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Preconcentration Techniques

DETERMINATION OF GEOSMIN AND 2-METHYLISOBORNEOL IN WATER BY HEADSPACE LIQUID-PHASE MICROEXTRACTION COUPLED WITH GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Geosmin (GSM) and 2-methylisoborneol (MIB) were extracted from water samples, adsorbed in organic solvent microdrop by headspace liquid-phase microextraction (HS-LPME), and were analyzed by gas chromatography-mass spectrometry (GC-MS). Influence factors such as the extraction solvent types, headspace and microdrop volumes, stirring rate, equilibrium and extraction time, and ionic strength for HS-LPME efficiency were thoroughly evaluated. Under optimized extraction and detection conditions, the calibration curves of GSM and MIB were linear in the range of 5–1000 ng/L. The detection limits of GSM and MIB were 1.1 and 1.0 ng/L, respectively. Average recoveries of 95.45–113.7% (n = 5) were obtained and method precisions were also satisfactory. Trace levels of the off-flavor compounds at ng/L in tap water and raw water were successfully quantified.

Keywords: Gas chromatography-mass spectrometry; Geosmin; Headspace liquid-phase microextraction; 2-Methylisoborneol; Single-drop microextraction; Water samples

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INTRODUCTION

Surface water supplies, especially drinking water reservoirs, are more likely to be affected by substances causing undesirable tastes and odors. It is commonly accepted that the earthy-musty smell is associated with the presence of geosmin (GSM) and 2-methylisoborneol (MIB) (Mallevialle and Suffet 1987; Jensen et al. 1994; Bruchet 1999; Lu et al. 2009). These chemical by-products are often from the growth of blue-green algae, commonly found in lakes and reservoirs (Watson et al. 2003; Schrader and Dennis 2005; Uwins, Teasdale, and Stratton 2007). The mutagenicity and hepatotoxicity caused by MIB and GSM have been reported (Gagné et al. 1999; Huang, Lai, and Cheng 2007), but the impact on health has not been thoroughly investigated. Some people can smell the odor of these semi-volatile compounds in drinking water at 10 ng/L or lower. Therefore, a sensitive, reliable, and simple method is required for the determination of the presence and contents of MIB and GSM at low ng/L level.

Sample pretreatment is vital and necessary in order to measure very small amounts of these compounds in complex matrices, although the determination of MIB and GSM has been carried out by gas chromatography-mass spectrometry (GC-MS). Traditional pretreatment techniques, including closed-loop stripping analysis (CLSA) (Krasner, Wang, and Mcguire 1981; Zander and Pingert 1997), purge and trap (PT) (John, Payne, and Conn 1997; Salemi, Lacorte, and Bagheri 2006), liquid-liquid extraction (LLE) (Shin and Ahn 2000), and solid-phase extraction (SPE) (Palmentier, Taguchi, and Jenkins 1998), assist to improve determination but lack sensitivity and are time-consuming, resulting in low extraction recoveries. Recently, new techniques have emerged, such as solid-phase microextraction (SPME) (Zhang, Hu, and Yang 2005; Saito, Okamura, and Kataoka 2008; Sung, Li, and Huang 2005), liquid-phase microextraction (LPME) (Xie, He, and Huang 2007), and stir bar sorptive extraction (SBSE) (Nakamura and Nakaura 2001; Benanou, Acobas, and Roubin 2003). Probably, those based on SPME are the most popular methods for MIB and GSM determination (Pawliszyn 1997; Harmon 1997; Kataoka, Lord, and Pawliszyn 2000), with even a 2 cm fiber produced specially for the analysis of water off-odorants. The well-established SPME is solvent-free, rapid, and simple for sample enrichment, however, occasionally limited by the small amounts of polymer coating and the expensive costs of extraction fibers. The use of SBSE offers higher recoveries due to utilization of a stir bar coated with polydimethylsiloxane (PDMS), but it needs special thermal desorption device and a long time for extraction. The LPME using a microdrop of solvent to extract the analytes proved simple and inexpensive; however, it does not provide enough attention to the stability of the microdrop during extraction.

In this work, a headspace LPME (HS-LPME) method based on the analyte partitioning among the aqueous sample, headspace, and the organic microdrop was employed to extract MIB and GSM in environmental water, which ensures the microdrop is stable and avoids the exhaustive extraction. Several surface water samples including tap and raw water have been successfully subjected to the HS-LPME coupling with GC-MS. A series of parameters influencing extraction efficiency of the HS-LPME were investigated in detail, and the extraction recoveries were also compared with those of single-drop microextraction (SDME).

EXPERIMENTAL

Reagents and Instrumentation

The 2-Methylisoborneol (MIB, 99.9%, 100 μg/mL in methanol) and geosmin (GSM, 99.3%, 100 μg/mL in methanol) were purchased from Supelco (Bellefonte, PA, USA). The solutions were stored at 4°C and used after dilution with methanol. In order to eliminate volatilization losses, all aqueous samples were freshly prepared prior to use. All other reagents used were of high performance liquid chromatography (HPLC) grade.

The GC-MS analysis was performed with a Thermo Finngan Trace DSQ 2003 (Thermo Electron Co., USA). A 10 μL syringe with a bevel-needle tip for LPME was purchased from SGE Co. (Melbourne, Australia). Twenty milliliter (20 mL) headspace vials obtained from Supelco (Bellefonte, PA, USA) were used for extraction. Ultrapure water was produced by a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Analytical Conditions

The separation was conducted on a 30 m × 0.25 mm i.d. × 0.25 μm DB-5 MS capillary column (Agilent Technologies, Palo Alto, CA). The carrier gas was helium (purity 99.999%) at a flow rate of 1.0 mL/min. The injector temperature was 250°C, and all injections were carried out in the splitless mode. The GC oven temperature program was as follows: holding at 60°C for 1 min, raising to 130°C (15°C/min), and increasing to 200°C at 18°C/min. The transfer line temperature and ion source temperature were both 250°C. The mass spectrometer was operated in the selected ion monitoring (SIM) mode with electron impact (EI) ionization resource (electron energy 70 ev). SIM selected the ions at m/z 95, 107 and 135 for MIB, and 112 and 125 for GSM.

Extraction Processes

Headspace LPME (HS-LPME). The 10 mL of water sample was placed into a 20 mL headspace vial containing a magnetic stirrer (10 mm × 3 mm). The vial was then sealed with a silicon PTFE septum cap using a manual crimper. The sealed vial was placed in a magnetic agitator with a temperature controller and was held for a period of time for equilibrium. The 3 μL organic solvent was poured into a 10 μL microsyringe with a bevel-needle tip and then the microliter syringe was used to penetrate the septum. The syringe must be clamped steadily to fix the needle tip constantly in the headspace of the sample and then the plunger was depressed; it was held for a set time to let the analytes be extracted by the microdrop suspended at the beveled tip. After that, the microdrop was drawn back into the microsyringe with the needle still left in the headspace. Then, the microsyringe was removed from the vial and the extract was finally injected into the GC-MS system.

Single drop microextraction (SDME). The 2 μL organic solvent containing GSM and MIB was poured into a 10 μL microsyringe with an angle-cut needle tip, and then the microsyringe was inserted into the headspace, where the tip of the

needle was located close to the center of the headspace volume. The septum of the vial was penetrated through by needle until the tip was completely immersed into the solution. The plunger was depressed to cause the solvent to form a microdrop suspended from the tip.

Sample Collection and Preparation

Five different water samples were collected from Qingdao Sino-French Water Supply Co. Ltd., namely, Phase I water (mixture of Dagu River water and Jihongtan Reservoir water, 1:1, v/v), Phase II water (Laoshan Reservoir water), effluent water from Xianjiazhai, Yellow River water, and effluent water from Baisha River. And two samples were taken from Qingdao Liuting Water Co. Ltd., including the influent and effluent water (the raw water is underground water). All the water samples were filtered through a polypropylene filter (0.45 μm) for use.

RESULTS AND DISCUSSION

Optimization of HS-LPME

In order to optimize the HS-LPME extraction efficiency of MIB and GSM, several important parameters such as the extraction solvent types, headspace and microdrop volumes, stirring rate, equilibrium and extraction time, and ionic strength were systematically investigated.

Influence of extraction solvent types. The choice of an appropriate extraction solvent was initially considered for the HS-LPME method. The extraction normally takes place between small amounts of water-immiscible solvent and aqueous phase containing the analytes (Xu, Basheer, and Lee 2007). In addition to the ability to offer high partition ratios for analytes and the ability to separate from the analyte peaks in the chromatogram (Tankeviciute, Kazlauskas, and Vickackaite 2001), an excellent extraction solvent should also satisfy the following requirements (Xie et al. 2007): (1) excellent dissolving capacity for analytes for high enrichment and rapid extraction; (2) appropriate solvent viscosity to produce the suitable microdrop suspended at the tip of the needle and favor the depressing and withdrawing movement; and (3) low volatility for reducing or even avoiding solvent loss. In this work, toluene, cyclohexane, and hexane were tested in room temperature as the extraction solvents without agitation.

The extraction was performed in the headspace, so the extraction solvent should have relatively high boiling points and low vapor pressures to decrease solvent volatilization loss during extraction. At the same time, the most suitable solvents for GC should have relatively high vapor pressures (Psillakis and Kalogerakis 2002). Hexane has relatively high vapor pressure that is appropriate for GC, however, it is easily evaporated completely due to the low boiling point and, therefore, no GC-MS signal was detected. As seen from Figure 1, the higher extraction efficiency was attained by using cyclohexane. Cyclohexane possesses a relatively higher boiling point than hexane and higher vapor pressure than toluene; the two features are both desirable for GC. Therefore, cyclohexane was selected as the extraction solvent for further studies.

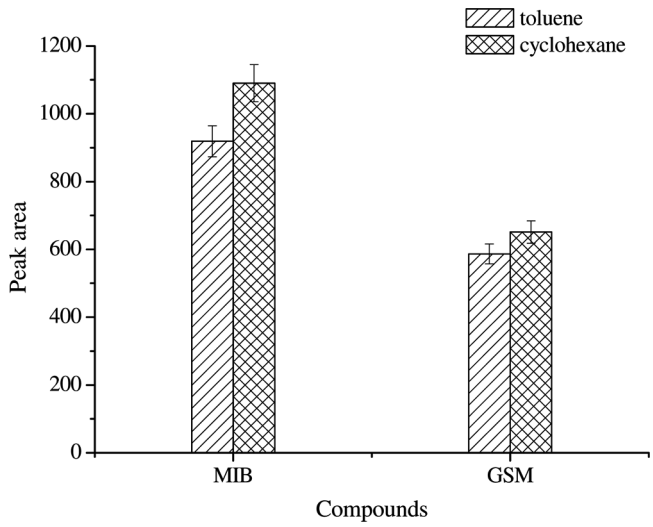

Figure 1. Influence of extraction solvent types on the extraction efficiency of HS-LPME. Other extraction conditions: 10 mL pure water solution containing standards of GSM and MIB at 200 ng/L of each in 20 mL headspace vial, 3 μL organic solvent, 30 min equilibrium time, and 10 min extraction time.

Influences of headspace and microdrop volumes. It is also important to investigate the influences of headspace and microdrop volumes on extraction efficiency since HS-LPME is based on the analyte partitioning among the aqueous sample, headspace, and the organic microdrop. During HS-LPME, headspace volume is the direct factor affecting the equilibrium concentration of analytes in headspace phase. Increase of headspace volume will favor analytes to volatilize towards headspace gas phase; however, overlarge headspace volume will "dilute" analytes and therefore decrease sensitivity. Also, it is known that the larger sample volume is in the headspace vial, the more the increase in the amounts of analytes. At the same time, various factors must be comprehensively considered for headspace efficiency including the vial column, headspace volume, sample volume, and so on. Therefore, it is important to determine the influence of phase ratio (liquid to headspace) on the extraction efficiency. In the present study, 20 mL headspace vial was chosen for the best extraction efficiency, in which 10 mL of headspace volume was employed large enough to prevent the direct contact between the microdrop and the liquid sample. As a result, the optimum volume ratio of liquid sample to headspace is 1:1 in the 20 mL headspace vial, which not only enabled the analytes in the headspace phase dominated in gas-liquid distribution, but also avoided the dilution effects caused by overlarge headspace volume and, therefore, offered the highest extraction efficiency and sensitivity.

In general, a microdrop with large volume would definitely impose a positive effect on the extraction of the analytes; however, it is also difficult to manipulate (He and Lee 1997). When the microdrop volume increased from 2.5 to 3.0 μL, the extraction efficiencies of MIB and GSM were both significantly increased; from 3.0 to 3.5 μL, the extraction efficiency of MIB increased while that of GSM

decreased. If the microdrop was too large, it would become difficult to suspend the microdrop at the tip of the microsyringe, so that it was very easy to fall apart. Therefore, the drop volume of 3.0 μL as a compromise was chosen for subsequent experiments.

Influence of stirring rate. Stirring rate plays an important role in the extraction of the analytes. Sample agitation can enhance extraction efficiency and shorten extraction time. The agitation can accelerate the mass transfer in the aqueous phase and induce convection into the headspace and thus shorten the time for achieving a thermodynamic equilibrium (Psillakis and Kalogerakis 2002; Xie et al. 2007). For the purpose of the present investigation, 3.0 μL cyclohexane was exposed each time for 10 min to the headspace of 10 mL water sample spiked at 200 ng/L with the standard solution and stirred at different agitation rates including 0, 720, 900, and 1000 rpm. It was observed that the extraction efficiency increased with the increase of stirring rate. However, over-stirring would also accelerate the volatilization of the headspace extraction solvent and affect the stability of the microdrop at the tip of the needle, which would enlarge experimental errors. For this reason, a stirring rate of 1000 rpm was employed in further work.

Influence of equilibrium and extraction time. Time is also an important factor affecting extraction efficiency of HS-LPME method, and it is necessary to determine the time when the amount of analytes in organic solvent drop will reach maximum. The equilibrium time was measured as the time span from capping of the vial with analyzed samples in it until to the point of insertion of the microsyringe with extraction solvent in it. The extraction time was determined by exposing the organic drop in the headspace for a period of time until that the microdrop was to be retracted into the needle. Herein, the equilibrium time in fact means the pre-equilibrium time before headspace extraction. During experimentation, the influence of different equilibrium time was investigated under the constant extraction time of 10 min, as well as, the influence of different extraction times, which was investigated under the the constant equilibrium time of 30 min.

The influence of the equilibrium and extraction time was investigated. Under the conditions of stirring and equilibrium for a certain time, MIB and GSM could volatilize to the headspace of the vial and, therefore, accelerate the analysis. Different time spans were tested, including 0, 10, 20, and 30 min, and as a result, the extraction efficiency increased with the increase of the equilibrium time. Instead, for longer time, the efficiency decreased. As a result, we selected the optimum equilibrium time of 30 min.

During a HS-LPME process, the distribution equilibrium of enriched analytes could be established among the sample solution, headspace, and organic solvent drop. Consequently, within a time span, equilibrium would be reached, which requires the satisfaction of the following: avoidance of the loss of microdrop and longer sampling period, providing sufficient extraction efficiency; and the ability to perform the HS-LPME procedure (Sung et al. 2005). The extraction time span displayed great influence on enrichment amounts, that is, the longer the extraction time was, the more likely the enrichment was close to equilibrium and, therefore, the higher extraction efficiency. However, for longer extraction time, the volatilization of extraction drop would definitely impose a negative effect on the extraction of

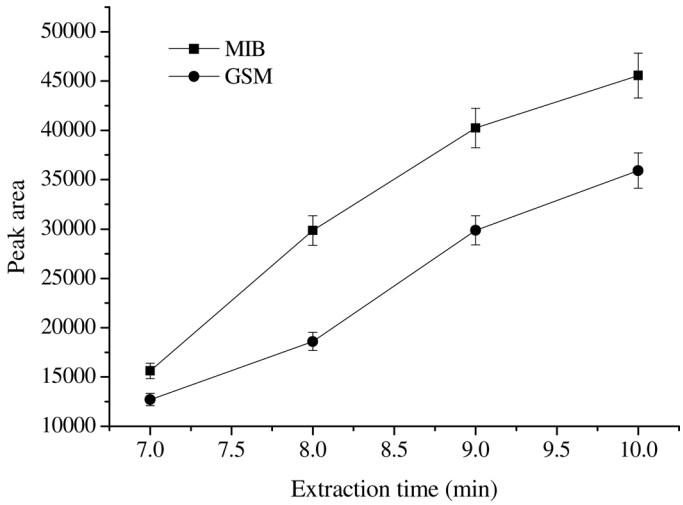

Figure 2. Influence of extraction time on the extraction efficiency of HS-LPME. Other extraction conditions: 10 mL saturated NaCl solution containing standards of GSM and MIB at 200 ng/L of each in 20 mL headspace vial, 3 μL cyclohexane drop, 30 min equilibrium time, and 1000 rpm stirring rate.

the analytes; meanwhile, the extraction repeatability became poor. As shown in Figure 2, the peak areas of both analytes increased with the increase of the extraction time in the range of 7 to 10 min. For the longer time, the microdrop volume decreased drastically and, thereby, deteriorated extraction efficiency. As a result, the optimum extraction time was chosen at 10 min.

Influence of ionic strength. Ionic strength is also a major factor affecting extraction efficiency. The influence of ionic strength was determined by preparing standards with NaCl solutions at different concentrations (w/v %) ranging from 0 to saturated concentration. The odorous analytes displayed a significant increase in extraction efficiency with the addition of NaCl, and the maximum peak areas of both MIB and GSM were achieved when the solution was saturated with NaCl. The increased ionic strength of the sample solution decreased the water solubility of the analytes and, consequently, enhanced the extraction efficiency due to the salting-out effect (Xie et al. 2007; Fontana et al. 2009). The suitability of the HS-LPME technique for the extraction of compounds in water relied on the transfer of analytes from the aqueous phase to the gaseous phase, resulting in higher extraction efficiency for these compounds in the headspace. Accordingly, saturated NaCl solution was employed for further work.

Comparison of Extraction Performance Between HS-LPME and SDME

The aforementioned optimized extraction conditions for HS-LPME were employed in subsequent work, namely, after equilibrium for 30 min, 3 μL cyclohexane microdrop exposed for 10 min to the 10 mL headspace volume of a 10 mL

saturated NaCl solutions containing standard mixture, with stirring at 1000 rpm, under room temperature. To further evaluate the performance of HS-LPME, SDME was used as a comparison. Samples were extracted for the highest efficiency (data not shown) under the optimum experimental conditions summarized as: extraction solvent, toluene; microdrop volume, 2 μL; stirring rate, 900 rpm; extraction temperature, 50°C; saturated NaCl solution; extraction time, 30 min. In terms of the extraction recovery, that of HS-LPME was higher than SDME; the values of the former were approximately 4 times and 3 times those of the latter for MIB and GSM, respectively. Therefore, HS-LPME was selected to extract the real water samples.

The HS-LPME is based on the analyte partitioning between the aqueous sample and the organic microdrop, which is not an exhaustive extraction technique. In HS-LPME, the analytes can be effectively extracted from the aqueous sample into the single-drop solvent by suspending a microdrop of organic solvent at the tip of a microsyringe needle and placing it into the headspace of a stirred sample solution. After extraction, the microdrop solvent is retracted into the needle and then injected directly into a GC system, so it does not involve any labor intensive and time-consuming steps. The developed method employed less extraction solvent and the headspace favored the semi-volatile compounds of GSM and MIB to cleanup and concentration and, thus, improved extraction efficiency. Moreover, the HS-LPME proved robust compared with the unstable microdrop in SDME.

Evaluation of Method Performance

Under the aforementioned optimized HS-LPME conditions, total ion current (TIC) chromatogram of the two compounds from standard solution is shown in Figure 3. The method performance was investigated including reproducibility, linear

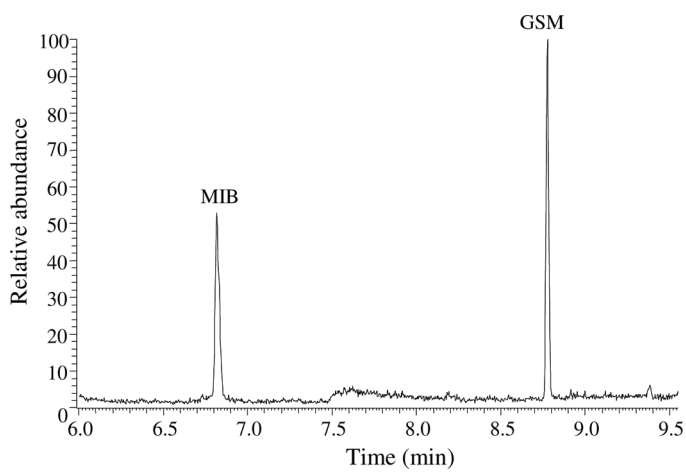

Figure 3. TIC chromatogram obtained by HS-LPME coupled to GC-MS under the SIM mode for the standards of MIB and GSM at 200 ng/L of each. Extraction conditions: 3 μL cyclohexane solvent microdrop, 10 mL headspace volume, 1000 rpm stirring rate, 30 min equlibrium time, 10 min extraction time, and saturated NaCl solution.

range, regression equation, correlation coefficient, and detection limit. A series of solutions with GSM and MIB spiked in the river water were tested. Good linear relationships between peak areas and concentrations of both analytes were obtained in the range of 5–1000 ng/L, namely, $y = 122.4\ x - 457.7$ with $R^2 = 0.9973$ for GSM and $y = 150.3\ x - 395.6$ with $R^2 = 0.9970$ for MIB. The limits of detection (LODs) defined for a signal to noise (S/N) ratio of 3:1 were evaluated in the river water for 1.1 ng/L GSM and 1.0 ng/L MIB. The relative standard deviations (RSDs) were 4.1% and 4.8% for GSM and MIB, respectively, based on the peak areas for five replicates of a standard solution at 300 ng/L of each.

The LODs obtained by the present method were comparable with those similar microextraction techniques coupled to GC-MS reported recently, even if slightly higher by just 1 order, and the method also gave wide linear range, as seen from Table 1. Additionally, the extraction time of HS-LPME is generally shorter than that of SPME, SBSE, or HS-SPME, and the cost is dramatically lower. Moreover, the reported HS-LPME linked to GC-MS technique presented 19 times lower LODs for both odorants (Table 1), which is probably due to the different sample matrices of standard solution of *Streptomyces* sp. and *Anabaena* PCC7120, while we analyzed them in river matrix. Still, the proposed method proved to be an excellent cleanup and enrichment method with great potential for the analysis of GSM and MIB in water samples.

Application to Water Samples

To further evaluate the method applicability, simultaneous extraction and determination of the earthy and musty compounds in drinking water and source water were conducted. As seen in Figure 4, neither MIB nor GSM were found in effluent water from Qingdao Liuting Water Co. Ltd. (a); both were detected in different degrees in effluent water from Baisha River (b); Yellow River water (c); and mixed water from Dagu River and Jihongtan Reservoir (1:1, v/v) (d). Contents of MIB and GSM in seven water samples obtained by the external standard method are listed in Table 2. MIB and GSM were not detected after treatment in Laoshan Reservoir water, as well as in the influent/effluent water of underground water from

Table 1. Comparisons of LODs and linear ranges with several microextraction techniques coupled to GC-MS for analysis of GSM and MIB

Pretreatment technique	LOD (ng/L)	Linear range (ng/L)	Sample source	Ref.
SBSE	GSM: 0.15 MIB: 0.33	0.5–100	River water	Nakamura and Nakamura 2001
HS-SPME	GSM: 0.32 MIB: 0.66	1–500	Tap and lake water	Sung et al. 2005
HS-SPME	GSM: 0.6 MIB: 0.9	0–500	Tap and pond water	Saito et al. 2008
HS-LPME	Both: 0.05	10–5000	*Streptomyces* sp. and *Anabaena* PCC7120	Xie et al. 2007
HS-LPME	GSM: 1.1 MIB: 1.0	5–1000	Tap and raw water	Present study

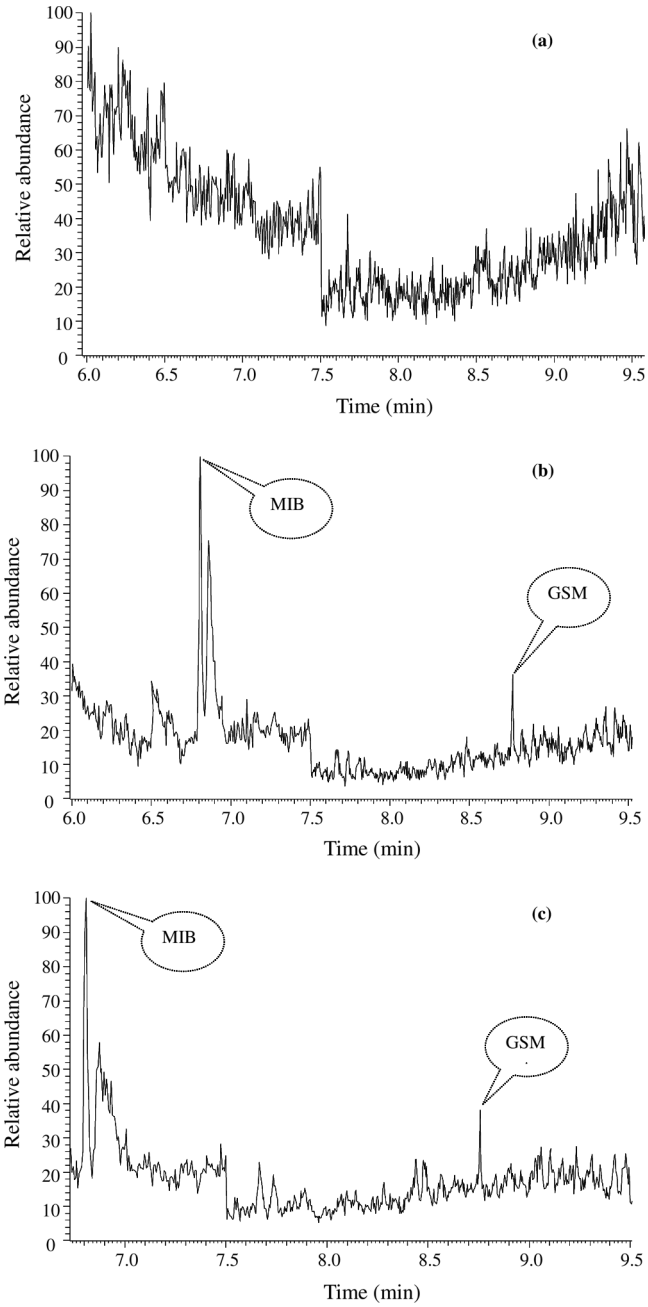

Figure 4. TIC chromatograms obtained by HS-LPME coupled to GC-MS under the SIM mode for the real water samples including (a) effluent water from Qingdao Liuting Water Co. Ltd., (b) effluent water from Baisha River, (c) Yellow River water, and (d) mixed water from Dagu River and Jihongtan Reservoir (1:1, v/v). Extraction conditions were the same as those described in Figure 3.

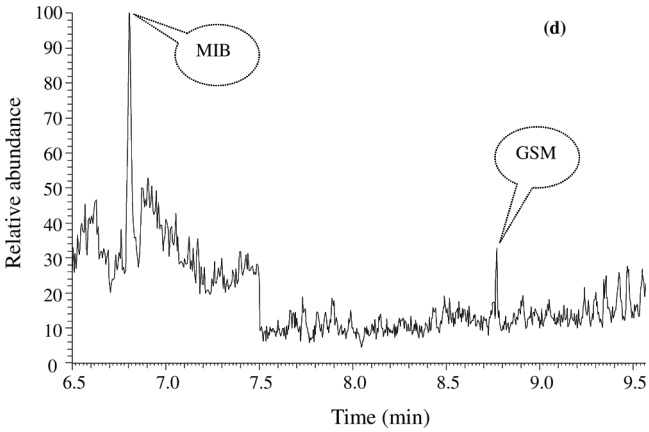

Figure 4. Continued.

Liuting water Co. Ltd. The GSM was detected at 7 ng/L, respectively, in the other four water samples. Amounts of 12, 18, and 15 ng/L MIB were detected from the Dagu River water mixed with Jihongtan Reservoir water, the Yellow River, and the effluent water of Baisha River, respectively, while 9 ng/L MIB were detected from the effluent water of Xianjiazhai, which indicated that the surface water supplies were more likely to be affected by substances causing undesirable tastes and odors (Zhang, Hu, and Yang 2006). Also, as seen from Table 2, the relatively poor precision is presumably due to some factors, such as the low concentration levels of analytes in the several water samples and the limited number of parallel determination experiments. Human's olfactory system often discerns MIB and GSM at concentrations as low as 4–10 ng/L in water (Xie et al. 2007), so it is necessary to treat the studied water samples by utilizing chemicals or adsorbents to control the MIB and GSM, in order that the levels of both compounds meet taste and odor standards set by the Environmental Protection Agency (EPA) (Sung et al. 2005).

Recoveries and RSDs of the HS-LPME coupled to GC-MS method for the determination of the two off-flavor substances are summarized in Table 3. The

Table 2. Contents of MIB and GSM determined by HS-LPME coupled to GC-MS in seven real water samples (ng/L)[a]

Source[b]	#1	#2	#3	#4	#5	#6	#7
MIB	12 ± 4[c]	ND[d]	9 ± 4	18 ± 9	15 ± 5	ND	ND
GSM	7 ± 3	ND	7 ± 3	7 ± 4	7 ± 2	ND	ND

[a]HS-LPME conditions were the same as those described in Figure 4.

[b]#1 Mixed water from Dagu River and Jihongtan Reservoir (1:1, v/v); #2 Laoshan Reservoir water; #3 Effluent water from Xianjiazhai; #4 Yellow River water; #5 Effluent water from Baisha River; #6 Influent water from Qingdao Liuting water Co. Ltd.; and #7 Effluent water from Qingdao Liuting water Co. Ltd.

[c]Averaged from five determinations.

[d]Not detected.

Table 3. Recovery and precision of the HS-LPME coupled to GC-MS method for the determination of MIB and GSM in the two real water samples ($n = 5$)[a]

Source	Compound	Added (ng/L)	Recovery (%)	RSD (%)
Yellow River water	MIB	20	103.70	3.6
	GSM	20	95.45	4.2
	MIB	200	99.60	4.0
	GSM	200	96.74	2.8
Tap water[b]	MIB	10	104.50	2.1
	GSM	10	113.70	2.6
	MIB	100	99.73	2.8
	GSM	100	100.60	6.3

[a]HS-LPME conditions were the same as those described in Figure 4.
[b]Effluent water samples treated from Qingdao Liuting Water Co. Ltd.

MIB and GSM were spiked into Yellow River water at 20 and 200 ng/L, and the effluent water of Liuting Water Co. Ltd. at 10 and 100 ng/L, respectively. The average recoveries ranged from 95.45% and 113.7% with RSDs of less than 6.3% for GSM. As for MIB, the recoveries ranged from 99.60% to 104.5% with RSDs between 2.0% and 4.0%. This method was demonstrated to be reproducible, accurate, sensitive, and practical for the separation and determination of both analytes in environmental water samples. Coupling of HS-LPME with GC-MS has the advantages of low cost and without secondary pollution, which can be applied to the determination of trace level MIB and GSM at ng/L and applicable to drinking or source water quality monitoring and determination.

CONCLUSIONS

A HS-LPME coupling with GC-MS method was developed for the analysis of MIB and GSM in water, which proved simple, fast, inexpensive, to utilize low consumption of toxic organic solvents, and be effective for the analysis of the odorous compounds in water samples. Under the optimum conditions, the two earthy-musty compounds could be separated rapidly, with good linearity and reproducibility and low ng/L levels detection limits. No further pretreatment procedure was required before sample detection, and the analysis of several drinking and source water samples was successfully realized. The method was demonstrated to be greatly applicable to the routine screening and determination of MIB and GSM in water quality research.

REFERENCES

Benanou, D., F. Acobas, and D. M. R. Roubin. 2003. Analysis of off-flavors in the aquatic environment by stir bar sorptive extraction–thermal desorption–capillary GC/MS/olfactometry. *Anal. Bioanal. Chem.* 376: 69–77.

Bruchet, A. 1999. Solved and unsolved cases of taste and odor episodes in the files of Inspector Cluzeau. *Water Sci. Technol.* 40: 15–22.

Fontana, A. R., R. G. Wuilloud, L. D. Martínez, and J. C. Altamirano. 2009. Simple approach based on ultrasound-assisted emulsification-microextraction for determination of polibrominated flame retardants in water samples by gas chromatography–mass spectrometry. *J. Chromatogr. A* 1216: 147–153.

Gagné, F., J. Ridal, C. Blaise, and B. Brownlee. 1999. Toxicological effects of geosmin and 2-methylisoborneol on rainbow trout hepatocytes. *Bull. Environ. Contam. Toxicol.* 63: 174–180.

George, J. E., G. Payne, and D. Conn. 1997. Cost-effective low-level detection of geosmin and MIB in water by large volume purge and trap GC/MS. *Proceedings of American Water Works Association*. Water Quality Technology Conference, November 9–12, Denver, CO.

Harmon, A. D. 1997. In *Techniques for Analyzing Food Aroma*, ed. R. Marsili. 81. New York: Marcel Dekker.

He, Y., and H. K. Lee. 1997. Liquid-phase microextraction in a single drop of organic solvent by using a conventional microsyringe. *Anal. Chem.* 69: 4634–4640.

Huang, W. J., C. H. Lai, and Y. L. Cheng. 2007. Evaluation of extracellular products and mutagenicity in cyanobacteria cultures separated from a eutrophic reservoir. *Sci. Total Environ.* 377: 214–223.

Jensen, S. E., C. L. Anders, L. J. Goatcher, and S. E. Hrudey. 1994. Actinomycetes as a factor in odour problems affecting drinking water from the North Saskatchewan River. *Water Res.* 28: 1393–1401.

Kataoka, H., H. L. Lord, and J. Pawliszyn. 2000. Applications of solid-phase microextraction in food analysis. *J. Chromatogr. A* 880: 35–62.

Krasner, S. W., C. J. H. Wang, and M. J. Mcguire. 1981. Development of a closed-loop stripping technique for the analysis of taste-and odor-causing substances in drinking water. In *Advances in the Identification and Analysis of Organic Pollutants in Water*. Vol. 12, ed., L. H. Keith. AnnArbor, MI: Ann Arbor Science Publishers, Inc.

Lu, W. H., J. P. Ma, R. H. Xiao, and S. W. Zhu. 2009. Progress in pretreatment techniques for analysis on odorous compounds in environmental water. *J. Instru. Anal.* 28(5): 621–626.

Mallevialle, J., and I. H. Suffet, eds. 1987. *Identification and Treatment of Tastes and Odors in Drinking Water*. Denver, CO: American water works association research foundation/lyonnaise des Eaux, AWWA.

Nakamura, S., and N. Nakamura. 2001. Determination of 2-methylisoborneol and geosmin in water by gas chromatography-mass spectrometry using stir bar sorptive extraction. *J. Sep. Sci.* 24: 674–677.

Palmentier, J. P. F. P., V. Y. Taguchi, and S. W. D. Jenkins. 1998. The determination of geosmin and 2-methylisoborneol in water using isotope dilution high resolution mass spectrometry. *Water Res.* 32: 287–294.

Pawliszyn, J. 1997. *Solid Phase Microextraction—Theory and Practice*. New York: Wiley–VCH.

Psillakis, E., and N. Kalogerakis. 2002. Developments in single-drop microextraction. *TrAC Trends Anal. Chem.* 21: 54–64.

Saito, K., K. Okamura, and H. Kataoka. 2008. Determination of musty odorants, 2-methylisoborneol and geosmin, in environmental water by headspace solid-phase microextraction and gas chromatography–mass spectrometry. *J. Chromatogr. A* 1186: 434–437.

Salemi, A., S. Lacorte, and H. Bagheri. 2006. Automated trace determination of earthy-musty odorous compounds in water samples by on-line purge-and-trap-gas chromatography-mass spectrometry. *J. Chromatogr. A* 1136: 170–175.

Schrader, K. K., and M. E. Dennis. 2005. Cyanobacteria and earthy/musty compounds found in commercial catfish (Ictalurus punctatus) ponds in the Mississippi Delta and Mississippi-Alabama Blackland Prairie. *Water Res.* 39: 2807–2814.

Shin, H. S., and H. S. Ahn. 2000. Simple, rapid, and sensitive determination of odorous compounds in water by GC-MS. *Chromatographia* 59: 107–113.

Sung, Y. H., T. Y. Li, and S. D. Huang. 2005. Analysis of earthy and musty odors in water samples by solid-phase microextraction coupled with gas chromatogyaphy/ion trap mass spectrometry. *Talanta* 65: 518–524.

Tankeviciute, A., R. Kazlauskas, and V. Vickackaite. 2001. Headspace extraction of alcohols into a single drop. *Analyst* 126: 1674–1677.

Uwins, H. K., P. Teasdale, and H. Stratton. 2007. A case study investigating the occurrence of geosmin and 2-methylisoborneol (MIB) in the surface waters of the Hinze Dam, Gold Coast, Australia. *Water Sci. Technol.* 55: 231–238.

Watson, S. B., J. Ridal, B. Zaitlin, and A. Lo. 2003. Odours from pulp mill effluent treatment ponds: The origin of sifnificant levels of geosmin and 2-methylisoborneol (MIB). *Chemosphere* 51: 765–773.

Xie, Y. Q., J. He, and J. Huang. 2007. Determination of 2-methylisoborneol and geosmin produced by streptomyces sp. And Anabaena PCC7120. *J. Agric. Food Chem.* 55: 6823–6828.

Xu, L., C. Basheer, and H. K. Lee. 2007. Developments in single-drop microextraction. *J. Chromatogr. A* 1152: 184–192.

Zander, A. K., and P. Pingert. 1997. Membrane-based extraction for detection of tastes and odors in water. *Water Res.* 31: 301–309.

Zhang, L. F., R. K. Hu, and Z. G. Yang. 2005. 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. *J. Chromatogr. A* 1098: 7–13.

Zhang, L. F., R. K. Hu, and Z. G. Yang. 2006. Routine analysis of off-flavor compounds in water at sub-part-per-trillion level by large-volume injection GC/MS with programmable temperature vaporizing inlet. *Water Res.* 40: 699–709.