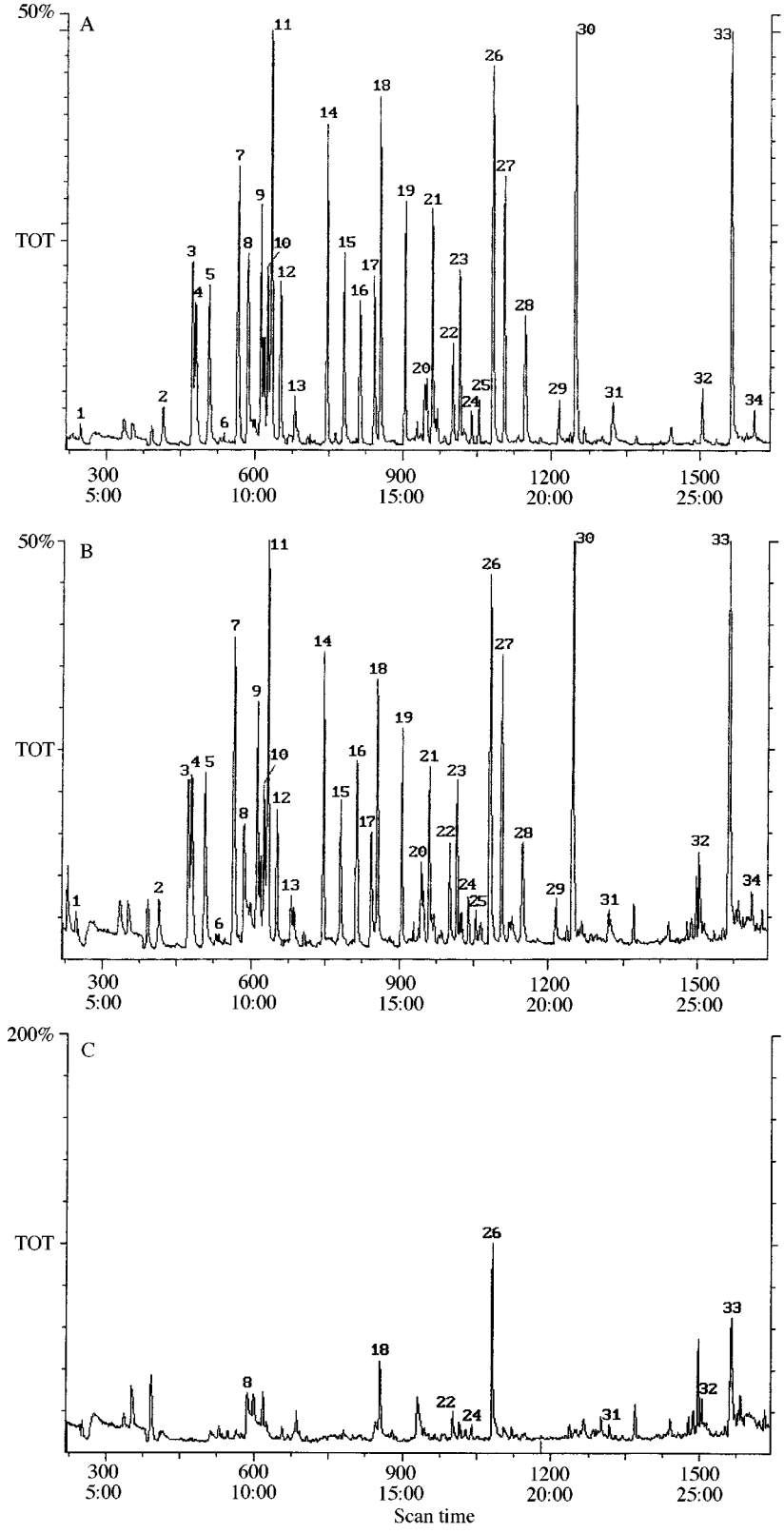

Fig. 7 Typical GC–ITDMS chromatograms obtained by headspace SPME for spiked samples of bidistilled water (A) and river water (B) and non-spiked river water sample (C). Spiking level was 20 ng l^{-1} for MIB and geosmin, 40 ng l^{-1} for β-ionone and 200 ng l^{-1} for the other compounds studied. For peak numbers, see Table 3.

of extraction time),[14] and LLME-GC-ITDMS (1 l of water sample and > 1 h of extraction and concentration time).[15]

Fig. 7 shows the ITD chromatograms obtained after extraction of spiked samples of bidistilled water (A) and river water (B) and non-spiked river water samples by the proposed headspace SPME procedure. The chromatograms shown in Fig. 7 indicate that the GC resolution and peak shapes are perfectly acceptable, and the chromatogram of the spiked river water sample shows minimal background interferences when compared to that of the spiked bidistilled water sample.

As shown in Fig. 7, in the non-spiked river water sample, compounds including 6-methyl-5-hepten-2-one, nonanal, borneol, MIB, decanal, 2,4-decadienal, geosmin and geranylacetone were detected. Table 4 shows the results obtained by triplicate analysis. The concentrations of MIB and geosmin determined were 5.9 ± 0.8 and 4.1 ± 0.6 ng l^{-1}, respectively. In addition, the same river water samples were also analyzed using an LLME method as described in the experimental section, and the results are also shown in Table 4. The data in Table 4 show that the concentrations obtained with headspace SPME were comparable to those obtained by LLME.

Finally, to check the uniformity of response of different fibers, four fibers (one of which had been used more than 200 times) from two lots were compared. The extraction efficiency and RSD were found to be similar.

Conclusions

A method for the determination of trace levels of 34 taste and odor-causing compounds belonging to four major classes has been developed. By using a PDMS-DVB-coated fiber, the headspace SPME method, in conjunction with GC-ITDMS analysis, reveals a high degree of precision, good linearity over a wide range of concentration and high sensitivity. Using only 40 ml of water sample, detection limits obtained in river water are in the low ng l^{-1} range for all the compounds examined in this study. Compared to other methods currently in use for the determination of taste- and odor-causing compounds present in trace levels in water, this method offers a number of practical advantages: smaller sample volume, shorter extraction time, simplicity of extraction and low cost.

Table 4 Taste- and odor-causing compounds determined in river water by headspace SPME-GC-ITDMS and LLME-GC-ITDMS

No.	Compound	Headspace SPME/ng l^{-1}	LLME/ ng l^{-1}
8	6-Methyl-5-hepten-2-one	34 ± 5	39 ± 6
18	Nonanal	58 ± 7	67 ± 8
22	Borneol	38 ± 4	33 ± 6
24	MIB	5.9 ± 0.8	4.9 ± 0.7
26	Decanal	92 ± 11	121 ± 14
31	2,4-Decadienal	37 ± 6	46 ± 6
32	Geosmin	4.1 ± 0.6	5.4 ± 0.8
33	Geranylacetone	51 ± 7	62 ± 7

Mean ± *s* (*n* = 3).

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