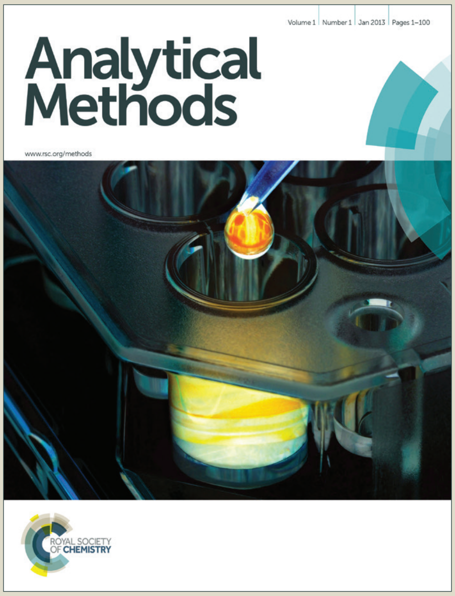
Analytical Methods

Accepted Manuscript



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Application of SPE followed by large-volume injection GC/MS for analysis of Geosmin and 2-Methylisoborneol in water

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ABSTRACT

A new method comprising of solid phase extraction (SPE) and subsequent large volume injection-gas chromatograph/mass spectrometer (LVI-GC/MS) was developed to analyze 2-methylisoborneol (2-MIB) and geosmin in water. The method with the injection volume of 25 μL showed a good linearity (i.e., $R^2 > 0.999$) over the concentration range of 0.5-20 ng L^{-1} and good repeatability and recovery. The MDLs of the method for 2-MIB and geosmin were determined 0.87 and 0.62 ng L^{-1}, respectively, which are lower than one tenth of the compounds' published odor thresholds (i.e., 5-10 ng L^{-1}). If the injection volume was further increased, even lower MDLs could be obtained. In short, considering its ease of use, and high accuracy and sensitivity, the proposed SPE-LVI-GC/MS method can be easily applied for routine analysis of the target compounds in water.

Keywords: 2-MIB, geosmin, SPE, large volume injection, SPME, GC/MS,

1. INTRODUCTION

Taste and odor of drinking water have been a concern for both consumers and water supply authorities. As the national economy grows around the world, more public complaints on tastes and odors from drinking water are received. The public reluctance to directly consume tap water is mainly due to its musty or earthy odors and tastes. For example, most citizens in Korea do not drink water right from their taps; as of 2008, only 1.4% of the people consume tap water without further treatment [1]. The earthy and musty odors from tap water are characteristics of 2-methylisoborneol (2-MIB) and geosmin produced by actinomycetes, cyanobacteria, and fungi in source water [2-6]. They can cause odor sensation to the public even at an extremely low concentration; the odor threshold for 2-MIB or geosmin is 5-10 ng L^{-1}, which is 10^{-4}–10^{-3} times lower than that of methyl tertiary-butyl ether [7-9]. Due to low odor thresholds of 2-MIB and geosmin, it is critical that drinking water suppliers to have an easy analytical method to accurately determine concentrations of odorous compounds on a routine basis.

The quantitative analysis of 2-MIB and geosmin in water has been carried out with capillary gas chromatograph/mass spectrometer (GC/MS) methods because of their high separation power and sensitivity [10]. Since the target analytes usually exist at extremely low concentration (often at ng L^{-1} levels), however, the sensitivity of the GC-MS method remains challenging. In addition, an extensive sample preparation step is often required before injecting the sample into the GC/MS system. A few sample pretreatment techniques have been suggested and applied to analyze 2-MIB and geosmin in water [11-13]. Examples include closed loop stripping analysis (CLSA) [14], purge and trap [13, 15], open stripping analysis [16], simultaneous distillation extraction (SDE) [17], liquid- liquid extraction (LLE) [5, 18], liquid-liquid microextraction (LLME) [19], continuous liquid-liquid extraction (CLLE) [19, 20], solid-phase extraction (SPE) [4, 18, 21], solid-phase microextraction (SPME) [13, 22, 23] and stir bar sorptive extraction (SBSE) [24-26].

Although the specific procedure of each technique for sample pretreatment is different, the principles are basically similar. Target analytes are first extracted from aqueous samples, such as drinking water, surface water, ground water, and wastewater, and subsequently trapped on or in a sorbent. Then, the target analytes are concentrated before injected into an instrument for quantitation. In fact, some of them (e.g., SDE, LLE, CLLE) are very labor intensive, and require large sample volume. In addition, LLE and CLLE require specially designed apparatus and the use of potentially harmful solvents [26, 27]. Albeit, these methods often suffer from deteriorated sensitivity and repeatability and result in to some extent large errors; it is simply because the sample volume is required to be reduced to 1-2 µL before GC analysis [28].

Currently, the methods requiring less or no solvents, e.g., SPE, SPME, and SBSE, are more prevalent nowadays. In practice, SPME coupled with GC/MS is more commonly applied to quantitate 2-MIB and geosmin in water samples, since it allows extraction and pre-concentration of the analytes to be carried out in one step. Although the method has been successfully applied for extracting and pre-concentrating 2-MIB and geosmin, its use for accurate quantitative analysis is still limited. Two different phase equilibriums (one between liquid to headspace and the other between headspace and adsorbant of a fiber), extraction (such as temperature), variations in sample matrixes, etc. result in large variations in results; the reported relative standard deviations (RSDs) were as large as 40% for pond water [29].

An easy way to overcome the above-mentioned limitation is injecting a sample of larger volume than typical injection, e.g., 1 µL. Recently, a programmable temperature vaporizing (PTV) technique was developed to facilitate large-volume injection (LVI) [30-32], resulting in significantly improved sensitivity of GC analysis. For example, sub-ppt levels of 2-MIB and geosmin in water could be determined using CLLE coupled with GC/MS equipped with a

PTV device [20].

This paper aims to develop a new analytical method to quantify 2-MIB and geosmin in raw and tap waters by coupling SPE with LVI-GC/MS technique. The developed method utilized a GC/MS system with a specially designed LVI liner (so called Stomach Insert) and a PTV to quantitate the target analytes that were pre-concentrated with SPE. Using this method, improvement in the sensitivity of GC/MS measurements to determine 2-MIB and geosmin could be achieved with the minimum use of environmentally-harmful solvents. The developed method was validated and compared with the headspace SPME/GC/MS method. Finally, the method of the present study was applied to analyze 2-MIB and geosmin in samples of source waters.

2. MATERIALS AND METHODS

2.1. Standards and reagents

Both 2-MIB and geosmin standards were purchased from Sigma-Aldrich (St. Louise, MO, USA). The stock solution of 1 μg mL^{-1} for method development was prepared by diluting 100 μg mL^{-1}, when needed. However, the working solutions of 0.5, 1, 5, 10, and 20 ng mL^{-1} were daily prepared by diluting the stock solution. The diluting water of 18.2 MΩ cm^{-1} was produced using the Aquarius^{TM} purification system (Advantec, Kashiwa-shi, Japan). Acetone and hexane as extracting solvents of target analytes were purchased from TEDIA (Fairfield, OH, USA). Phenanthrene-d$_{10}$ and polyethylene glycol 200 were acquired from Sigma-Aldrich (St. Louise, MO, USA).

2.2. Instrument

In this study, a GC/MS system (GCMS-QP2010Plus, Shimadzu, Kyoto, Japan), equipped with a PTV for facilitating LVI developed by AiSTI (Fig. 1a; LVI-S200, AiSTI, Wakayama, Japan), was used to quantify 2-MIB and geosmin in water; particularly, a spiral-shaped liner, named Stomach Insert made by AiSTI (Fig. 1b; Wakayama, Japan), was used for LVI. By twisting a conventional liner, the liner could hold inside a large volume of a liquid sample. Once a sample was injected in the Stomach Insert, hot air was supplied into the PTV unit to increase inside temperature according to a pre-set temperature program. Then, solvent was vaporized and target analytes were introduced to a capillary column to achieve separation.

[Figure 1 here]

The PTV was connected to an auto-sampler (AOC-20i, Shimadzu, Kyoto, Japan) with a 50 μL syringe (SGE, Victoria, Australia). The operating condition of the PTV along with the temperature program is provided in Table 1. The procedure consisted of the following steps; injection, solvent vaporization, split transfer, and cleaning. During injection and vaporization of solvent, the split purge line was open. In these steps, the PTV temperature was raised from 70 to 210 ^{o}C for about 1.2 min and was still below the boiling point of 2-MIB or of geosmin; boiling points of 2-MIB and geosmin were 207 and 210 ^{o}C, respectively. Using this approach, the target analytes could be concentrated in the Stomach Insert liner while the solvent was removed through the split purge. After solvent was completely vaporized, the analytes remaining in the liner were transferred to the capillary column as the PTV temperature was rapidly raised to 270 ^{o}C, at which the temperature was held for 20 min to clean up the insider of the liner.

For separation of 2-MIB and geosmin, a Shim-5 MS column (30 m × 0.25 mm i.d., 0.25 μm film thickness; Shimadzu, Kyoto, Japan) was used with helium as a carrier gas. The GC/MS analysis was performed in both SCAN and SIM modes. The detailed operating condition for the GC/MS along with the oven temperature program is also provided in Table 1.

[Table 1 here]

For comparison, SPME followed by GC/MS analysis was also applied to the water samples. The procedure to extract the target analytes from the headspace of water samples using SPME fibers along with GC condition is provided as Supporting Information (Table SM-1).

2.3. Sample pretreatment procedure

The SPE method with a PBX cartridge (20 mg; AiSTI, Wakayama, Japan) was applied to selectively extract 2-MIB and geosmin from a water sample of 100 mL (Fig. 2). The extraction procedure is briefly described below.

[Figure 2 here]

Prior to extracting target chemicals, the SPE cartridge was washed twice with 2 mL pure water, and dried for 5 min. Then, a sample of 100 mL underwent the loading process under approximately 3 kPa in order to allow target analytes to be adsorbed on to the SPE cartridge. The SPE cartridge was then mounted on a vacuum manifold, washed twice with 2 mL water, and dried for 5 min. After drying, the SPE cartridge was eluted with a 1-mL mixture of acetate and hexane (3:7). A 2-μL acetone mixture containing 0.2% polyethylene glycol 200 as an analyte protectant and 10-ppm phenanthrene-d_{10} as an internal standard was added to the eluted sample; in particular, the analyte protectant was added to prevent matrix-induced chromatographic response enhancements caused by the undesirable interactions of matrix compoenets with active sites in the PTV inlet and the GC column. The sample volume was subsequently adjusted to 1 mL by adding a mixture of acetate and hexane (3:7). Finally, the sample was injected into the LVI-GC/MS for quantitation of target compounds.

2.4. Validation of proposed analytical method

The performance of the sample extraction and analytical method for quantitation of 2-MIB and geosmin developed in this study was evaluated by determining linearity of calibration curves, repeatability and recovery efficiencies, RSDs, instrumental limit of quantifications (LOQs), and method detection limits (MDLs).

For developing the calibration curves for 2-MIB and geosmin, standards of each compound at five different concentrations (0.5-20 ng L^{-1}) were prepared by diluting appropriate amounts of the stock solution. All standards were prepared in duplicate. For the repeatability test, 7 standard samples of 5 ng L^{-1} and 3 standard samples of 50 ng L^{-1} were prepared by adding each of the two compounds to water, and were analyzed using the proposed method. Recovery tests were performed with source water and produced drinking water. Test samples were prepared by spiking 2-MIB and geosmin in raw or tap water at three different levels (i.e., 5, 10, and 50 ng L^{-1}); five samples were prepared for each level. For repeatability and recovery tests, raw water samples were collected from a water reservoir.

The instrumental LOQ was determined by calculating the signal-to-noise (S/N) ratio for the standard solution of the lowest concentration in the calibration curve; 10 times of a signal to noise (S/N) ratio was considered as the LOQ for each target compound. Since each compound has different instrumental responses, determining the MDL of each compound was separately carried out. For MDL determination, solutions containing the target compounds of 1 ng L^{-1} each were prepared in target compounds-free raw water samples (total organic carbon of about 2 ± 0.1 mg L^{-1}). The MDL with a 99% confidence level that the concentration of a target analyte was considered greater than zero was calculated.

3. RESULTS AND DISCUSSION

3.1. Chromatogram from analysis of 2-MIB and Geosmin

Figure 3 shows the chromatogram for 2-MIB and geosmin, obtained by 25 μL injection (Table 1). Sharp peaks for both target compounds were observed; even at the concentration of 0.5 ng L^{-1}, discernable peaks could be observed for both target compounds.

[Figure 3 here]

In Fig. 4, target ions for 2-MIB and geosmin are shown; the concentration of each analyte was 100 ng L^{-1}. For each of the target compounds, the most abundant fragment ion was used as the quantifier and two additional mass ions were selected as qualifiers (Table 1). Mass ions used for quantification, i.e., 112 and 95 *m/z* for 2-MIB and geosmin, respectively, are clearly shown in Fig. 4. For the confirmation of target compounds, the tolerance intervals for mass ion ratios between quantifier and qualifiers were set ± 30%. Considering the injection volume size used in this study (i.e., 25 μL), the sensitivity of the proposed method was promising; using the current PTV system, the injection volume could be increased up to 250 μL.

[Figure 4 here]

3.2. Validation of the proposed method

The linearity of the calibration curves, the repeatability, the recovery, LOQ, and the

MDL for each target compound were evaluated to validate the suitability of the developed method. Calibration standards were prepared at five different concentrations (0.5-20 ng L^{-1}) to cover the respective dynamic range for both analytes. The linearities of the calibration curves developed for 2-MIB and geosmin were excellent; R^2s of both calibration curves were all > 0.999 (See Fig. SM-1).

The repeatability test was carried out with standard solutions of two different concentrations, i.e., 5, and 50 ng L^{-1} (Table 2). The proposed method showed good repeatability for both target compounds. In the case of 2-MIB, RSD values were 6.9% and 6.2% for 5 and 50 ng L^{-1}, respectively, while those for geosmin were 4.5% and 3.7%. The repeatability of the proposed method was also tested with raw water samples spiked with the target analytes. Larger RSDs, especially at lower level were observed possibly due to presence of other constituents of the water samples. Noticeably, RSDs were still within 15% (Table 2). At the level of 5 ng L^{-1}, the error value calculated from the repeatability test with raw water was more than two times larger than that with pure water.

[Table 2 here]

The recovery test was performed with both raw water and tap water samples, which were prepared by spiking 2-MIB and geosmin. Before the water samples were used, their 2-MIB and geosmin concentrations were analyzed. 2-MIB and geosmin concentrations of the raw water were 44.6 ± 0.3 (n = 5) and 2.6 ± 0.2 (n = 5) ng L^{-1}, respectively. However, the two target analytes were not detected from the tap water. After background concentrations of the target compounds in the water samples were determined, each water sample was spiked with 2-MIB and geosmin. The expected concentration increases of the samples were 5, 10, and 50 ng L^{-1}. In general, the method showed to some degree better recovery ratio for geosmin than that for 2-MIB (Table 3). In the test performed with raw water, the proposed method showed 72-104% recovery ratio for 2-MIB, and 93-105% for geosmin. On the other hand, it showed 61-67% for 2-MIB and 74-85% for geosmin, when tests were performed with tap water. The relatively lower recovery for tap water samples was attributed to the interaction between target compounds or adsorption sites on SPE material and residual chlorine. Lin et al. also reported that residual chlorine causes enlarged errors in 2-MIB and geosmin analysis [33]. If residual chlorine was removed from water samples, much better recovery efficiency could be obtained.

[Table 3 here]

The instrumental LOQs were determined by considering the peak area corresponding 10 times the S/N ratios for 2-MIB and geosmin. The calculated LOQs for 2-MIB and geosmin were 7.7 and 6.7 ng L^{-1}, respectively. Similar levels of LOQs were also reported with a method based on headspace-SPME coupled to GC/MS [22].

For the determination of MDLs of the developed method for 2-MIB and geosmin, a total of 7 raw water samples were prepared. The obtained MDLs for 2-MIB and geosmin were 0.87, and 0.62 ng L^{-1}, and were compared well with those reported by others. Especially, for the SPME followed by GC/MS analysis, which is the most commonly applied approach, the reported MDLs for 2-MIB and geosmin are 0.5-5 ng L^{-1} and 0.5-3.3 ng L^{-1}, respectively (Table 4). In this study, the method using SPME-GC/MS was also applied, and its MDLs for 2-MIB and geosmin were calculated as 1.5 and 0.6 ng L^{-1}, respectively, which are comparable with those reported by others. However, the main disadvantage of SPME is reduced limited concentration capability due to the small amount of polymer coating on the fiber. In addition, the SPME fiber coating is easily breakable and hence has limited lifetime.

[Table 4 here]

Among a variety of analytical methods for 2-MIB and geosmin presented in Table 4, SBSE-GC/MS method is mentionable. SBSE is one-step extraction process utilizing a magnetic stirring rod, which is incorporated into a glass jacket coated with a 0.5-mm layer of polydimethylsiloxane (PDMS). In fact, SBSE-GC/MS method has been considered as an alternative choice to conventional extraction methods. Although the principle of SBSE is similar to that of SPME which uses PDMS sorbent, the amount of sorbent used in SBSE is much higher than that of SPME, resulting in higher enrichment factors and sensitivity and low MDLs [36, 37]. Nonetheless, it also suffers from the same issues with those of SPME, e.g., easy breakableness and limited lifetime of adsorbent.

Considering that its MDLs for 2-MIB and geosmin were determined with raw water samples and the sample volume was only 25 μL, the analytical method based on SPE-LVI-GC/MS proposed in this study can be readily employed in a routine monitoring program for the odorants in source water. If the injection volume is increased, the sensitivity of the method could be increased; the injection volume can be increased up to 250 μL. From a practical point of view, however, the proposed method can be applied without increase of injection volume for better sensitivity because the current guidelines for 2-MIB and geosmin are about 10 times higher than its MDLs.

3.3. Application of proposed method for analysis of 2-MIB and geosmin in real water.

The proposed method was applied to quantify the target compounds in raw water samples collected from upstream sites of Han River; it is located approximately 30 km away from the eastern boundary of the Seoul Metropolitan. The sample temperature was about 23

^{o}C and dissolved oxygen and total organic carbon concentrations were 8.6 ± 0.2 mg L^{-1} and 2.1 ± 0.2 mg L^{-1}, respectively. The concentrations of 2-MIB and geosmin determined using the developed method were 59.3-65.6 and 8.9-9.4 μg L^{-1}, respectively. This result is comparable with those reported by a study previously conducted for Han River [39]. As stated in Section 3.1, the tolerance interval for the ion ratios between quantifier and each of two qualifiers was set at 30% for both 2-MIB and geosmin in raw water samples. The ion ratios calculated for 2-MIB were within the rages of 19-27% and 10-14% whereas those for geosmin were 15.0-25.7% and 13.4-21.7%, indicating the preset tolerances of absolute ion abundances ratios set for both odorants satisfied.

4. CONCLUSION

A new method consisting of SPE and subsequent LVI-GC/MS was developed to analyze 2-MIB and geosmin in water. The proposed method showed a good linearity over the wide calibration range for 2-MIB and geosmin, and good repeatability and recovery. Large volume injection practiced in the proposed method resulted in a good sensitivity for the target analytes. The MDLs of the method for 2-MIB and geosmin are lower than one tenth of the compounds' published odor thresholds, and are comparable with or lower than those obtained using SPME-GC/MS. However, the proposed method is free from the concern about breaking of adsorbent on a fiber frequently witnessed in the practice with SPME. Overall, due to its relative ease of practice and high accuracy and sensitivity, the proposed method can be easily applied to a water quality monitoring program for the odorants.

ACKNOWLEDGEMENT

This work was supported by the R&D program of MOTIE/KEIT (R&D program number: 10037331, Development of Core Water Treatment Technologies based on Intelligent BT-NT-

IT Fusion Platform).

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Table 1. Operating conditions for PTV and GC/MS used in this study

Operating Parameters for PTV	
Injector Temp. Program	70 to 240 ^{o}C 120 ^{o}C min^{-1}, to 270 ^{o}C 50 ^{o}C min^{-1}, and held for 20 min
Injector Solvent Purge Time, sec	7
Injection Volume, µL	25
Operating Parameters for GC/MS	
Oven Temp. Program	held at 50 ^{o}C for 3 min, to 180 ^{o}C at 10 ^{o}C min^{-1}, and to 310 ^{o}C at 25 ^{o}C min^{-1}, and held for 5 min
Column Flow, mL min^{-1}	1
Carrier Gas Saver at Split Ratio of 20, min	4
Split Ratio	150
Ion Source Temp., ^{o}C	280
Interface Temp., ^{o}C	290
Scan Range, *m/z*	50-250
SIM, *m/z*	97, 112 (quantifier), 125 for geosmin 95 (quantifier), 108, 135 for 2-MIB

Table 2. Results of repeatability tests for 2-MIB and gesmin (n = 5)

	2-MIB				Geosmin			
	Pure water		Raw water		Pure water		Raw water	
Level, ng L^{-1}	SD[a], ng L^{-1}	RSD[b], %	SD, ng L^{-1}	RSD, %	SD, ng L^{-1}	RSD, %	SD, ng L^{-1}	RSD, %
SPE-LVI-GC/MS								
5	0.29	6.9	0.7	14.6	0.2	4.5	0.67	14.2
50	3.2	6.2	3.2	6.5	1.9	3.7	3.8	8.0
SPME-GC/MS								
5	0.48	9.7			0.14	3.0		
50	1.9	3.8			4.0	8.0		

a: standard deviation
b: relative standard deviation

374 **Table 3.** Results of recovery test for 2-MIB and gesmin (n = 5)

	2-MIB			Geosmin		
Levels, ng L^{-1}	5	10	50	5	10	50
Raw water, %	104.4	72.1	72.9	104.7	93.0	95.3
Tap water, %	61.3	66.5	62.2	85.3	74.1	79.8

375

376

Table 4. Method detection limit values for 2-MIB and geosmin reported in literature and obtained in this study

2-MIB, ng L^{-1}	Geosmin, ng L^{-1}	Method	Matrix	Reference
1.0	5.0	LLE-GC/MS	Pure water	[18]
1.0	1.0	LLE-GC/ITMS	Pure water	[34]
5.0	5.0	CLSA-GC/MS	Pure water	[14]
1.0	1.1	Headspace LLME-GC/MS	Raw water	[35]
0.5	0.5	SPME-GC/MS	Raw water	[36]
0.9	0.6	Headspace SPME-GC/MS	Pure water	[22]
9.7	0.94	SPME-GC/MS	Pure water	[36]
1.52	**0.6**	**SPME-GC/MS**	**Raw water**	**This study**
9	2	USADLLME-GC/MS*	Pure water	[38]
0.25	0.1	SBSE-GC/MS	Pure water	[24]
0.18	0.09	SBSE-GC/MS	Pure Water	[36]
0.04-0.16	0.03-0.11	SBSE-GC/MS	Mineral water	[37]
0.3	0.05	CLLE-LVI-GC/MS	Pure water	[20]
0.91	**0.63**	**SPE-LVI-GC/MS**	**Raw water**	**This study**

* USADLLME-GC/MS; ultrasound-assisted dispersive liquid–liquid microextraction coupled to GC/MS.

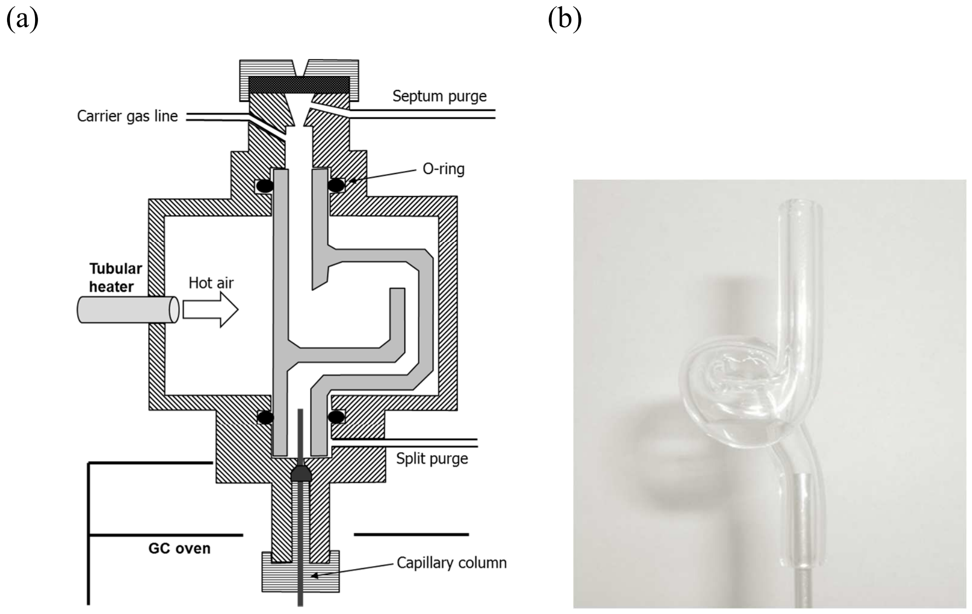
Figure legend

Fig. 1. Schematic diagram for PTV unit (a) and picture of Stomach Insert (b) used in this study

Fig. 2. Extraction procedure for 2-MIB and geosmin in water

Fig. 3. Chromatogram of 2-MIB and geosmin analyzed by GC/MS

Fig. 4. Target mass ions for 2-MIB and geosmin analyzed by GC/MS



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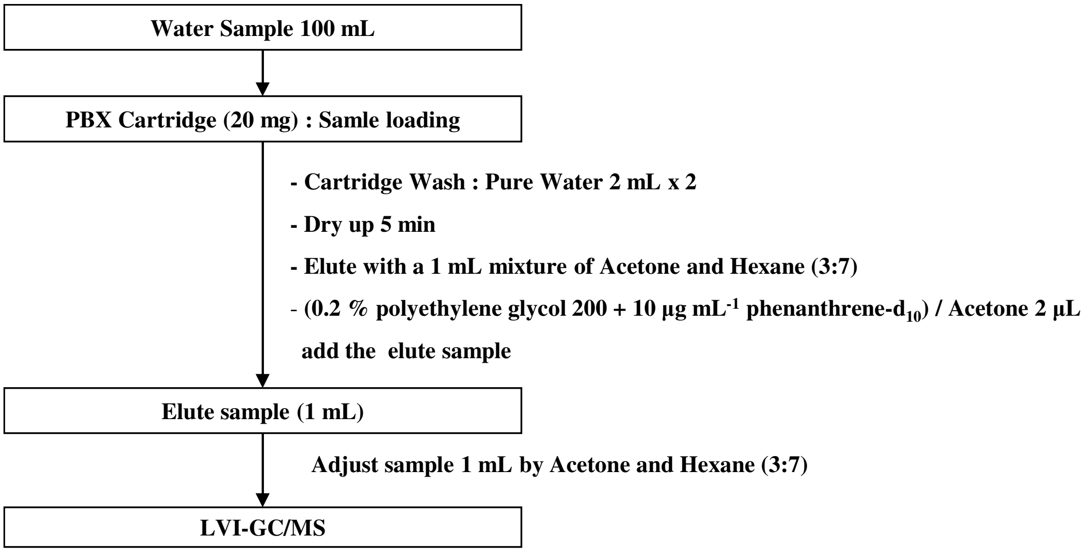


Fig. 2. Extraction procedure for 2-MIB and geosmin in water

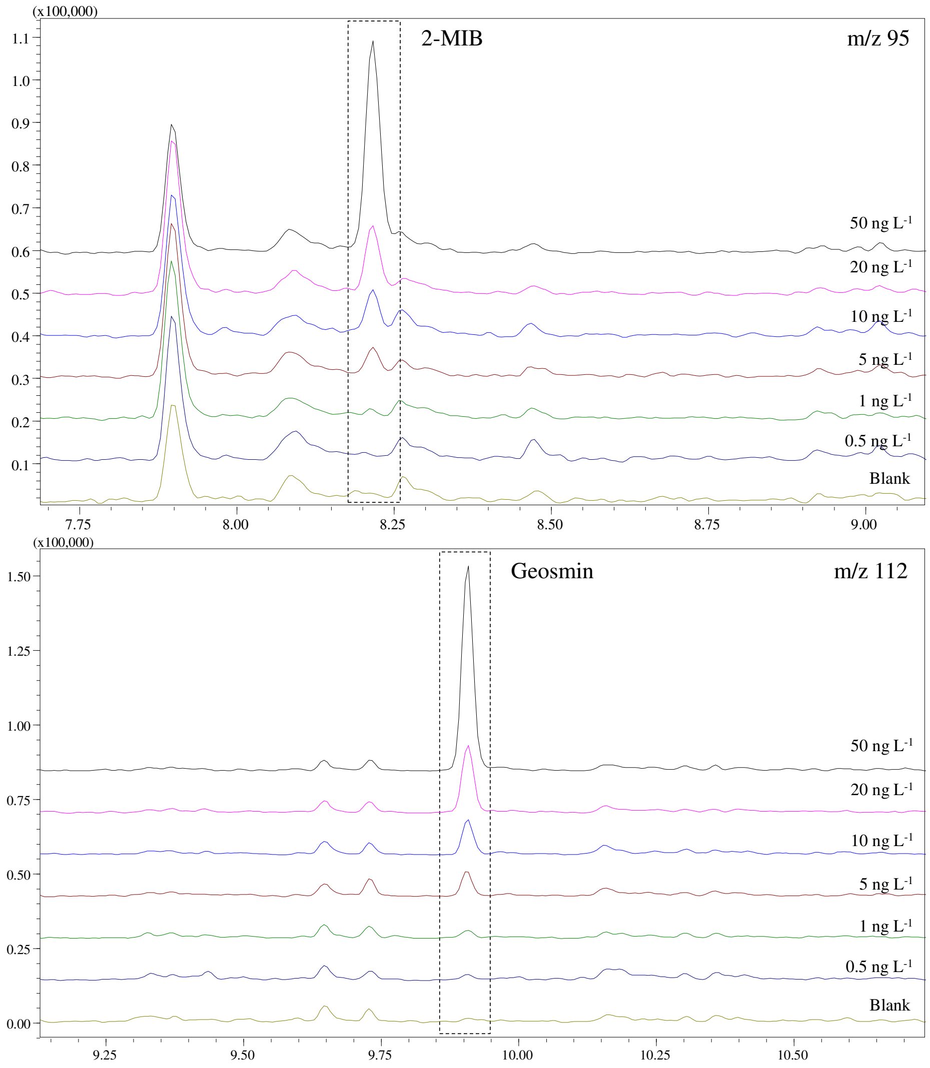
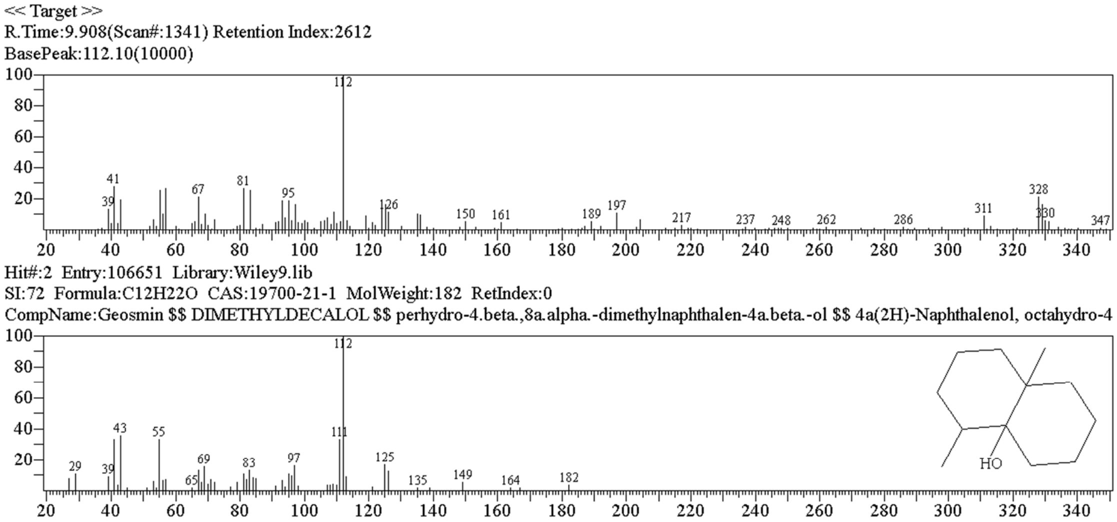


Fig. 3. Chromatogram of 2-MIB and geosmin analyzed by GC/MS

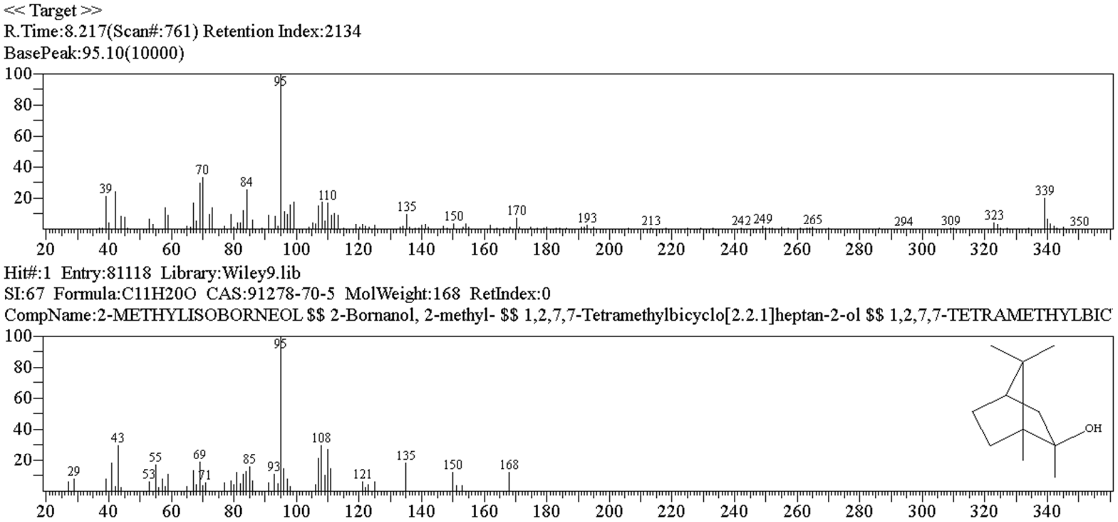
(a) Target mass ions for Geosmin



<< Target >>
R.Time:9.908(Scan#:1341) Retention Index:2612
BasePeak:112.10(10000)

Hit#:2 Entry:106651 Library:Wiley9.lib
SI:72 Formula:C12H22O CAS:19700-21-1 MolWeight:182 RetIndex:0
CompName:Geosmin $$ DIMETHYLDECALOL $$ perhydro-4.beta.,8a.alpha.-dimethylnaphthalen-4a.beta.-ol $$ 4a(2H)-Naphthalenol, octahydro-4

(b) Target mass ions for 2-MIB



<< Target >>
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BasePeak:95.10(10000)

Hit#:1 Entry:81118 Library:Wiley9.lib
SI:67 Formula:C11H20O CAS:91278-70-5 MolWeight:168 RetIndex:0
CompName:2-METHYLISOBORNEOL $$ 2-Bornanol, 2-methyl- $$ 1,2,7,7-Tetramethylbicyclo[2.2.1]heptan-2-ol $$ 1,2,7,7-TETRAMETHYLBIC

Fig. 4. Target mass ions for 2-MIB and geosmin analyzed by GC/MS