

Research Article

Analysis of Five Earthy-Musty Odorants in Environmental Water by HS-SPME/GC-MS

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The pressing issue of earthy and musty odor compounds in natural waters, which can affect the organoleptic properties of drinking water, makes it a public health concern. A simple and sensitive method for simultaneous analysis of five odorants in environmental water was developed by headspace solid-phase microextraction (HS-SPME) coupled to chromatography-mass spectrometry (GC-MS), including *geosmin* (GSM) and 2-methylisoborneol (2-MIB), as well as dimethyl trisulfide (DMTS), β -cyclocitral, and β -ionone. Based on the simple modification of original magnetic stirrer purchased from CORNING (USA), the five target compounds can be separated within 23 min, and the calibration curves show good linearity with a correlation coefficient above 0.999 (levels = 5). The limits of detection (LOD) are all below 1.3 ng L^{-1} , and the relative standard deviation (%RSD) is between 4.4% and 9.9% ($n = 7$) and recoveries of the analytes from water samples are between 86.2% and 112.3%. In addition, the storage time experiment indicated that the concentrations did not change significantly for GSM and 2-MIB if they were stored in canonical environment. In conclusion, the method in this study could be applied for monitoring these five odorants in natural waters.

1. Introduction

Earthy and musty odors in drinking water are often associated with the metabolites which are produced in the degradation of cyanobacteria, actinomyces, fungi, and blue-green algae [1–3], including *geosmin* (GSM) and 2-methylisoborneol (2-MIB), commonly found in lakes and reservoirs [4, 5]. Moreover, attention now is drawn to the compounds dimethyl trisulfide (DMTS), β -cyclocitral, and β -ionone, which are also associated with algal blooms caused by eutrophication progress [6–9], and they often simultaneously break out in environmental waters [4, 10]. *Beta-ionone*, for instance, potentially derived from carotenoids, is the significant component of flavor and aroma in some fruits and vegetables [11, 12]. In studies conducted according to the SIDS initial assessment report [13], *beta-ionone* has only low acute toxicity after oral ingestion by animal experiments and none of volunteers

showed a positive reaction. More specifically, the two main exposures, occupational exposure may occur during manufacture and industrial using, which is the skin contact and inhalation and is limited by enclosed systems and personal protective measures, as well as consumer exposure in food and some house wares which is also low since small amounts around 5 ppm (parts per million) in food and at usual concentrations of up to 0.3% in cosmetics. However, the odor threshold concentration (OTC) is extremely low, 10 ng L^{-1} or less for GSM and 2-MIB [14], for instance, which can be detected by human nose. The low threshold of detection can result in consumer complaints about the terrible malodors in recreational waters, aquatic products, and tap water, especially during the outbreak period of algal blooms [8, 15, 16], even if some other quality indicators of water, such as turbidity, number of algal cells, and suspended matter, are acceptable. Therefore, the identification and quantification of these trace

TABLE 1: The CAS number, molecular weight, boiling point, and odor threshold of the six compounds.

Compounds	CAS number	Molecular formula	Molecular weight	Boiling point ^a (°C)	OTC ^c (ng L ⁻¹)
DMTS	3658-80-8	C ₂ H ₆ S ₃	126	177	10
IBMP	24683-00-9	C ₉ H ₁₄ N ₂ O	166	236	1
2-MIB	2371-42-8	C ₁₁ H ₂₀ O	168	210	9
β -Cyclocitral	432-25-7	C ₁₀ H ₁₆ O	152	215	1.9 × 10 ⁴
GSM	19700-21-1	C ₁₂ H ₂₂ O	182	270 ^b /249	4
β -Ionone	14901-07-6	C ₁₃ H ₂₀ O	192	239 ^b /263	7

^a Calculated by EPISuit v.4.10 (2011) developed by the US EPA 2011, and boiling points by Stein and Brown method.

^b This boiling point was obtained by EPISuit v.4.10.

^c OTC: odor threshold concentration, detected by sensory and cited from Mallevalle [14] and Young et al. [6].

compounds are essential since they dramatically influence the esthetic quality and consumer acceptability of drinking water.

For now, a variety of techniques have been established and applied for enrichment and extraction of earthy and musty compounds. Among these techniques, closed-loop stripping analysis (CLSA) and some of its modified versions have been widely used for trace odorants such as GSM and 2-MIB in water samples. The result showed that CLSA was a good tool for analysis of GSM and 2-MIB at a low level [17]. Some other methods such as purge and trap (P&T) coupled to gas chromatography with mass spectrometry [18, 19] or to GC-FID [20], liquid-liquid microextraction (LLME) [21], stir bar sorptive extraction (SBSE) [22–24], and solid-phase extraction (SPE) [25] can also be taken to detect the earthy and musty odors in water at nanogram-per-liter level. Although these techniques greatly improve the limits and sensitivity of detection, some shortcomings restrict extensive usage of these methods, including unsuitable for the analysis of low-boiling-point odors and time-consuming (SPE, SBSE) [26, 27], lacking stability of droplet during extraction (LLME), and the sodium chloride, could be spurge onto the upside of purge tube and subsequently the sodium chloride was dragged in tubes and valves, causing abrasion by using P&T [10, 18, 28]. As technology advances, solid phase microextraction (SPME) was first developed and reported that headspace SPME (HS-SPME) was effective for collecting volatile organic compounds from Penicillium [29]. HS-SPME has become one of the most popular techniques in pretreating and enriching the odorants in water [30–34], because of no solvent during extraction by HS-SPME which cannot be achieved by LLME and simpler operation when comparing other methods like as SPE, CLSA, and SBSE, and the most important merit is that the targets can be enriched selectively by suitable fiber, which cannot be obtained by SPE and LLME. There are few reports regarding the HS-SPME to detect five or more odor compounds simultaneously in water samples, and some reports limited to two common odors as GSM and 2-MIB [31, 33–35]. However, the noteworthy is that their study indicated that the HS-SPME had excellent performance in studying trace odors in natural waters.

This study details a simple and sensitive method for simultaneous analysis of five odors in environmental water by using HS-SPME coupled to GC-MS, including GSM and 2-MIB, as well as DMTS, β -cyclocitral, and β -ionone. The

proposed method has been validated by variables on the five compounds, such as limit of detection (LOD), recovery, measurement precision (%RSD), and it also has been applied to environmental waters. In addition, the storage time experiment indicated that the concentrations did not change significantly for both GSM and 2-MIB if they were stored in canonical environment in ten days.

2. Materials and Methods

2.1. Chemicals, HS-SPME Apparatus, and Samples. The six standard compounds, GSM, 2-MIB, β -cyclocitral, and 2-isobutyl-3-methoxypyrazine (IBMP, as the internal standard) were obtained from Sigma-Aldrich (100 mg L⁻¹ in methanol); DMTS and β -ionone were also purchased from Sigma-Aldrich in the highest purity available. One mg L⁻¹ mixed stock standard solutions of five target compounds was prepared in methanol, and all of them were stored in the dark at 4°C. The details of the six compounds are shown in Table 1.

Deionized water was prepared on a water purification system (Gradient A10) supplied by Millipore (Billerica, MA, USA). Sodium chloride (analytical grade, China), which was added to the samples before extraction, was conditioned by heating at 450°C for 4 h before use. SPME apparatus was purchased from Supelco (USA), including fiber DVB/CAR/PDMS, PMDS/DVB and PMDS, fiber holder, sampling stand, magnetic stirrer, injection catheter, and 60 mL specialized vials for SPME.

Water samples from three waterworks in Wuxi city (120:18E-31:35N) were analyzed by using the proposed method, one source water, one product water, and one tap water were collected from each waterworks, nine samples in total. Water samples were filtered through 0.45 μ m glass-fiber-filter (GF/C, Whatman, England) if necessary and kept in 350 mL sample vials with PTFE-faced silicone septum and stored at 4°C before analysis.

2.2. SPME Procedures. After putting NaCl and a stir bar in a 60 mL vial, 40 mL of mixed standard solutions or environmental water samples was added, and IBMP (20 ng L⁻¹ in 40 mL water sample) was added to every sample when using internal standard method. The vial was sealed with PTFE septum cap and placed in a water bath. Several minutes after the

TABLE 2: The parameters of the MS scan function (SIM mode) for the determination of analytes.

Compounds	t_R (min)	Segment (min)	Selected ions	R^b	RSD% ($n = 7$)	LOD ^c (ng L ⁻¹)
DMTS	13.669	12.1–14.0	126 ^a , 79,111	0.9998	9.9 ^c , 12.1 ^d	1.3
IBMP	18.003	17.0–18.1	124 ^a , 94,151	—	—	0.1
2-MIB	18.542	18.1–18.7	107 ^a , 95,135	0.9995	4.9 ^c , 5.9 ^d	0.5
β -Cyclocitral	18.991	18.7–20.0	137 ^a , 152,123	0.9990	4.4 ^c , 6.7 ^d	0.2
GSM	22.102	20.0–22.3	112 ^a , 126,97	0.9990	8.2 ^c , 8.9 ^d	0.2
β -Ionone	22.596	22.3–25.0	177 ^a , 91,135	0.9811	7.1 ^c , 9.8 ^d	0.4

^aQuantitative ions (m/z).

^bCalibration curves with compounds concentration: 5, 10, 20, 50, and 100 ng L⁻¹.

^cRSD: relative standard deviation, using IBMP as the internal standard. Compound concentration: 20 ng L⁻¹.

^dWithout internal standard. Compound concentration: 20 ng L⁻¹.

^eLOD: limit of detection was calculated on the basis of $S/N = 3$, this value is a mathematical approximation.

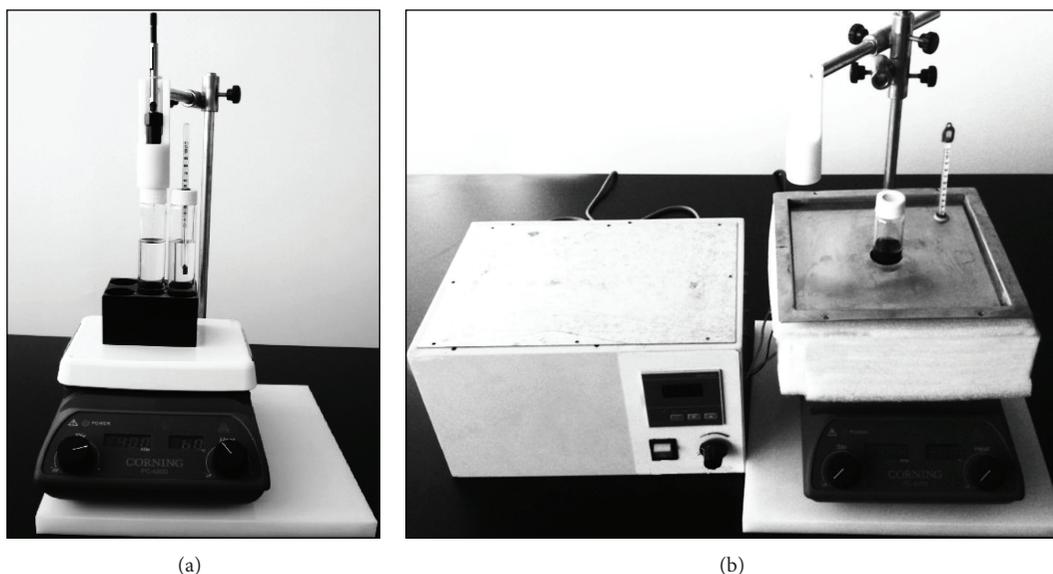


FIGURE 1: (a) The original magnetic stirrer from CORNING and (b) modified one.

temperature was achieved in the vial, the outer needle of fiber was used to penetrate the septum and the fiber was exposed to the headspace for extraction. After exposure, the fiber was immediately inserted into GC injection port for desorption.

2.3. Gas Chromatography-Mass Spectrometry. A Varian 300 GC/MS/MS (Varian Inc. CA, USA) with ion trap and mass spectrometer was obtained with a Varian VF-5 MS capillarity column (30 m \times 0.25 mm \times 0.5 μ m). The temperature of the injector was 230°C and adjusted to splitless mode at the eighth minute. The carrier gas was helium at a flow of 1 mL min⁻¹. The temperature of the oven started at 40°C and was held for 5 min. Then the temperature was 8°C min⁻¹ to achieve 160°C (total time 20 min) followed by 20°C min⁻¹ to achieve 260°C (25 min in total). The electron impact (EI)-MS conditions were as follows: ion-source temperature, 230°C; MS transfer line temperature, 250°C; solvent delay time, 5 min; ionizing voltage, 70 eV. The mass spectrogram in full scan mode was obtained at the m/z range of 60–260. According to the MS scan function (SIM mode), the process was divided into six main segments as shown in Table 2. The method of internal

standard [31, 33] was applied to construct calibration curve and determine concentrations of five odorants in water.

3. Results and Discussion

3.1. Improvements in HS-SPME Apparatus. The HS-SPME apparatus was obtained from Supelco, as shown in Figure 1(a). The original apparatus has some demerits in practice, which can be classified as follows: firstly, it would take relatively long time to reach or adjust the proposed temperature, especially in low environmental temperature such as in winter, because the body of sample vial is almost fully exposed to the environment and difficult to keep a stable temperature; secondly, the temperature of sample or the extraction is recorded by the thermometer in adjacent vial, and this is not reliable or it cannot guarantee the same temperature in both of them since the two vials are independent of each other in respective dynamic system due to uneven heating and natural air flow. However, some studies [31, 33, 35] had never addressed the above issues. Therefore, we tried to transform the original apparatus into a novel one. As shown in

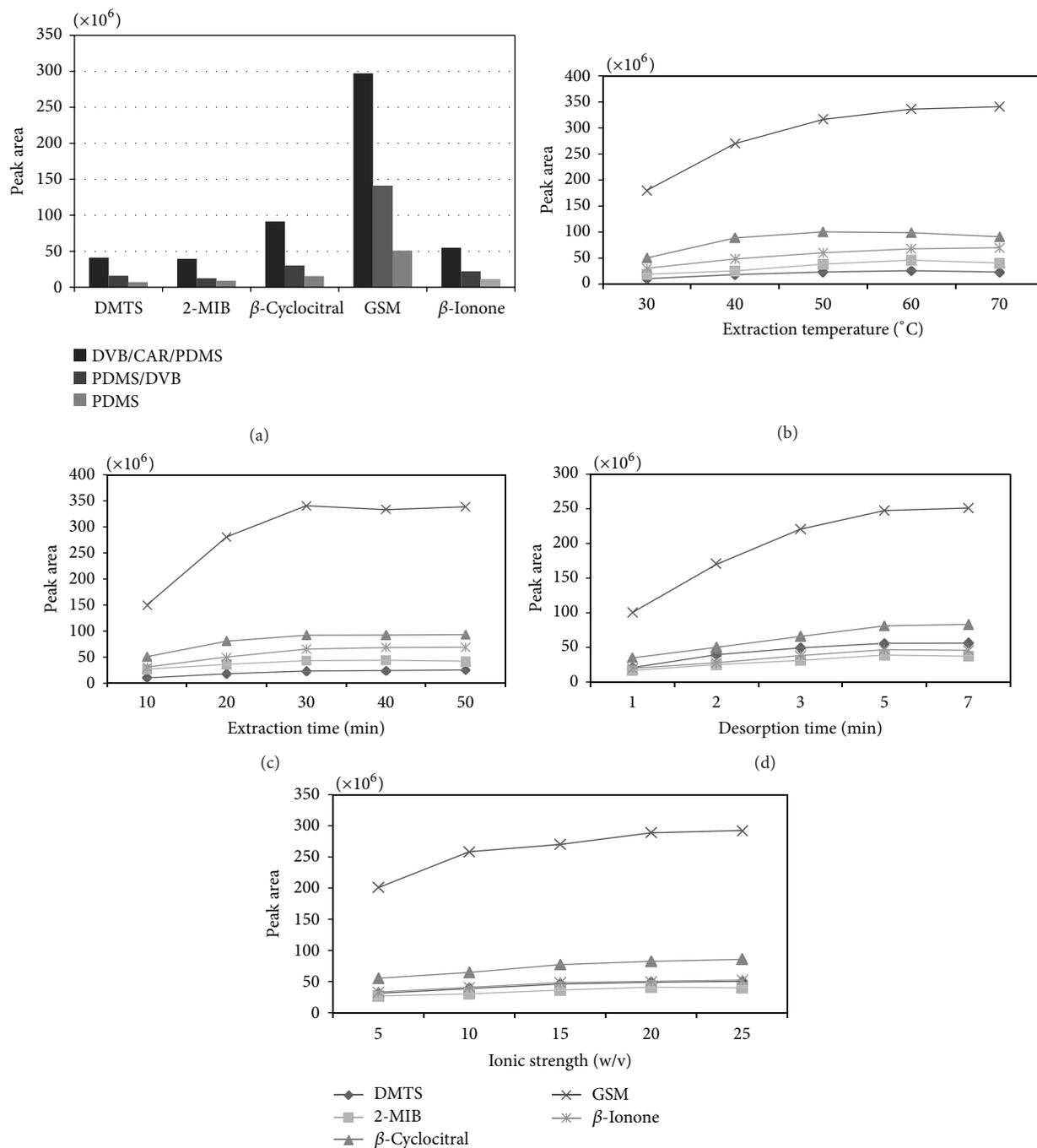


FIGURE 2: The effect of (a) fiber, (b) extraction temperature, (c) extraction time, (d) desorption time, and (e) ionic strength on the HS-SPME/GC-MS of five target compounds, and 100 ng L^{-1} of mixed standard solutions was analyzed by (a) fiber exposition at 60°C , 30 min, for 25% (w/v) ionic strength, (b) fiber exposition at 25% (w/v) ionic strength for 30 min, (c) fiber exposition at 60°C for 25% (w/v) ionic strength, and (d) and (e) at 60°C for 30 min.

Figure 1(b), the digital magnetic stirrer was retained to obtain accurate and comparable values which can contrast with other peer reports. However, we apply the thermostat water bath to control the vial temperature freely, and it can be quickly and accurately adjusted to proposed temperature if we study the effect of the extraction temperature, which can efficiently overcome the weak points above and put its merits into full use.

3.2. Selection of the Fiber. Fiber coatings dominate the effect of extraction or recoveries of analytes. According to the principles of fiber selection from Supelco, that is, the polarity and thickness of the stationary phase coating on the fiber, and also based on the earlier reports [31, 33, 36], three commercial fibers (DVB/CAR/PDMS, PDMS/DVB, and PDMS) were chosen for evaluation in this study. Figure 2(a) showed the extraction yield of three fibers (expressed by peak area), and it

TABLE 3: The concentration and recovery of earthy and musty odors in water samples (all samples were tested two times).

Compounds	Tap water			Deionized water		
	Concentration (ng L ⁻¹)	Recovery (%)		Concentration (ng L ⁻¹)	Recovery (%)	
		20 ng L ⁻¹	100 ng L ⁻¹		20 ng L ⁻¹	100 ng L ⁻¹
DMTS	7.8	92.8	95.4	2.4	91.7	90.2
2-MIB	6.4	104.3	92.0	2.5	110.1	93.5
β -Cyclocitral	1.2	109.8	94.3	n.d.	112.3	107.9
GSM	1.5	90.8	99.7	n.d.	107.0	104.1
β -Ionone	n.d. ^a	85.7	83.2	n.d.	86.2	88.3

^a n.d. means below the lower-limit of the calibration range.

was concluded that DVB/CAR/PDMS fiber extracted almost all of analytes with the best performance. Thus, this coated fiber was chosen in our study and for further experiments.

3.3. Effect of Extraction Temperature. As shown in Figure 2(b), we studied the HS-SPME analyses run at a selected temperature. The extraction efficiency of five targeted analytes increased as extraction temperature from 30°C to 60°C, especially sharply increasing between 30°C and 40°C, and slowly growing until 60°C. However, a decrease was observed between 60°C and 70°C for 2-MIB and β -cyclocitral. The potential reasons can be as follows: firstly, the increased amount of water vapor would be assembled on the fiber as temperature growing, which would reduce the extraction efficiency; secondly, the different molecular weight of odorants was deemed to be inconsistently susceptible to fiber [37]; thirdly, this can be understood by the partition coefficient between the fiber and analytes. In other words, according to the formula $K_{fs} = K_0 \exp[-\Delta H/R(1/T - 1/T_0)]$ [38], the partition coefficient (K_{fs}) would change if extraction temperature alters from T_0 to T , because potential energy of analyte on coating material would be less than that in the sample if the K_{fs} value is more than one. Therefore, the value of K_{fs} would decrease as the extraction temperature increases, which can result in decreased extraction efficiency as a similar situation reported by Chai and Pawliszyn [39]. Consequently, 60°C was the optimal choice as obtained in Figure 2(b), when considering the extraction temperature.

3.4. Effect of Extraction Time. As shown in Figure 2(c), we studied the SPME analyses run at selected time, the extraction efficiency of five analytes increased rapidly as extraction time from 10 min to 20 min, especially for GSM and β -cyclocitral, while a slow increase was observed for them between 20 and 40 min except GSM even declining, and the trend was tending towards stability after 40 min. However, the equilibrium time for this fiber maybe 30 min or more, but we desired shorter extraction time to maximize sample. Therefore, an extraction time 30 min was selected for experiments, and also this allowed the GC-MS analysis (25 min) to be performed nearly in the approximate time as HS-SPME procedure.

3.5. Effect of Desorption Time. As shown in Figure 2(d), desorption time (1, 2, 3, 5, and 7 min) profile is studied. Although their growth was inconsistent in the first five minutes, the peak area of five target compounds remained unchanged when desorption time is after 5 min. In other

words, 5 min was enough for desorption. Thus, 5 min was selected as the optimal time.

3.6. Effect of Ionic Strength. The suitable salt addition could improve the transfer of analytes from the aqueous phase to the gaseous phase so this can result in a higher concentration of the odors in the headspace. Responses were calculated upon the condition of 5, 10, 15, 20, and 25% (w/v) ionic strength. As shown in Figure 2(e), the overall trend inclined to be horizontal in selected ionic strength, and, also, it was fairly clear that 25% (w/v) was most suitable for the extraction process, and this concentration of salt was selected for the future experiments.

4. Method Validation

The proposed method had been validated in terms of accuracy, linearity, LOD, %RSD, and recovery, and the relevant analytical parameters were shown in Table 2. To be more specific, linearity was studied by extracting the five odor standard solutions at five concentration levels, ranging from 5 to 100 ng L⁻¹. Calibration curves showed adequate coefficients of correlation (R) higher than 0.999 with RSDs below 9.9% ($n = 7$); this showed satisfactory precision. The five odorants gave excellent responses to GC-MS detection. The LOD of these compounds were calculated on the basis of $S/N = 3$ in SIM mode at a low concentration and were below 1.3 ng L⁻¹.

In addition, the method was applied to determine the target compounds in water samples from waterworks in Wuxi city. To confirm the validity of this method, we need to study the possible matrix effect in the water samples, and the result showed that there was no interfering peak from the sample matrix (Figure 3(a)). Moreover, according to the scan mode, the six target compounds in water samples can be identified and retrieved from MS spectrum library (Figure 3(b)). The recoveries of the five odors are between 83.2% and 112.3% in Table 3. Also, nine water samples from three waterworks were analyzed. The results are listed in Table 4, and, in conclusion, the proposed method has been proved to be rapid, sensitive, and reproducible enough to detect the trace compounds at nanogram-per-liter level.

5. Attenuation Experiment

The routine water samples often need a short-term for storage, because of the great quantity, the transportation delay

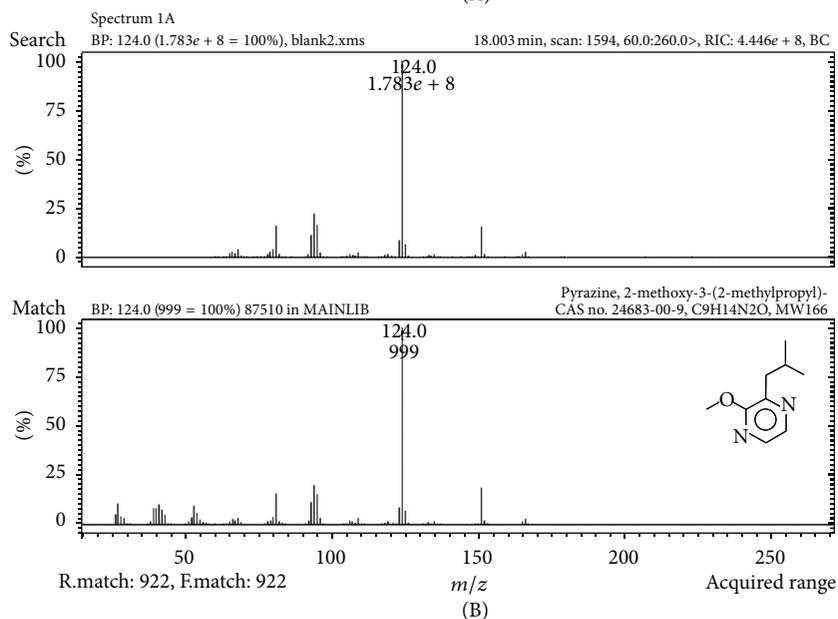
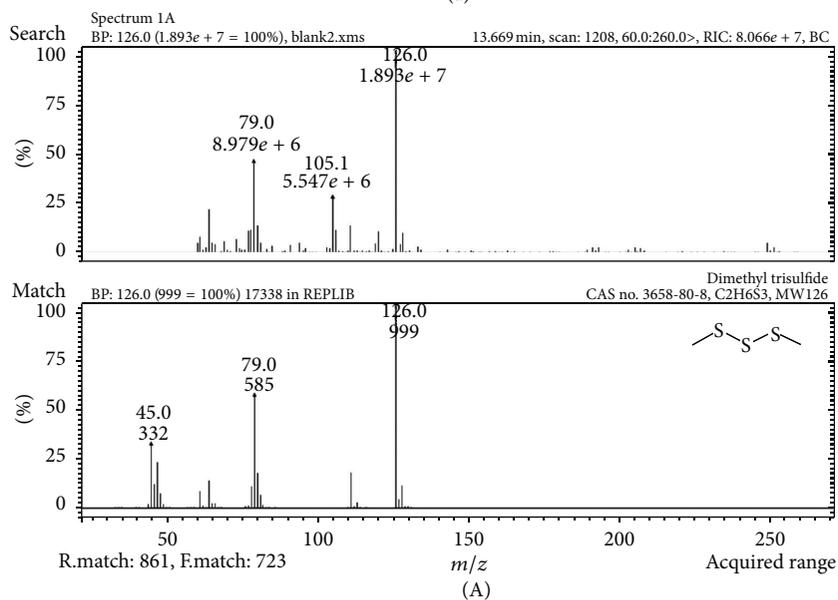
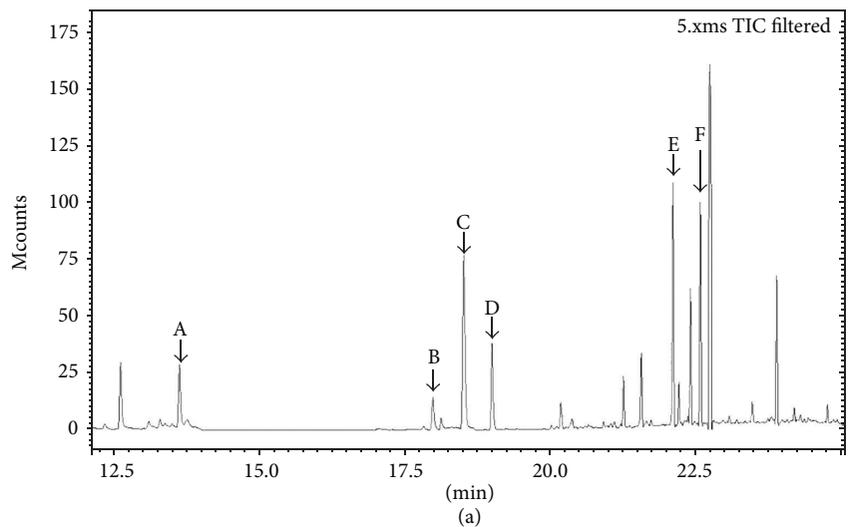


FIGURE 3: Continued.

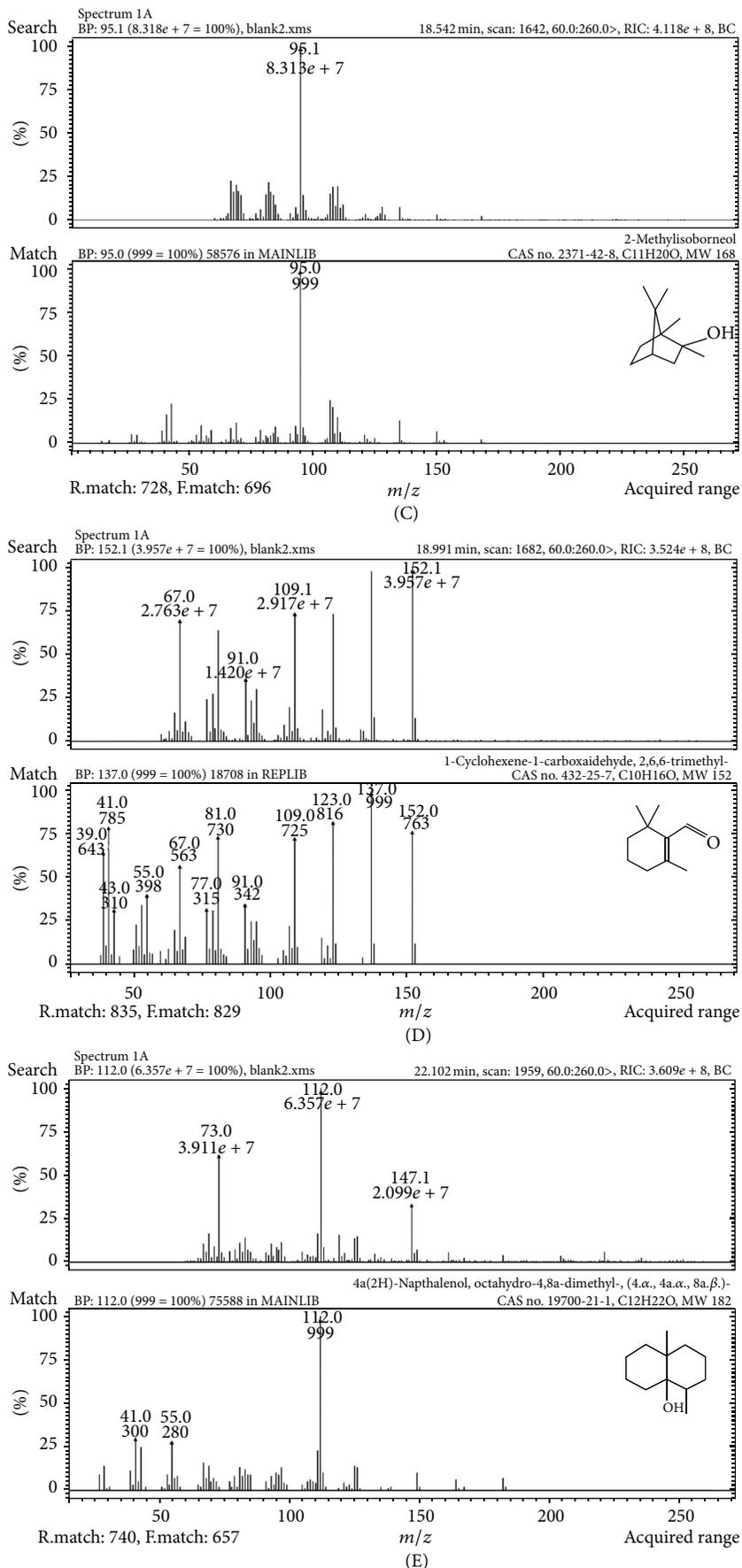


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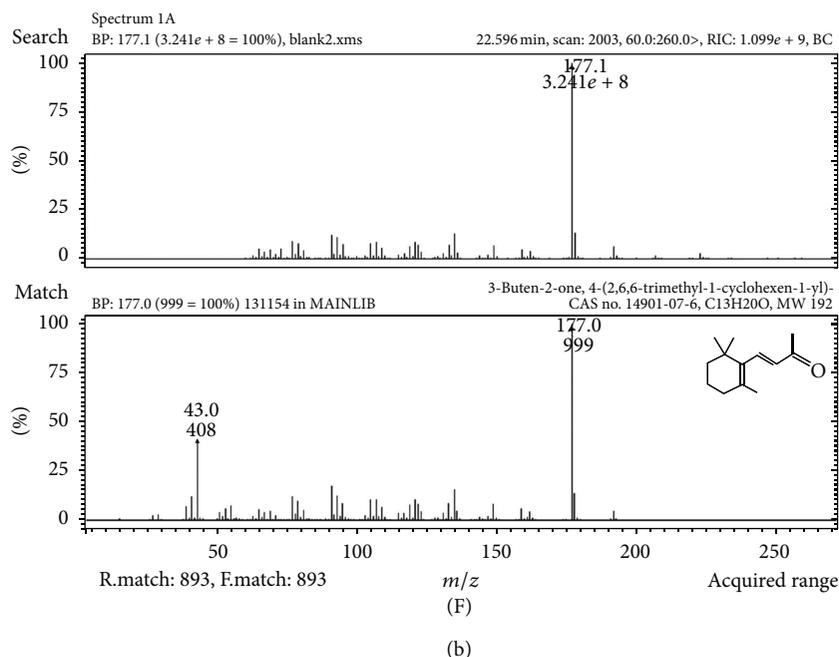


FIGURE 3: (a) MS-chromatogram of water sample (total ion current of the MS in the select ion mode) and (b) mass spectra of the six target compounds. Shown are (A) DMTS, (B) IBMP, (C) 2-MIB, (D) β -cyclocitral, (E) GSM, and (F) β -ionone for both (a) and (b).

TABLE 4: The concentration of the five odors detected in waterworks from Wuxi city (all samples were test two times).

Compounds	Waterworks A ^e (ng L ⁻¹)			Waterworks B (ng L ⁻¹)			Waterworks C (ng L ⁻¹)		
	A1 ^a	A2 ^b	A3 ^c	B1 ^a	B2 ^b	B3 ^c	C1 ^a	C2 ^b	C3 ^c
DMTS	37.5	27.8	30.9	22.4	38.7	51.6	250.3	—	30.7
2-MIB	298.2 ^d	9.8	4.0	104.6	3.9	5.9	1.6	4.2	1.1
β -Cyclocitral	338.8 ^d	68.6	6.4	120.4	12.2	0.9	n.d.	n.d.	n.d.
GSM	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
β -Ionone	112.9	n.d.	n.d.	98.2	n.d.	n.d.	n.d.	n.d.	n.d.

^{a, b, c} Represent source water, product water, and tap water, respectively.

^d The samples above the upper-limit of the calibration range were diluted twice before the further test.

^e Waterworks A is located at Taihu Lake, Wuxi city.

that the samples are collected from sampling field to the lab, and time consuming on samples pretreatment. In addition, the musty odors GSM and 2-MIB are the required inspection items for drinking water in some countries, as in China and some other developing countries. Therefore, we conducted another experiment called attenuation or storage time experiment, to study the concentration decay subsequently.

To be more specific, two kinds of material vials had been applied to collect environmental samples, including glass vial for routine sampling and plastic vial (PET, polyethylene glycol terephthalate) which was convenient for specialists or citizens in case of some emergencies such as algae outbreak, ship leakage, flood, and earthquake, for the sake of collecting the typical samples. The water samples were obtained from Taihu Lake, Wuxi city. The mercuric chloride had been added to original water samples to inhabit microbial growth before the storage time experiment series. The result was shown in Table 5.

According to the result of analysis of variance calculated by SPSS 19.0, we did not find any statistically significant differences of the concentrations for both of GSM and 2-MIB during the storage time, and the P value was 0.92 and 0.98, respectively, for the plastic vial, whereas the glass vial was 0.69 and 0.80, respectively. Therefore, it is effective and reliable to detect GSM and 2-MIB in ten days if the water samples would be preserved in plastic or glass vial, and other required conditions, including sealed cap and 4°C in the dark.

6. Conclusion

A simple and sensitive method for simultaneous analysis of five odors in environmental water was developed by HS-SPME coupled to GC-MS, including GSM and 2-MIB, as well as DMTS, β -cyclocitral, and β -ionone; and it is more practical to detect trace odors in environmental water for future study,

TABLE 5: Result^a for water storage time (all samples were tested three times).

Storage time ^b (d)	Linearity (R)		Plastic vial ^c (ng L ⁻¹)		Glass vial ^c (ng L ⁻¹)	
	GSM	2-MIB	GSM	2-MIB	GSM	2-MIB
0	0.9997	0.9999	108.26	109.36	98.62	101.17
1	0.9991	0.9993	95.32	107.33	92.59	107.88
2	0.9998	0.9998	98.32	94.02	94.62	89.61
3	0.9997	0.9934	105.62	107.04	98.63	95.17
4	0.9987	0.9995	104.85	96.13	96.86	95.86
5	0.9986	0.9995	108.26	106.07	97.31	94.69
6	0.9941	0.9998	98.98	109.36	95.26	94.51
7	0.9997	0.9987	105.24	97.01	96.54	96.18
10	0.9917	0.9974	96.13	105.95	98.05	91.74

^aThe concentration of target compounds in original water, GSM and 2-MIB, n.d., and 1.1 ng L⁻¹, respectively.

^bThe 0 day means the day of sampling, 1 day means one day after 0 day, and so on.

^cThe 100 ng L⁻¹ mixed standard of GSM and 2-MIB was added to both plastic and glass vial.

if modifying the original magnetic stirrer into a new one. Moreover, the storage time experiment indicated that the concentrations did not change significantly for GSM and 2-MIB if they were stored in canonical environment in ten days.

Abbreviation

GSM:	Geosmin
2-MIB:	2-Methylisoborneol
DMTS:	Dimethyl trisulfide
IBMP:	2-Isobutyl-3-methoxypyrazine
CLSA:	Closed-loop stripping analysis
LLME:	Liquid-liquid microextraction
SBSE:	Stir bar sorptive extraction
SPE:	Solid-phase extraction
P&T:	Purge and trap
HS-SPME:	Headspace solid phase microextraction
GC-MS:	Chromatography-mass spectrometry
LOD:	Limit of detection
RSD:	Relative Standard Deviation
OTC:	Odor threshold concentration.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this article.

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References

- [1] G. Izaguirre and W. D. Taylor, "A guide to geosmin- and MIB-producing cyanobacteria in the United States," *Water Science and Technology*, vol. 49, no. 9, pp. 19–24, 2004.
- [2] N. N. Gerber, "Geosmin an earthy-smelling substance isolated from actinomycetes," *Biotechnology and Bioengineering*, vol. 9, article 321, 1967.
- [3] N. N. Gerber and H. A. Lechevalier, "Geosmin, an earthy-smelling substance isolated from actinomycetes," *Applied microbiology*, vol. 13, no. 6, pp. 935–938, 1965.
- [4] A. Peter, O. Köster, A. Schildknecht, and U. von Gunten, "Occurrence of dissolved and particle-bound taste and odor compounds in Swiss lake waters," *Water Research*, vol. 43, no. 8, pp. 2191–2200, 2009.
- [5] K. K. Schrader, S. A. Rubio, R. H. Piedrahita, and A. M. Rimando, "Geosmin and 2-methylisoborneol cause off-flavors in cultured largemouth bass and white sturgeon reared in recirculating-water systems," *North American Journal of Aquaculture*, vol. 67, no. 3, pp. 177–180, 2005.
- [6] W. F. Young, H. Horth, R. Crane, T. Ogden, and M. Arnott, "Taste and odour threshold concentrations of potential potable water contaminants," *Water Research*, vol. 30, no. 2, pp. 331–340, 1996.
- [7] J. L. Graham, K. A. Loftin, M. T. Meyer, and A. C. Ziegler, "Cyanotoxin mixtures and taste-and-odor compounds in cyanobacterial blooms from the midwestern united states," *Environmental Science and Technology*, vol. 44, no. 19, pp. 7361–7368, 2010.
- [8] J.-M. Davies, M. Roxborough, and A. Mazumder, "Origins and implications of drinking water odours in lakes and reservoirs of British Columbia, Canada," *Water Research*, vol. 38, no. 7, pp. 1900–1910, 2004.
- [9] C. Höckelmann and F. Jüttner, "Off-flavours in water: Hydroxyketones and β -ionone derivatives as new odour compounds of freshwater cyanobacteria," *Flavour and Fragrance Journal*, vol. 20, no. 4, pp. 387–394, 2005.
- [10] J. Chen, P. Xie, Z. Ma et al., "A systematic study on spatial and seasonal patterns of eight taste and odor compounds with rel-

- ation to various biotic and abiotic parameters in Gonghu Bay of Lake Taihu, China,” *Science of the Total Environment*, vol. 409, no. 2, pp. 314–325, 2010.
- [11] A. J. Simkin, S. H. Schwartz, M. Auldridge, M. G. Taylor, and H. J. Klee, “The tomato carotenoid cleavage dioxygenase 1 genes contribute to the formation of the flavor volatiles β -ionone, pseudoionone, and geranylacetone,” *Plant Journal*, vol. 40, no. 6, pp. 882–892, 2004.
- [12] E. Lewinsohn, Y. Sitrit, E. Bar et al., “Not just colors—carotenoid degradation as a link between pigmentation and aroma in tomato and watermelon fruit,” *Trends in Food Science and Technology*, vol. 16, no. 9, pp. 407–415, 2005.
- [13] “SIDS Initial Assessment Report for SIAM 20,” Paris, France: pp. 8–15, 2004.
- [14] J. Mallevialle, *Identification and Treatment of Tastes and Odors in Drinking Water*, chapter 5, American Water Works Association, Denver, Colo, USA, 1987.
- [15] E. D. Mackey, H. Baribeau, G. F. Crozes, I. H. Suffet, and P. Piriou, “Public thresholds for chlorinous flavors in U.S. tap water,” *Water Science and Technology*, vol. 49, no. 9, pp. 335–340, 2004.
- [16] I. Freuze, S. Brosillon, D. Herman, A. Laplanche, C. Démocrate, and J. Cavard, “Odorous products of the chlorination of phenylalanine in water: formation, evolution, and quantification,” *Environmental Science and Technology*, vol. 38, no. 15, pp. 4134–4139, 2004.
- [17] D. Mitjans and F. Ventura, “Determination of fragrances at ng/L levels using CLSA and GC/MS detection,” *Water Science and Technology*, vol. 52, no. 10–11, pp. 145–150, 2005.
- [18] X. Deng, G. Liang, J. Chen, M. Qi, and P. Xie, “Simultaneous determination of eight common odors in natural water body using automatic purge and trap coupled to gas chromatography with mass spectrometry,” *Journal of Chromatography A*, vol. 1218, no. 24, pp. 3791–3798, 2011.
- [19] T. Luo, Z.-R. Zhou, and S.-B. Lin, “Determination of volatile organic compounds in drinking water by purge and trap gas chromatography/mass spectrometry,” *Wei Sheng Yan Jiu*, vol. 35, no. 4, pp. 504–507, 2006.
- [20] H. W. Liu, Y. T. Liu, B. Z. Wu et al., “Process sampling module coupled with purge and trap-GC-FID for in situ auto-monitoring of volatile organic compounds in wastewater,” *Talanta*, vol. 80, pp. 903–908, 2009.
- [21] C. Cortada, L. Vidal, and A. Canals, “Determination of geosmin and 2-methylisoborneol in water and wine samples by ultrasound-assisted dispersive liquid-liquid microextraction coupled to gas chromatography-mass spectrometry,” *Journal of Chromatography A*, vol. 1218, no. 1, pp. 17–22, 2011.
- [22] R. R. Madrera and B. S. Valles, “Determination of volatile compounds in apple pomace by stir bar sorptive extraction and gas chromatography-mass spectrometry (SBSE-GC-MS),” *Journal of Food Science*, vol. 76, no. 9, pp. C1326–C1334, 2011.
- [23] A. M. Casas Ferreira, M. Möder, and M. E. Fernández Laespada, “GC-MS determination of parabens, triclosan and methyl triclosan in water by in situ derivatisation and stir-bar sorptive extraction,” *Analytical and Bioanalytical Chemistry*, vol. 399, no. 2, pp. 945–953, 2011.
- [24] P. Grossi, I. R. B. Olivares, D. R. de Freitas, and F. M. Lancas, “A novel HS-SBSE system coupled with gas chromatography and mass spectrometry for the analysis of organochlorine pesticides in water samples,” *Journal of separation science*, vol. 31, no. 20, pp. 3630–3637, 2008.
- [25] B. Chen, W. Wang, and Y. Huang, “Cigarette filters as adsorbents of solid-phase extraction for determination of fluoroquinolone antibiotics in environmental water samples coupled with high-performance liquid chromatography,” *Talanta*, vol. 88, pp. 237–243, 2012.
- [26] R. López, M. Aznar, J. Cacho, and V. Ferreira, “Determination of minor and trace volatile compounds in wine by solid-phase extraction and gas chromatography with mass spectrometric detection,” *Journal of Chromatography A*, vol. 966, no. 1–2, pp. 167–177, 2002.
- [27] A. L. Capriotti, C. Cavaliere, P. Giansanti, R. Gubbiotti, R. Samperi, and A. Laganà, “Recent developments in matrix solid-phase dispersion extraction,” *Journal of Chromatography A*, vol. 1217, no. 16, pp. 2521–2532, 2010.
- [28] A. Salemi, S. Lacorte, H. Bagheri, and D. Barceló, “Automated trace determination of earthy-musty odorous compounds in water samples by on-line purge-and-trap-gas chromatography-mass spectrometry,” *Journal of Chromatography A*, vol. 1136, no. 2, pp. 170–175, 2006.
- [29] C. L. Arthur and J. Pawliszyn, “Solid-phase microextraction with thermal-desorption using fused-silica optical fibers,” *Analytical Chemistry*, vol. 62, pp. 2145–2148, 1990.
- [30] X. Lu, C. Fan, J. Shang, J. Deng, and H. Yin, “Headspace solid-phase microextraction for the determination of volatile sulfur compounds in odorous hyper-eutrophic freshwater lakes using gas chromatography with flame photometric detection,” *Microchemical Journal*, vol. 104, pp. 26–32, 2012.
- [31] K. Saito, K. Okamura, and H. Kataoka, “Determination of musty odorants, 2-methylisoborneol and geosmin, in environmental water by headspace solid-phase microextraction and gas chromatography-mass spectrometry,” *Journal of Chromatography A*, vol. 1186, no. 1–2, pp. 434–437, 2008.
- [32] S. Nakamura and S. Daishima, “Simultaneous determination of 22 volatile organic compounds, methyl-tert-butyl ether, 1,4-dioxane, 2-methylisoborneol and geosmin in water by headspace solid phase microextraction-gas chromatography-mass spectrometry,” *Analytica Chimica Acta*, vol. 548, no. 1–2, pp. 79–85, 2005.
- [33] Y.-H. Sung, T.-Y. Li, and S.-D. Huang, “Analysis of earthy and musty odors in water samples by solid-phase microextraction coupled with gas chromatography/ion trap mass spectrometry,” *Talanta*, vol. 65, no. 2, pp. 518–524, 2005.
- [34] S. W. Lloyd, J. M. Lea, P. V. Zimba, and C. C. Grimm, “Rapid analysis of geosmin and 2-methylisoborneol in water using solid phase micro extraction procedures,” *Water Research*, vol. 32, no. 7, pp. 2140–2146, 1998.
- [35] S. B. Watson, B. Brownlee, T. Satchwill, and E. E. Hargesheimer, “Quantitative analysis of trace levels of geosmin and MIB in source and drinking water using headspace SPME,” *Water Research*, vol. 34, no. 10, pp. 2818–2828, 2000.
- [36] L. Zhang, R. Hu, and Z. Yang, “Simultaneous picogram determination of “earthy-musty” odorous compounds in water using solid-phase microextraction and gas chromatography-mass spectrometry coupled with initial cool programmable temperature vaporizer inlet,” *Journal of Chromatography A*, vol. 1098, no. 1–2, pp. 7–13, 2005.
- [37] R. A. Murray, “Limitations to the use of solid-phase microextraction for quantitation of mixtures of volatile organic sulfur compounds,” *Analytical Chemistry*, vol. 73, no. 7, pp. 1646–1649, 2001.
- [38] J. Pawliszyn, *Principle and Application of Solid Phase Microextraction*, Chemical, Beijing, China, 2012.

- [39] M. Chai and J. Pawliszyn, "Analysis of environmental air samples by solid-phase microextraction and gas chromatography/ion trap mass spectrometry," *Environmental Science and Technology*, vol. 29, no. 3, pp. 693–701, 1995.



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