Simultaneous determination of ten taste and odor compounds in drinking water by solid-phase microextraction combined with gas chromatography-mass spectrometry

Xichao Chen, Qian Luo*, Shengguang Yuan, Zi Wei, Hanwen Song, Donghong Wang, Zijian Wang

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: 06xichao@163.com

Abstract

Taste and odor (T&O) problems in drinking water frequently occur because of many compounds present in the water, of which *trans*-1,10-dimethyl-*trans*-9-decalol (geosmin) and 2-methylisoborneol (MIB) are well-known. In this study, a fast and effective method was established for simultaneous determination of 10 T&O compounds, including geosmin, MIB, 2,4,6-trichloroanisole (TCA), 2-methylbenzofuran, 2-isopropyl-3-methoxypyrazine (IPMP), 2-isobutyl-3-methoxypyrazine (IBMP), *cis*-3-hexenyl acetate, *trans,trans*-2,4-heptadienal, *trans, cis*-2,6-nonadienal, and *trans*-2-decenal in water samples by headspace solid-phase microextraction (SPME) coupled with gas chromatography-mass spectrometry. An orthogonal array experimental design was used to optimize the effects of SPME fiber, extraction temperature, stirring rate, NaCl content, extraction time, and desorption time. The limits of detection ranged from 0.1 to 73 ng/L were lower than or close to the odor threshold concentrations (OTCs). All the 10 T&O compounds were detected in the 14 water samples including surface water, treatment process water and tap water, taken from a waterworks in Lianyungang City, China. MIB and geosmin were detected in most samples at low concentration. Six T&O compounds (IPMP, IBMP, *trans,cis*-2,6-nonadienal, 2-methylbenzofuran, *trans*-2-decenal, and TCA) were effectively decreased in water treatment process (sedimentation and filtration) that is different from *cis*-3-hexenyl acetate, MIB and geosmin. It is noted that the TCA concentrations at 15.9–122.3 ng/L and the *trans,cis*-2,6-nonadienal concentrations at 79.9–190.1 ng/L were over 10 times higher than their OTCs in tap water. The variation of the analytes in the all water samples, especially distribution system indicated that distribution system cannot be ignored as a T&O compounds source.

Key words: taste and odor compound; drinking water; SPME-GC/MS; geosmin; 2,4,6-trichloroanisole

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Introduction

Taste and odor (T&O) compounds are troublesome in water supplies in many parts of the world because they dramatically impact the acceptability of the drinking water to the consumers (Sung et al., 2005; Deng et al., 2011). Geosmin (earthy) and 2-methylisoborneol (MIB) (musty) have been identified as major T&O compounds in drinking water from surface water sources, and mainly result from the metabolism and biodegradation of certain types of microorganisms (Peter et al., 2009). Conventional water treatment processes such as chlorination, coagulation and sedimentation are ineffective for removal of MIB and geosmin (Srinivasan and Sorial, 2011) and other T&O compounds like *trans,trans*-2,4-heptadienal (fishy) (Wat-

son et al., 2001). In addition, T&O compounds could be produced during water treatment processes and/or from the water distribution network (Proulx et al., 2012). Previously, most studies focusing on T&O compounds have been limited to earthy and musty compounds, including MIB, geosmin, 2-isopropyl-3-methoxypyrazine (IPMP), 2-isobutyl-3-methoxypyrazine (IBMP) and 2,4,6-trichloroanisole (TCA). These compounds can easily cause T&O problems in lakes and reservoirs because of their extremely low odor threshold concentrations (OTCs) (Palmentier and Taguchi, 2001; Sun et al., 2012). Few studies have investigated other off-flavors such as the unsaturated aldehydes *trans,trans*-2,4-heptadienal, *trans,cis*-2,6-nonadienal (grassy) and *trans*-2-decenal (sweet) that are produced by algae and/or fish in natural aquatic environments (Hartvigsen et al., 2000; Watson et al., 2001). *cis*-3-Hexenyl acetate (grassy) is an odor compound de-

rived from decaying grass (Suffet et al., 2004), and 2-methylbenzofuran (smoky) has been identified as an odorant in cereal grains (Magan and Evans, 2000) and raw scallops (Morita and Aishima, 2002). There are currently no regulations for T&O compounds even the most common geosmin and MIB only with reference concentrations in the Standards for Drinking Water Quality (GB5749-2006), partly because they have not been associated with immediate health effects (Srinivasan and Sorial, 2011).

There are several reports on the occurrence of sulfur T&O compounds in natural waters. Concern increased after a water crisis in Wuxi, China in 2007 that was caused by an algal bloom in Taihu Lake that affected the aesthetic qualities of the water (Yang et al., 2008; Zhang et al., 2010). Dimethyl trisulfide and related alkyl sulfide compounds, but not MIB and geosmin, were the key odor-causing compounds in this incident (Yang et al., 2008; Yu et al., 2009). Therefore, more T&O compounds should be concerned and detected. In a study of cyanobacterial blooms in Midwest lakes in the USA, toxins and T&O compounds co-occurred frequently, which indicates that odor may serve as a warning that harmful toxins are present (Graham et al., 2010). The OTCs of T&O compounds are at ng/L level or even less (Zhang et al., 2005; Salemi et al., 2006). Because sensitivity to these compounds can vary among people and even in one person with time, it is not possible to determine an exact concentration or a very restricted concentration range for the OTCs.

Sensory gas chromatography coupled to mass spectrometry (GC/MS) analysis was used for the simultaneous identification of trace organics and description of their odors (Young et al. 1999; Yu et al., 2009). However, GC/MS is not sensitive enough to measure very small amounts of T&O compounds without enrichment (Godayol et al., 2011). To date, a wide variety of extraction and enrichment techniques, including closed-loop stripping (Malleret et al., 2001), purge and trap (P&T) (Chen et al., 2010a), membrane-based extraction (Zander and Pingert, 1997) and stir bar sorptive extraction (Ochiai et al., 2001) have been established and applied to some T&O compounds. Some of these methods have poor sensitivity, while some are time-consuming and labor-intensive (Deng et al., 2011). The stability and durability of solid-phase microextraction (SPME) limit its wider application although as a popular sample preparation technique (Sun et al., 2012). Choosing a fiber suitable for the simultaneous analysis of odorants is also difficult because of the wide polarity and volatility ranges of the analytes (Deng et al., 2011). In earlier studies, a number of one-factor-at-a-time experiments were conducted to investigate individual factors (Watson et al., 2000; Sung et al., 2005). However, this strategy overlooks interactions among the factors (George et al., 2004). Six of the SPME factors including extraction temperature, extraction time, desorption time, stirring rate, NaCl content, and fiber coating have an impact on

their enrichment. An orthogonal array experimental design (OAD) is an alternative way that can be used to overcome this limitation.

In the present study, an analytical method was developed for simultaneous quantification of 10 T&O compounds from different chemical families in water samples. The SPME-GC/MS method was applied to investigate occurrence and concentrations of 10 T&O compounds in water samples. The species and concentrations of T&O compounds were simultaneously analyzed in raw water, the water treatment processes (sedimentation, filtration and ozone) and tap water in plant adopting chlorine as disinfectant. Possible factors influencing the production of and/or decreases in T&O compounds are also discussed based on investigation of water treatment plants in representative north city (Lianyungang) that employ typical disinfection methods in China.

1 Materials and methods

1.1 Chemicals

Geosmin, MIB, TCA, IPMP, IBMP, 2-methylbenzofuran, cis-3-hexenyl acetate, trans,cis-2,6-nonadienal, trans,trans-2,4-heptadienal and trans-2-decenal standards were purchased from AccuStandard (New Haven, CT, USA). The details for these compounds are given in **Table S1**. Methanol (HPLC grade) was acquired from Fisher Scientific (Fair Lawn, NJ, USA). Milli-Q water was obtained from a Milli-Q Plus water purification system (Millipore, Billerica, MA, USA). Stock standard solutions were prepared by weight and stored at 4°C. Working solutions were made daily by diluting the standard solutions to the required concentrations with Milli-Q water.

1.2 Sample collection and preparation

Sampling was performed in the city of Lianyungang, China, in June, 2012. Surface water, treatment process water, and tap water were collected in 40 mL amber glass bottles with polytetrafluoroethylene-lined caps. The samples were stored at 4°C after collection and then analyzed within 14 days. The water qualities of these samples are summarized in **Table S2**. Surface water samples (a) to (g) were collected along the Qiangwei River, which is the water source for the third water treatment plant (Lianyungang, China). The suspended solid particles on the filter membrane for these samples gave off a light fishy smell. Treatment process water samples were collected from settled water (h), filtered water (i), ozonated water (j) and finished water (k). No suspended solid particles or obvious smells were detected for these samples. Tap water samples were collected from the taps of customers supplied by the third water treatment plant. These samples (l) to (n) were collected along the pipeline from upstream to downstream.

1.3 Solid-phase microextraction procedure

SPME experiments were performed with a manual fiber holder. Because the molecular weights (MW) of the analytes were between 110 and 211.5, we tested the following commercially available SPME fibers: polydimethylsiloxane (PDMS, 100 μm, MW 60–275), PDMS/divinylbenzene (PDMS/DVB, 65 μm, MW 50–300), polyacrylate (PA, 85 μm, MW 80–300), carboxen/PDMS, (CAR/PDMS, 75 μm, MW 30–225), and DVB/CAR/PDMS (2 cm-50/30 μm, MW 40–275). The fiber holder and coatings were supplied by Supelco (Bellefonte, PA, USA). Before use, each fiber was exposed to a splitless/split injection port of GC under helium flow and conditioned for the recommended time at recommended temperatures according to the manufacturer's instructions to remove contaminants and stabilize the solid phase.

Sample vials (15 mL) with magnetic stirring bars were filled with aliquots of standard solution containing the 10 analytes or sample solution (10 mL). The vials were tightly capped with a polypropylene cap with hole and a polytetrafluoroethylene/silicone septum. The SPME fiber was then exposed to the headspace. A hot plate/stirrer (Corning, NY, USA) was used to maintain a constant temperature and a constant stirring rate. When the extraction was complete, the fiber was immediately introduced into the GC injection port for desorption at 270°C. To select the best SPME fiber, the extraction process was conducted at 65°C for 30 min with constant stirring at 700 r/min.

1.4 Orthogonal array design for solid-phase microextraction

An OAD was used to optimize the parameters that could affect the performance of the SPME experiment. The following five variables were selected for optimization of HS-SPME regardless of interactions: (1) extraction temperature; (2) extraction time; (3) desorption time; (4) stirring rate; and (5) NaCl content. A four-level $L_{16}(4^5)$ orthogonal array with repeated observations was employed to assign the five variables. The total peak area for 2-methylbenzofuran, *cis*-3-hexenyl acetate, *trans,trans*-2,4-heptadienal, IPMP, and *trans*-2-decenal was used as Group 1, while the total peak area for MIB, IBMP, TCA *trans,cis*-2,6-nonadienal, and geosmin was used as Group 2. **Table S3** illustrates the assignments of the experimental factors and levels for the 16 experimental trials.

1.5 Instrumentation

GC/MS analysis was performed on an Agilent 6890 series GC system coupled with a 5975 series mass selective detector. DB-5MS column (30 m × 0.25 mm i.d., 0.25 μm film thickness) and DB-FFAP column (30 m × 0.25 mm i.d., 0.25 μm film thickness) were purchased from Agilent Technologies, Santa Clara, CA, USA. GC was operated under the following conditions: splitless injection temperature, 270°C; total flow rate, 52.4 mL/min; column flow rate, 1.0 mL/min; and oven temperature program, 50°C for 6 min, ramped at 25°C/min to 200°C, and held for 3 min. The quadrupole mass spectrometer was equipped with an electron ionization source at 70 eV and operated as follows: ion source temperature, 230°C; transfer line temperature, 280°C; and solvent delay time, 6 min. The ions used for selected ion mode are optimized. The LOD was calculated at a signal-to-noise ratio of 3 (S/N > 3).

2 Results and discussion

2.1 Influence of solid-phase microextraction fiber conditions

The fiber coating is a critical factor for SPME, but the number of commercially available fiber coatings is limited (Li et al., 2008; Chen et al., 2010b). The coatings used in the present study covered a wide polarity range and included non-polar (PDMS), semi-polar (PDMS/DVB), polar (PA), and bipolar (CAR/PDMS and DVB/CAR/PDMS) coatings. All the five commercially available coatings were tested for simultaneous extraction of the 10 T&O compounds. The coating thickness also has an effect on the extraction efficiency. Lower molecular weight or volatile compounds usually require a thicker fiber coating, and larger molecular weight or semi-volatile compounds are more effectively extracted with a thinner coating. For GC use, there is only one coating thickness commercially available for PA, PDMS/DVB and DVB/CAR/PDMS. However, there are multiple coating thicknesses available for PDMS (100 μm, MW 60–275; 30 μm, MW 80–500; 7 μm, 125–600) and CAR/PDMS (75 μm, MW 30–225; 85 μm, MW 30–225). According to the polarities and molecular weights of the analytes, the relatively thicker coating for PDMS (100 μm, MW 60–275) and thinner coating for CAR/PDMS (75 μm, MW 30–225) were selected. An initial five-level $L_{25}(5^6)$ OAD was conducted with factors of extraction temperature, extraction time, desorption time, stirring rate, NaCl content, and fiber coating. Results indicated that only the type of fiber coating was a highly significant factor ($P \leqslant 0.001$), while the others were not significant ($P \geqslant 0.01$), and this confirmed that the choice of SPME coating is a key factor for determination of T&O compounds. Therefore, fibers were optimized individually and the other five factors were evaluated later. The bipolar coatings (CAR/PDMS and DVB/CAR/PDMS) gave higher extraction efficiencies than the single-polarity coatings PDMS, PDMS/DVB and PA (**Fig. 1**).

The two bipolar coatings behaved similarly. In particular, the efficiencies of both coatings for MIB were almost identical. The main difference was that the signal responses of the DVB/CAR/PDMS fiber were much higher than those for the other fiber, except for the MIB signal. This was expected because the outer 50 μm layer of DVB provides capacity for larger molecules or semi-volatile compounds (Gioacchini et al., 2005). By contrast, the inner
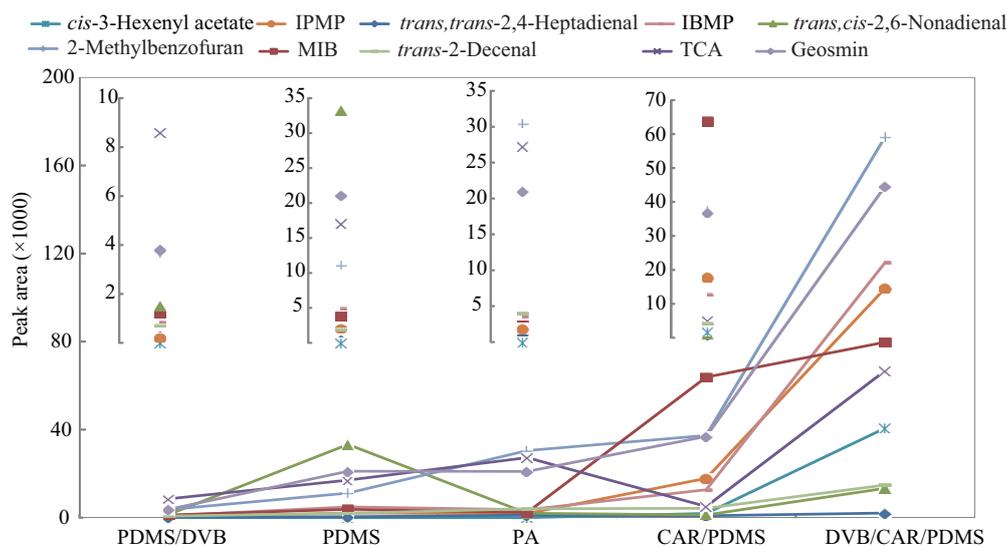
Fig. 1 Relative extraction efficiencies of 10 taste and odor analytes with five commercial fibers (PDMS, PDMS/DVB, PA, CAR/PDMS, and DVB/CAR/PDMS).

layer of CAR in DVB/CAR/PDMS was thinner (30 μm vs. 75 μm) than the layer in CAR/PDMS, which enhanced the extraction efficiency of the former fiber for semi-volatiles. Thus, the DVB/CAR/PDMS fiber was the most suitable for simultaneous determination of the 10 semi-volatile analytes. This was consistent with a previous study that indicated DVB/CAR/PDMS was the best fiber for five frequently reported T&O compounds (geosmin, MIB, TCA, IPMP and IBMP) (Sung et al., 2005). The present study expanded the fiber to another five compounds. Interestingly, these five frequently reported compounds clustered with relatively higher responses (**Fig. 1**). 2-Methylbenzofuran behaved similarly to these compounds because they all contain a ring structure. However, the 2 cm-50/30 μm DVB/CAR/PDMS fiber showed lower affinity for aliphatic compounds (*cis*-3-hexenyl acetate, *trans,cis*-2,6-nonadienal, *trans,trans*-2,4-heptadienal and *trans*-2-decenal). For the three unsaturated aliphatic alde-hydes, this can be explained by high polarity and reactivity of carbonyl compounds in water matrices, which makes derivatization necessary before their detection by chromatographic techniques (Cancho et al., 2002). Conse-quently, although the response of the 100 μm PDMS fiber for *trans,cis*-2,6-nonadienal was slightly higher, the 2 cm-

50/30 μm DVB/CAR/PDMS fiber was the best candidate for further optimization for all the analytes. Moreover, this fiber had higher affinity for cyclic compounds than aliphat-ic ones. For similar ring-structured T&O compounds such as β-ionone (Peter et al., 2009), 2,4,6-tribromoanisole (Malleret et al., 2001), the method is expected to be easily expanded to incorporate more compounds.

2.2 Optimized experimental conditions using a four-level $L_{16}(4^5)$ orthogonal array

The factors influencing SPME efficiency, including extrac-tion temperature, extraction time, desorption time, stirring rate, and NaCl content, were investigated. The data ob-tained from the four-level $L_{16}(4^5)$ OAD were evaluated by range analysis (**Fig. 2**) and ANOVA (**Table 1**). The extraction temperature, stirring rate, and NaCl content were highly significant at $P \leqslant 0.001$, whereas desorption time was significant at $P \leqslant 0.01$. The extraction time was less significant (only $P \leqslant 0.05$) within the studied range. As discussed above, the six cyclic compounds (2-methylbenzofuran, geosmin, MIB, TCA, IPMP and IBMP) showed higher responses than the four aliphat-ic ones (*cis*-3-hexenyl acetate, *trans,cis*-2,6-nonadienal, *trans,trans*-2,4-heptadienal and *trans*-2-decenal). There-

Table 1 Results of the $L_{16}(4^5)$ orthogonal array for factors influencing SPME

Source	Sum of squares	Degrees of freedom	Mean squares	F	P^a
Ext. temp.[b]	3.174×10^{13}	3	1.058×10^{13}	107.551	0.000***
Ext. time[c]	1.197×10^{12}	3	3.990×10^{11}	4.055	0.025*
Desorb. time[d]	2.073×10^{12}	3	6.910×10^{11}	7.024	0.003**
Stirring rate	6.222×10^{12}	3	2.074×10^{12}	21.080	0.000***
NaCl	6.949×10^{12}	3	2.316×10^{12}	23.545	0.000***
Error	1.574×10^{12}	16	9.838×10^{12}		
Total	1.995×10^{14}	32			

[a] *, ** and *** significant at $P \leqslant 0.05$, $P \leqslant 0.01$ and $P \leqslant 0.001$, respectively; [b] Ext. temp.: extraction temperature; [c] Ext. time: extraction time; [d] Desorb. time: eesorption time.
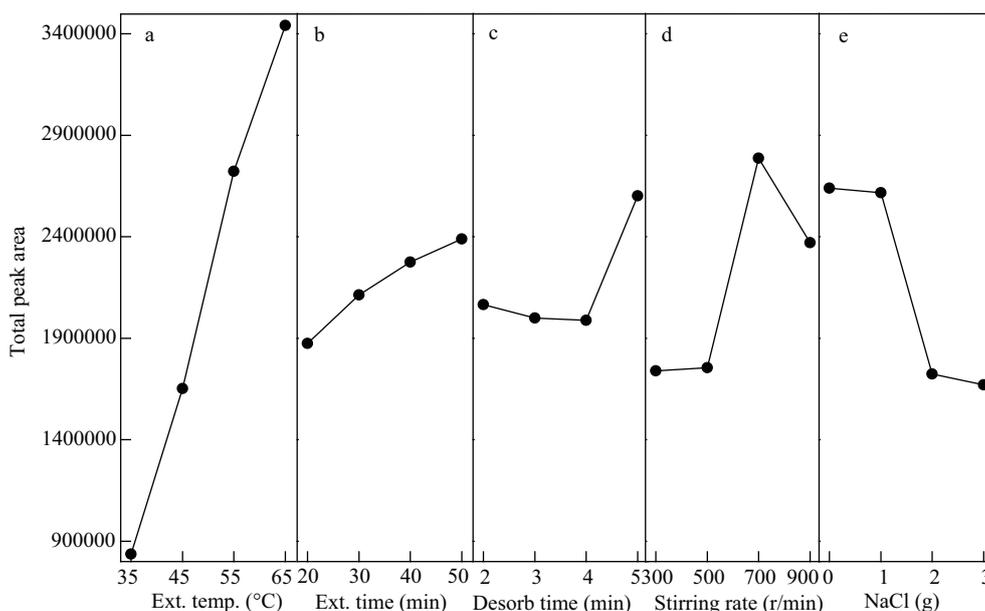
Fig. 2 Profiles of the total peak areas obtained in the range analysis of the orthogonal array. (a) extraction temperature; (b) extraction time; (c) desorption time; (d) stirring rate; (e) salt content.

fore, in the four-level $L_{16}(4^5)$ OAD, it is important to optimize these four aliphatic compounds for a simultaneous determination method even if compromises are made with the responses of the other six compounds. To optimize the experimental conditions, both the total peak area and the individual areas of the four aliphatic compounds were considered.

The extraction temperature was a crucial variable for SPME of T&O compounds since it had a noticeable influence on the target analytes as shown by the ANOVA results in **Table 1**. It has been reported that high temperature can have undesirable effects on the extraction efficiency of SPME fibers for some low molecular weight analytes with higher volatility because adsorption of analytes by the fiber coating is an exothermic process (Fang et al., 2003; Burbank and Qian, 2005; Vichi et al., 2005). However, in this study, a definite increase in total peak area occurred when the temperature increased from 35 to 65°C (**Fig. 2a**). The four aliphatic compounds showed similar trends (**Fig. 3a**). This is because migration from the solution to the headspace phase predominates for the semi-volatile analytes at the studied temperature range (Godayol et al., 2011). Moreover, higher temperature decreases the time to reach equilibrium. Although 65°C was not the equilibrium
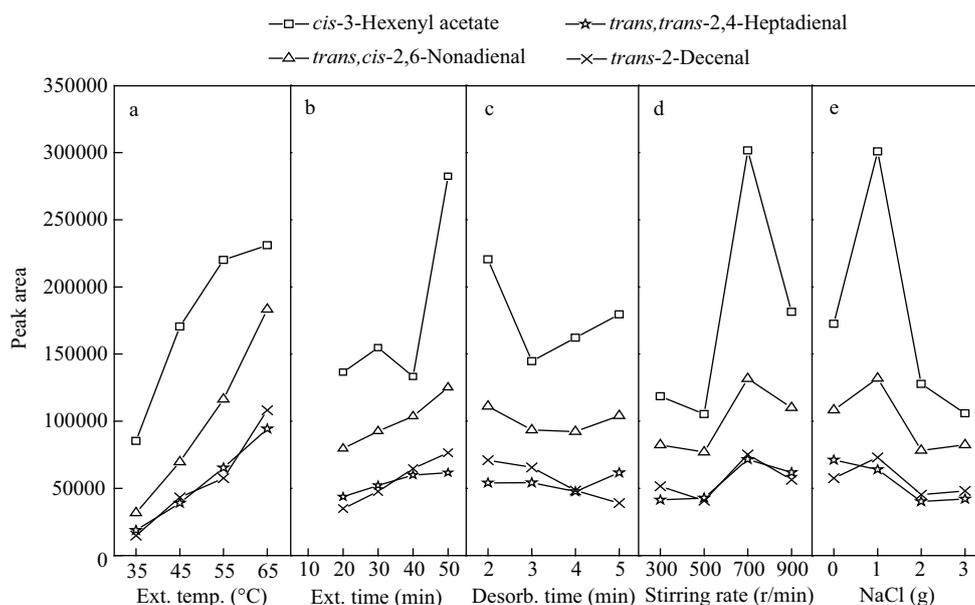

Fig. 3 Profiles of the four aliphatic analytes with low responses. (a) extraction temperature; (b) extraction time; (c) desorption time; (d) stirring rate; (e) salt content.

temperature, it was close to it. Saito et al. (2008) found that 70°C was the optimum temperature for MIB, geosmin and other volatile organic compounds. Temperatures higher than 65°C were not considered in this study because water vapor condensation on the fiber was observed at 65°C, and this could damage the GC/MS. Ultimately, 65°C was selected as the optimum temperature.

The extraction time with SPME usually varies from a few minutes to an hour or more, depending on the matrix, analytes, fiber phase, and desired sensitivity. The extraction time did not greatly affect the total peak area (**Table 1**). For semi-volatile compounds, it takes longer time to achieve equilibrium than volatile compounds. The extraction efficiency slowly increased as the extraction time increased, and this trend was observed both in the total peak area (**Fig. 2b**) and for the four aliphatic analytes (**Fig. 3b**). No large differences were observed when the extraction time was between 20 min and 50 min. The equilibrium time was 50 min or more, but routine analysis requires a short extraction time to maximize sample throughput. A proportional relationship has been demonstrated between the amount of analyte adsorbed into the SPME fiber and its initial concentration in the sample (Allard et al., 2012). Thus, an extraction time of 30 min was selected for quantification of the T&O compounds in non-equilibrium conditions. This parameter setting was selected in consideration of the equilibrium time, and operational convenience as a compromise between sufficient extraction and a reasonable overall analysis time.

Increasing the desorption temperature decreased the partition coefficient of the analyte between the fiber coating and the gaseous phase. Using the highest possible temperature without damaging the fiber coating is a solution to minimize the desorption time of the analyte from the fiber (Sarafraz-Yazdi et al., 2011). The manufacturer recommends a maximum temperature of 270°C for the 2 cm-50/30 μm CAR/PDMS/DVB fiber. Thus, the optimum desorption time was investigated at 1, 2, 3, 4 and 5 min at 270°C. For the four aliphatic analytes, there were few differences in the studied desorption time range (**Fig. 3c**), but for the total peak area there were a sharp increase between 4 min and 5 min (**Fig. 2c**). Importantly, carryover was observed at 4 min or below. Consequently, 5 min was selected as the optimal time.

The stirring rate was another significant factor for SPME of the analytes (**Table 1**). The extraction efficiency will increase with stirring of the sample solution, which accelerates diffusion of the analytes from the water solution to the SPME fiber coating and reduces the extraction time (Sarafraz-Yazdi et al., 2011). However, rapid stirring tends to be uncontrollable and might cause poor measurement precision (Saito et al., 2008). The stirring rate affected each T&O compound in similar way (**Fig. 2d** and **Fig. 3d**). The optimum extraction efficiencies for all 10 analytes were obtained with a stirring rate of 700 r/min.

The NaCl content was also a highly significant factor (**Table 1**). In general, NaCl increases the ionic strength of the sample, and makes organic substances less soluble and increases the partition coefficients by the 'salting out' effect (Rianawati and Balasubramanian, 2009). By contrast, the total peak area decreased when the NaCl content was increased in this study (**Fig. 2e**). This could be caused by the NaCl increasing the sample viscosity, ionizing the analytes, and making them dissolve in the water solution (Sarafraz-Yazdi et al., 2011). However, we found that addition of 1 g of NaCl was good for the four aliphatic analytes, especially for *cis*-3-hexenyl acetate (**Fig. 3e**). Therefore, 1 g of NaCl was added in subsequent experiments to increase the extraction efficiencies of the four aliphatic analytes without greatly influencing the total peak area.

2.3 Method evaluation

In the preconcentration step, the optimal SPME conditions including fiber (2 cm-50/30 μm DVB/CAR/PDMS), extraction temperature (65°C), extraction time (30 min), desorption time (5 min), stirring rate (700 r/min) and NaCl content (1 g) were applied to the following water samples. Since the studied compounds are polar moleculars, like aldehydes, alcohols and esters, they were not well resolved with polysiloxane-based columns. Better separation was obtained on a polar column (DB-FFAP) than on a non-polar column (DB-5MS). The optimized conditions gave good separation of the chromatographic peaks for all ten analytes, except for MIB and 2-methylbenzofuran (**Fig. 4a**). Nevertheless, quantification could be achieved with compound-specific target ions in the MS. The performance of the method with these conditions was investigated using standard aqueous solutions of the 10 analytes at different concentrations (1–1000 ng/L) (**Table 2**). Good linearity was observed for these substances and the correlation coefficients were found to exceed 0.9900 except for *trans,trans*-2,4-heptadienal (0.9898) at different ranges. The proposed method for more target compounds gave higher linear range and comparable or lower LODs compared with references (**Table 3**). For 8 of the 10 compounds with known OTCs, the LODs were near or below their OTCs. Moreover, apart from earthy and musty odor, the method can identify other odor-causing compounds. It is anticipated that the method could be expanded to incorporate more compounds that are associated with T&O problems in drinking water.

The precision of the method was evaluated by determination of the repeatability and reproducibility. Repeatability determinations involved measurement of 6 replicates consecutively while reproducibility determinations were 6 replicates over 3 different days. Considering of different linear ranges of different analytes, a low concentration (50 ng/L) and a high concentration (200 ng/L) were tested. Results in **Table 4** showed good

Table 2   Selected ions, linearity, determination coefficients, and limits of detection compared with odor threshold concentrations

Compound	Selected ions	Linear range (ng/L)	r^2	LOD (ng/L)	OTC (ng/L)
cis-3-Hexenyl acetate	67[a], 82	1–200	0.9977	6	1000–2000[b]
IPMP	137[a],152,124	5–800	0.9987	1	2–16[c]
trans,trans-2,4-Heptadienal	81[a],110,53	100–1000	0.9898	73	2500–5000[d]
IBMP	124[a],151,94	1–1000	0.9958	0.2	2–16[c]
trans,cis-2,6-Nonadienal	41[a],70,69	50–1000	0.9914	50	20[d]
2-Methylbenzofuran	131[a],132,103	1–1000	0.9939	0.1	Not available
MIB	95[a],108,135	1–800	0.9984	0.6	9–42[c]
trans-2-Decenal	41[a],55,70	5–800	0.9935	5	Not available
TCA	195[a],167,210	1–1000	0.9915	0.2	0.1–2[e]
Geosmin	112[a],125,182	1–1000	0.9976	0.4	4–10[c]

[a] Target ions for quantitation; [b] Khiari et al., 1995; [c] Salemi et al., 2006; [d] Burlingame et al., 1992; [e] Zhang et al., 2005.

Table 3   Comparison of analytical method, linearity, and LODs of T&O compounds

T&O compounds	Number of analytes	Performance	Analytical method	References
Geosmin, MIB, IPMP, TCA, IBMP	5	Linearity: 1–500 ng/L; LOD: 0.34–0.59 ng/L	SPME-GC/MS	Sung et al., 2005
Geosmin, MIB, IPMP, IBMP, TCA	5	Linearity: 1–200 ng/L; LOD: 0.5–1.5 ng/L	SPME-GC/MS	Sun et al., 2012
Geosmin, MIB, IPMP, IBMP, TCA, anisole, *trans, trans*-2,4-heptadienal	7	Linearity: 1–500 ng/L; LOD: 0.1–1 ng/L	Liquid-liquid extraction-GC/MS	Shin and Ahn, 2004
Dimethylsulfide, dimethyltrisulfide, MIB, geosmin, IPMP, IBMP, β-ionone, β-cyclocitral	8	Linearity: 1–500 ng/L; LOD: 0.3–1.1 ng/L	P&T-GC/MS	Chen et al., 2010a
Geosmin, MIB, IPMP, IBMP, β-ionone, β-cyclocitral, dimethylsulfide, dimethyltrisulfide	8	Linearity: 1–500 ng/L; LOD: 0.08–1.5 ng/L	P&T-GC/MS	Deng et al., 2011
Geosmin, MIB, IPMP, IBMP, TCA, 2-methylbenzofuran, *cis*-3-hexenyl acetate, *trans,cis*-2,6-nonadienal, *trans*-2-decenal, *trans, trans*-2,4-heptadienal	10	Linearity: 1–1000 ng/L; LOD: 0.1–73 ng/L	SPME-GC/MS	This study

Table 4   Accuracy and precision of the method

Compound	Repeatability (RSD%) (*n* = 6)		Reproducibility (RSD%) (*n* = 6)		Recovery (%) (*n* = 3)	
	50 ng/L	200 ng/L	50 ng/L	200 ng/L	Tap water	Surface water
cis-3-Hexenyl acetate	8.57	10.52	14.43	11.39	142.96 ± 12.36	157.95 ± 19.81
IPMP	8.92	6.94	9.20	4.36	96.68 ± 10.57	99.86 ± 12.32
trans,trans-2,4-Heptadienal	13.32	14.34	21.41	16.16	92.80 ± 5.48	94.86 ± 18.46
IBMP	8.16	6.89	7.82	4.81	85.99 ± 13.90	87.64 ± 11.59
trans,cis-2,6-Nonadienal	10.39	8.22	6.62	5.70	133.63 ± 5.84	128.50 ± 11.19
2-Methylbenzofuran	14.75	12.67	14.14	15.25	84.16 ± 3.77	105.05 ± 13.74
MIB	14.30	8.05	20.78	15.91	101.56 ± 12.30	112.30 ± 13.18
trans-2-Decenal	13.47	8.77	21.41	9.62	76.88 ± 5.11	117.61 ± 16.71
TCA	10.47	9.78	15.57	7.95	74.63 ± 2.52	85.86 ± 12.47
Geosmin	9.11	6.19	8.21	6.61	98.68 ± 17.08	90.29 ± 9.63

repeatability ranging from 6.89% to 14.75% for both concentrations. The reproducibility was still acceptable ranging from 4.36% to 16.16% for almost all the analytes at both concentrations. However, the reproducibility of *trans,trans*-2,4-heptadienal (21.41%), MIB (20.78%) and *trans*-2-decenal (21.41%) was relatively higher at 50 ng/L because of the polarity of the carbonyl group or hydroxyl group. Future work should consider the additional use of a suitable internal standard to increase the precision of the method.

For real water samples, matrix effects need to be investigated and controlled. The accuracy of the method for determination of real water samples was evaluated by measuring the recovery (*R*, %) of each analyte in tap water and surface water spiked with a concentration 100 ng/L (in triplicate). Recovery was calculated as:

$$R = \frac{C_{\text{spiked sample}} - C_{\text{sample}}}{C_{\text{spiking standard}}} \times 100\%$$

Good recoveries (84.16%–117.61%) were obtained for most of the analytes both in tap water and surface water, indicating that matrix effects were negligible using this method, and thus quantification could be done by external calibration in drinking water analysis. However, the recovery of TCA (74.63% in tap water and 85.86% in surface
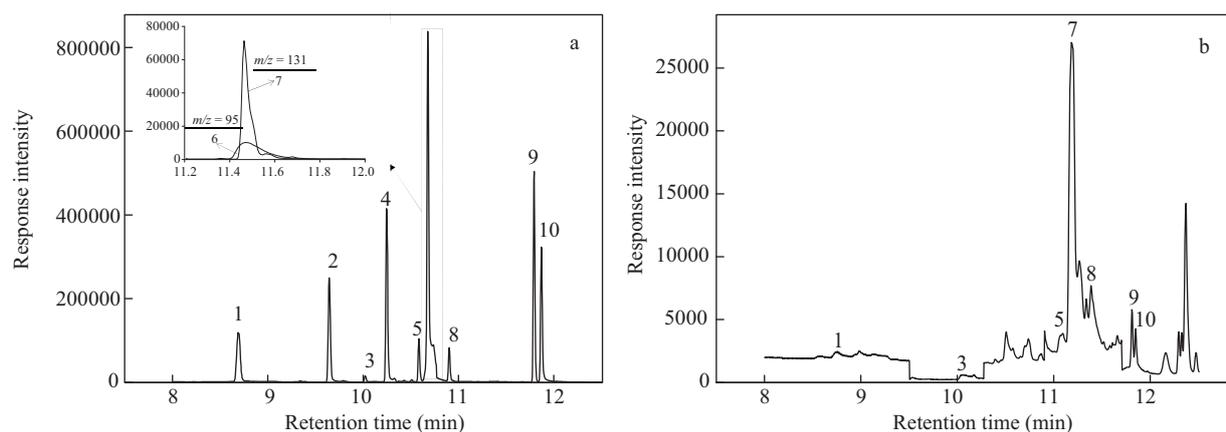
Fig. 4 Selected ion chromatogram of standard solution (a) and real water sample (b) for 10 T&O compounds using optimized conditions. Compounds in order are as follows: peak (1) *cis*-3-hexenyl acetate, (2) IPMP; (3) *trans,trans*-2,4-heptadienal; (4) IBMP; (5) *trans,cis*-2,6-nonadienal; (6) 2-methylbenzofuran (7) MIB; (8) *trans*-2-decenal; (9) TCA; (10) geosmin.

water) was relatively lower. Zhang et al. (2005) also obtained lower recoveries of haloanisole (about 60%) than those of geosmin and MIB (above 80%). The recoveries of *cis*-3-hexenyl acetate and *trans,cis*-2,6-nonadienal were a little bit higher than the other compounds, especially *cis*-3-hexenyl acetate. The higher recovery of *cis*-3-hexenyl acetate might be explained that the ester bond of *cis*-3-hexenyl acetate could be hydrolyzed at low concentrations.

2.4 Occurence, concentration and possible influence factor of T&O compounds in real water sample

The developed SPME-GC/MS method was applied to identify and quantify T&O compounds in source water, treatment process water and tap water collected from Lianyungang. In **Fig. 4b**, a chromatogram for a real water sample was shown. The concentration levels of these compounds (**Table 5**) ranged from not detected (n.d.) to several nanograms per liter or hundreds of nanograms per liter. In surface water, MIB and geosmin concentration ranged

from 3.2 to 51.8 ng/L and 13.4 to 26.7 ng/L, respectively. It was comparable with the published total concentrations of geosmin and MIB in the 8 water samples from Gonghu Bay of Lake Taihu ranged from 0 to 11.29 ng/L and 0 to 18.69 ng/L, respectively (Chen et al., 2010a). The only one of the nine investigated sites in Qinhuangdao was shown geosmin production, however, the peak geosmin concentration exceeding 7000 ng/L was detected in July 2007 (Yu et al., 2009). The MIB and geosmin in surface water from Qiangwei River were detected; however, the causes needed further investigation.

Another earthy and musty compound TCA was found at concentrations (from 12.2 to 195.9 ng/L) which were significantly higher than its OTC (0.1–2 ng/L). IBMP and IPMP are two kinds of pyrazines compounds that produce vegetable odor and vegetable to decaying odor, respectively. IBMP was described to be formed during microbial degradation of grass under anaerobic conditions, while IPMP was known to be a product of soil organ-

Table 5 Concentrations of 10 T&O compounds in real water samples (unit: ng/L)

Sampling sites		*cis*-3-Hexenyl acetate	IPMP	*trans,trans*-2,4-Heptadienal	IBMP	*trans,cis*-2,6-Nonadienal	2-Methyl-benzofuran	MIB	*trans*-2-Decenal	TCA	Geosmin
Surface	a	4.2	n.d.	437.5	31.4	153.5	199.0	3.7	36.1	122.3	20.4
water	b	4.0	n.d.	242.0	n.d.	183.8	10.9	10.0	19.3	12.2	13.6
	c	3.9	n.d.	316.9	17.7	257.9	33.0	3.2	5.3	24.8	14.4
	d	4.1	n.d.	324.0	n.d.	180.6	23.6	51.8	38.7	18.6	13.4
	e	3.9	n.d.	127.4	n.d.	83.5	14.4	17.6	21.0	14.0	13.5
	f	4.1	n.d.	313.7	19.7	131.2	158.2	3.5	126.2	77.9	17.9
	g	4.1	7.6	145.6	44.4	195.4	289.8	4.1	308.3	195.9	26.7
Treatment	h	4.0	n.d.	364.0	17.9	97.7	70.7	2.8	98.6	35.0	16.3
process	i	4.2	n.d.	377.2	15.5	50.5	23.1	3.2	22.8	17.0	14.2
water	j	3.8	n.d.	118.1	17.6	77.3	59.4	3.0	15.7	31.3	13.5
	k	4.3	n.d.	434.3	20.3	84.4	96.3	4.8	220.5	59.8	16.5
Tap	l	4.3	n.d.	340.1	16.6	103.3	20.8	3.5	15.0	15.9	13.2
water	m	12.5	6.8	353.0	39.1	190.1	176.1	6.8	112.8	122.3	24.5
	n	4.8	n.d.	353.0	18.9	79.9	21.6	2.9	18.2	17.1	14.3

a–g are surface water samples; n.d.: not detected.
Treatment processes are: (h) settled water, (i) filtered water, (j) ozonated water, and (k) finished water.

isms (actinomycetes) and has been found in many food and water samples (Khiari et al., 1997). In the current study, an equally low concentration of IPMP was detected in only site (g) with concentration at 7.6 ng/L, IBMP concentrations are between n.d. and 44.4 ng/L (g). This result is different from previous report by Chen et al. (2010a). It is certain that IPMP concentration was too low to produce odor during the studied period. Earthy and musty compounds such as MIB, geosmin, IPMP and IBMP are of major concern in previous T&O studies because of their extremely low OTCs (Sun et al., 2012). Interestingly, the dominant T&O compounds were *trans,trans*-2,4-heptadienal, *trans,cis*-2,6-nonadienal, *trans*-2-decenal and 2-methylbenzofuran in this study, not the most investigated earthy and musty compounds MIB or geosmin. In particular, the fishy compound *trans,trans*-2,4-heptadienal was present at the highest concentration levels (127.4 to 437.5 ng/L), which corresponded with the fishy smell we noted for the suspended solid particles on the filter membrane. The dominant odorous compounds in this study have received less attention before now probably because their OTCs are so high that they were overlooked as major T&O compounds. During this study period, *cis*-3-hexenyl acetate was not significant.

In treatment water, surface water (g) was the source water of the studied waterworks in Lianyungang, on the downstream of the Qiangwei River. Thus, that is why several compounds such as 2-methylbenzofuran, *trans*-2-decenal and TCA in source water (g) were at the highest concentration level among the surface water samples. Conventional treatment (sedimentation (h) and filtration (i)) combined with advanced treatment ozone-BAC (j) was used. Chlorine was applied in the finished water (k). As is commonly believed, conventional treatment is ineffective in controlling T&O compounds. However, effective IPMP, IBMP, *trans,cis*-2,6-nonadienal, 2-methylbenzofuran, *trans*-2-decenal, and TCA removal was demonstrated by sedimentation and filtration in this study. It is strange that the unsaturated aldehydes *trans,trans*-2,4-heptadienal seemed to be reduced by advanced treatment but rose again in finished water. The treatment processes had no significant effect on *cis*-3-hexenyl acetate, MIB and geosmin. These have been demonstrated that dissolved odorous compounds are affected by various factors, such as rate of odor production by algal cells, biodegradation by microbes, photolysis by sunlight, absorption by particles, disturbance by wave and volatilisation of odorous compounds themselves.

The analytes also existed in tap water. The TCA concentrations and the *trans,cis*-2,6-nonadienal concentrations were over 10 times higher than their OTCs. This is a more serious problem because T&O problems generated in distribution system are directly delivered to the customers. Sample (l) and (m) maintained almost stable or lower concentration levels compared with the finished

water (k). However, an increase was obtained in the middle of the pipeline at point (m) for all analytes. For 2-methylbenzofuran, *trans*-2-decenal and TCA, the concentrations were almost 10 times higher than the other two tap water samples. A possible explanation is that it was resulted from leaching plastic pipes or microbial activity in the distribution system (Peter and von Gunten, 2009). However, the causes needed further investigations to confirm it. Anyway, the water distribution network cannot be ignored as a T&O compounds source.

3 Conclusions

In the present study, 10 T&O compounds were simultaneously determined using HS-SPME-GC/MS. The best fiber for extracting T&O compounds with different polarities for non-target compound screening was 2 cm-50/30 μm DVB/CAR/PDMS. It should be noted that the method enabled LODs (0.1–73 ng/L) of the analytes below or close to their OTCs. Therefore, the method can be used by utilities to quickly and reliably detect T&O compounds and determine their concentrations before consumers can detect objectionable tastes and odors in drinking water. These compounds are widely detected in surface water and removed in water treatment process varying with compounds. In addition, T&O compounds exceeding OTCs in distribution systems posed a more serious problem to the customers.

Supporting materials

Supplementary data associated with this article can be found in the online version.

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