Sensitive Detection of 2-MIB and Geosmin in Drinking Water

Application Note

Environmental

Author

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Abstract

An automated SPME extraction method for easy and sensitive detection of gesomin and 2-Methylisoborneol (2-MIB) has been developed on the Agilent 7000B Triple Quadrupole GC/MS system coupled to an Agilent 7890A GC with the PAL Automated Sample Injector mounted on it. The method enables method detection limits (MDLs) of 0.1343 and 0.0937 parts per trillion (ppt) and the method quantitation limits (MQLs) were 0.4029 and 0.2811 ppt for 2-MIB and geosmin, respectively.

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Introduction

Geosmin and 2-Methylisoborneol (2-MIB) are naturally occurring terpenoid alcohols produced mainly by cyanobacteria (blue-green algae) and actinomycetes (bacteria) (Table 1) found in surface water sources. When these organisms bloom, they can cause earthy-musty odors in the water that are difficult to remove by conventional water treatment procedures. The human olfactory can detect these compounds at ppt levels (5 ng/L for 2-MIB and 30 ng/L for geosmin). The identification, quantification and removal of geosmin and 2-MIB from water are essential since they affect the organoleptic properties and consumer acceptability of drinking water.

Substantial research on the removal of geosmin and 2-MIB has been conducted in Korea, because seasonal variations of 2-MIB and geosmin comprise one of the biggest problems in drinking water originating from the Han River. The government of Korea has set maximum allowable limits for these compounds in drinking water (Table 1) that require sensitive and accurate monitoring of very low levels of 2-MIB and geosmin. Elsewhere, there is limited regulation. In the US, the Environmental Protection Agency (EPA) has not defined maximum permissible concentration levels for geosmin and 2-MIB in drinking water. Instead, the EPA uses Total Odor Number (TON), a method based on the persistence of an odor after dilution, and limits the TON to a value of 3.

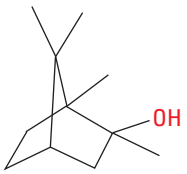
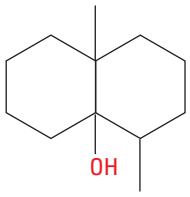
This application note describes a method for the analysis of these two compounds using automated solid phase microextraction (SPME) on the PAL Automated Sample Injector. The separation was then performed on an 7890A GC coupled to a 7000B Triple Quadrupole GC/MS system. Method detection limits (MDLs) and MQLs are well below one ppt with a sample analysis run time less than 60 minutes, including sample preparation by SPME.

Experimental

Reagents and Standards

A 2-MIB and geosmin standard mixture was purchased from Supelco (p/n 47525U). Sodium chloride was purchased from Merck. Stock standard solutions were prepared in methanol from JT Baker at 10 ppb (µg/L). The mixed calibration samples were prepared in distilled water at seven concentrations, ranging from 0.5 to 40 ppt (ng/L). The divinylbenzene (DBV) Carboxen 50/30 µm, 1-cm StableFlex SPME microfiber was obtained from Supelco (p/n 57329-U).

Table 1. Compound Information

Compound name	2-Methylisoborneol (2-MIB)	Geosmin
Formula	$C_{11}H_{20}O$	$C_{12}H_{22}O$
Molecular weight	168	182
Exact mass	168.151415	182.167066
CAS	2371-42-8	19700-21-1
Odor	Earthy	Camphor
Maximum allowed limit in drinking water in Korea	20 ppt	20 ppt
Required maximum LOQ in Korea	2 ppt	1 ppt
Structure		

Instruments

This method was developed using the PAL Automated Sample Injector (Figure 1), as well as the Agilent 7890A GC coupled to a 7000B Triple Quadrupole GC/MS system. The instrument conditions are shown in Tables 2 and 3.

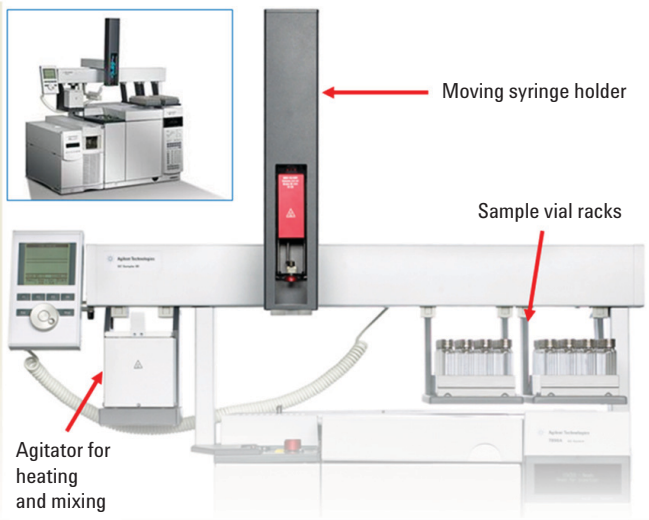


Figure 1. The PAL Automated Sample Injector with SPME accessory mounted on the Agilent 7890A GC (inset), and its labeled components.

Table 3. GC and MS Instrument Conditions

GC run conditions	
Analytical columns	30 m × 0.25 mm, 0.25 µm HP-5MS (p/n 19091S-433)
Injection mode	Split mode, ratio 5:1
Inlet temperature	250 °C
Flow mode	Constant flow, 1 mL/min, helium
Oven temperature	50 °C for 1 minute 10 °C/min to 200 °C, hold for 1 minute 20 °C/min to 220 °C, hold for 1 minute
Carrier gas	Helium in constant flow mode, 1 mL/min
Transfer line temperature	250 °C
MS conditions	
Scan mode	Electron impact, *m/z* 40 *m/z* through/250 *m/z*
MRM mode	Electron impact, Multiple reaction monitoring (MRM)
Collision gas	N_2 at 1.5 mL/min
Quench gas	He at 2.25 mL/min
MS temperatures	Source 230 °C Quadrupole 150 °C

Table 2. PAL Automated Sample Injector SPME Conditions

Pre incubation time	60 seconds
Incubation temperature	80 °C
Agitator speed	500 rpm
Agitator on time	5 seconds
Agitator off time	2 seconds
Vial penetration	20 mm
Extraction time	1,200 seconds
Injection penetration	54 mm
Dersorption time	300 seconds
Post desorption fiber condition time	600 seconds
Fiber	DBV/Carboxen 50/30 µm (Gray)

SPME

Solid phase microextraction (SPME) is an adsorption/desorption process using coated fibers fitted into a syringe-like device that facilitates automation on LC and GC auto-sampling systems such as the PAL. The generalized automated procedure is shown in Figure 2. Pass the outer needle protecting the fiber through the septum that seals the vial. Depress the syringe plunger to expose the fiber directly to the sample or to the headspace above the sample, and organic analytes are adsorbed onto the fiber coating. Once equilibrium is attained, draw the fiber back into the needle and withdraw from the sample vial. The needle/fiber assembly is then introduced into the GC injector, and the adsorbed analytes are thermally desorbed into the inlet.

Sample Preparation

A 10-mL water sample spiked with a calibration sample was placed in a 20-mL sample vial, 3 grams of sodium chloride was added, and the vial was placed in the sample rack for the PAL Automated Sample Injector. After agitation on the PAL for 1 minute at 80 °C, the SPME fiber was inserted and exposed to the headspace for 20 minutes to extract the odor compounds. Fiber desorption occurs after the fiber assembly is inserted into the injection port of the GC and held isothermally at 250 °C for 5 minutes (Figure 2). The injection port was in split mode (ratio = 5:1). The instrument conditions for the PAL Automated Sample Injector are shown in Table 3.

Analysis Parameters

The GC/MS/MS analysis parameters are shown in Table 4.

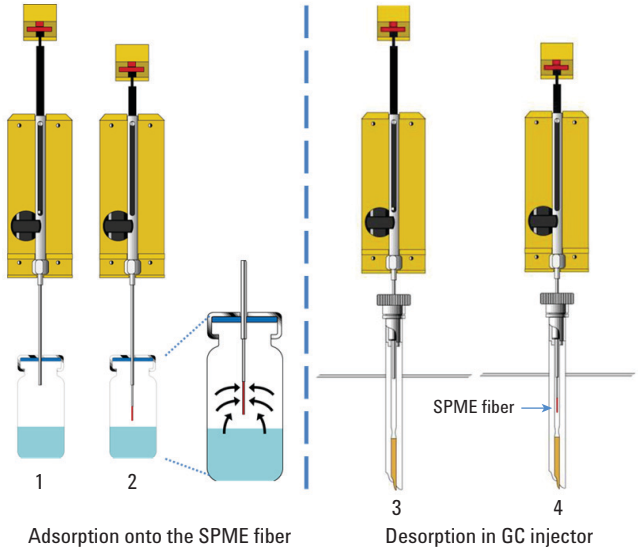


Figure 2. Solid phase microextraction (SPME) adsorption and subsequent desorption in the GC injector. The outer needle protecting the fiber is first passed through the septum that seals the vial (1). The syringe plunger is depressed to expose the fiber directly to the sample or to the headspace above the sample, and organic analytes are adsorbed onto the fiber coating (2). Once equilibrium is attained, the fiber is drawn back into the needle and withdrawn from the sample vial. The needle/fiber assembly is then introduced into the GC injector (3), and the adsorbed analytes are thermally desorbed into the inlet (4).

Table 4. GC/MS/MS Analysis Parameters

Time segment	Retention time (min)	Compound	Precursor ion	Product ion	dwell	Collision energy
1	11.163	2-MIB	95	67	20	10
1				55	20	20
2	14.182	Geosmin	112	97	20	10
2				83	20	10

Results and Discussion

Sample Preparation

One key to the ease of use and reproducibility of this method is the automation of the solid phase micro-extraction (SPME) on the PAL Automated Sample Injector. This system offers three injectors, including the liquid injector, a static head-space injector, and the SPME accessory used in this method. The top-mounted system fits neatly on Agilent GC systems (Figure 1). Advantages of automated SPME include high-throughput extractions, and lower cost and less impact on the environment since liquid extraction solvents are not required. Increased analytical sensitivity is also achieved, because all adsorbed analytes are transferred into the analytical system, and precision is improved due to automation.

Separation and Spectra

Geosmin and 2-MIB are well separated from each other and other volatile components, as shown in Figure 3. The extracted ion current for the parent ion of each compound exhibits a single peak. For the retention time check, total ion current (TIC) data was collected in the scan range from *m/z* 40 to 250.

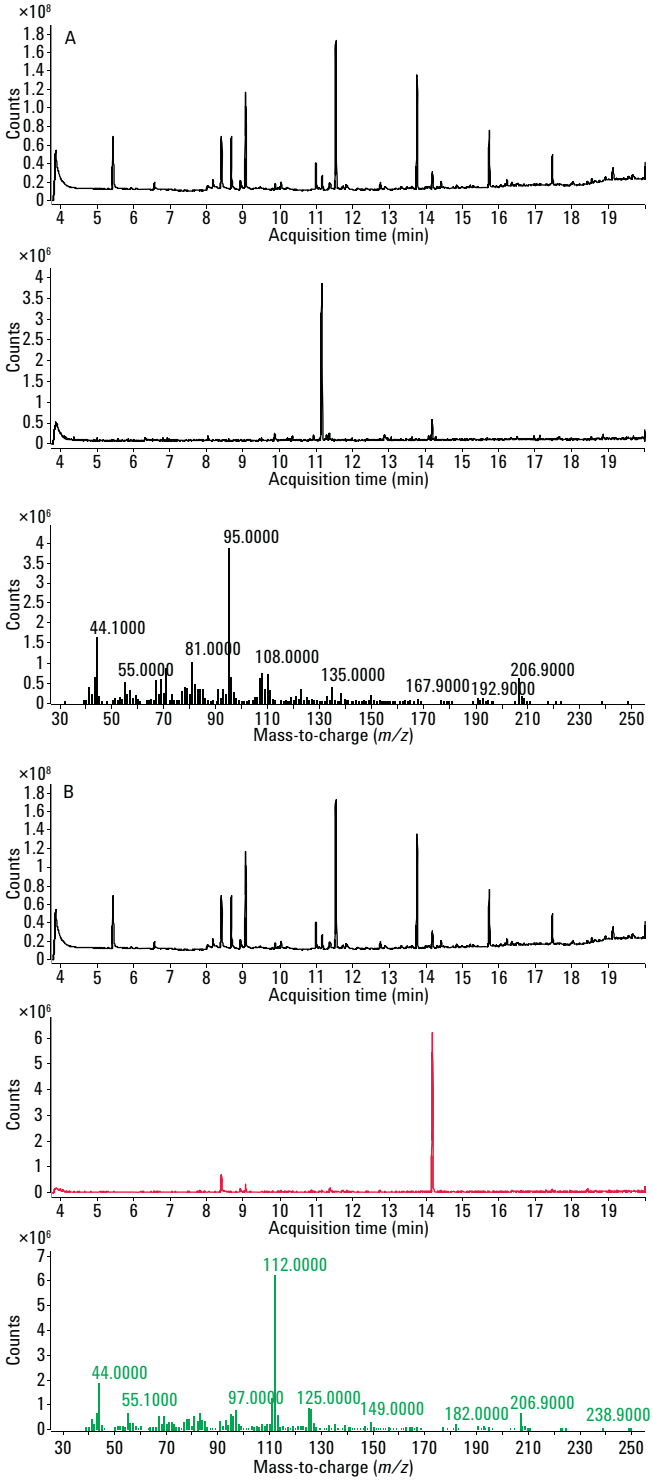


Figure 3. A) 2-MIB total ion current (TIC), extracted ion current (EIC) (m/z 95), and MS spectrum. B) Geosmin TIC, EIC (m/z 112), and MS spectrum.

Selection of Product Ions

The product ion scan spectra at multiple collision energies (CEs) for the target compounds led to the selection of product ions *m/z* 67 (CE 10V) and m/z 55 (CE 20V) for the precursor ion *m/z* 95 of 2-MIB for the multiple reaction monitoring (MRM) method (Figure 4). Product ions *m/z* 97 (CE 10V) and *m/z* 83 (CE 10V) were chosen for the precursor ion *m/z* 112 of Geosmin.

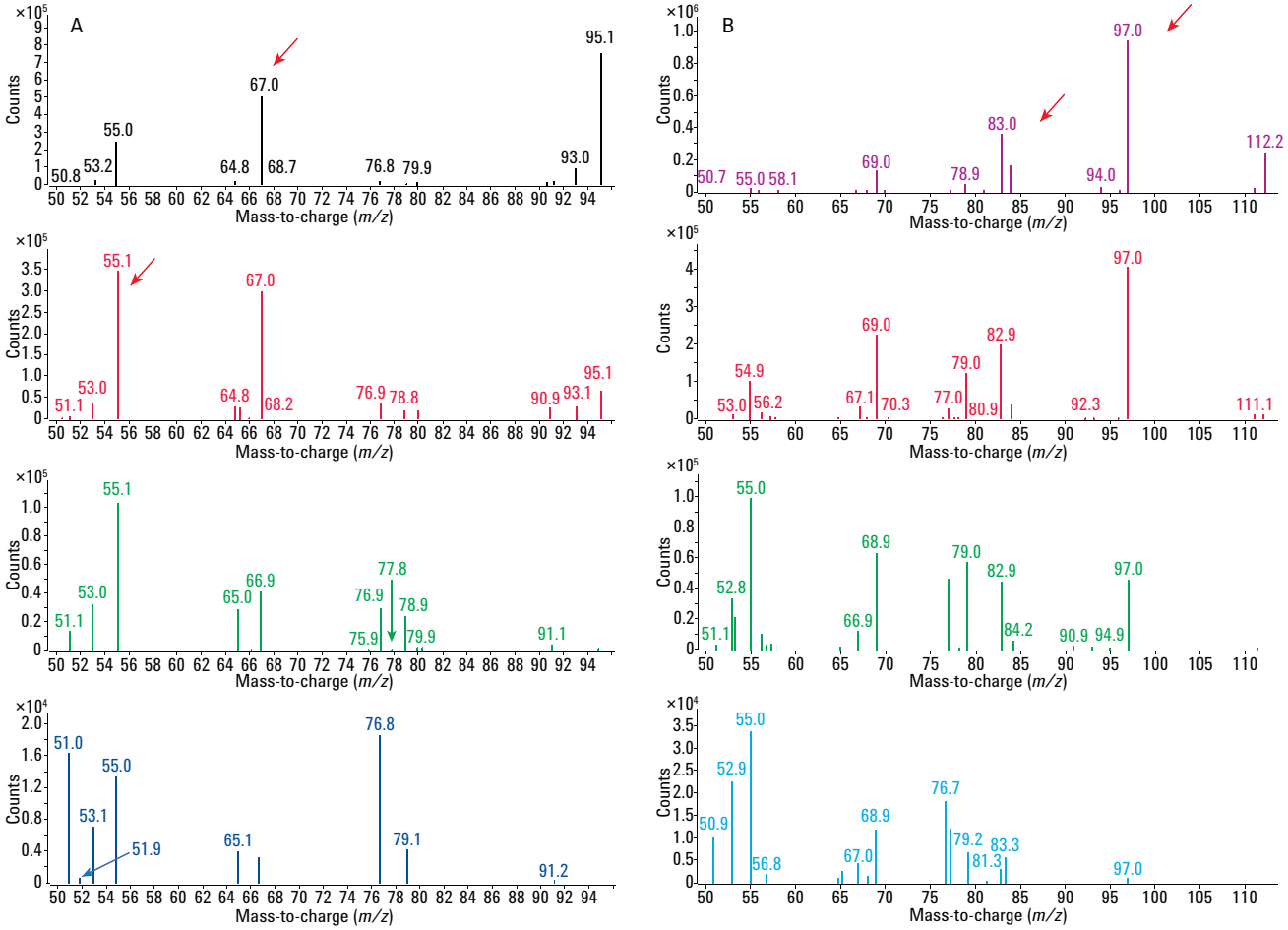


Figure 4. A) 2- MIB product ion spectra (CE 10, 20, 30, 40V). B) Geosmin product ion spectra (CE 10, 20, 30, 40V).

Linearity of Quantitation

Excellent linearity of the peak areas versus concentration was obtained, with $R^2 > 0.998$ for both target compounds for seven concentrations across a range from 0.5 ppt (ppt; ng/L) to 40 ppt (Figure 5).

Sensitivity

Five replicates of each target compound were analyzed at 5 ppt to determine the method detection limits (MDLs) and method quantitation limits (MQLs). The MDL is defined as the standard deviation of the five replicates, times three. The MQL is defined as three times the MDL. The MDLs were found to be 0.1343 and 0.0937 ppt, and the MQLs were 0.4029 and 0.2811 ppt for 2-MIB and geosmin (Table 5).

Conclusions

This method provides easy, accurate and sensitive odor compound analysis in drinking water using the 7000 Triple Quadrupole GC/MS system. The automated SPME extraction on the PAL Automated Sample Injector enables facile, reproducible and rapid sample preparation. The use of SPME coupled with Multiple Reaction Monitoring (MRM) improves extraction efficiency, reduces chemical interferences in the mass spectrum and improves overall signal-to-noise levels. The end result is significantly lower detection limits than comparable liquid-liquid extraction and MS methods. The method defined herein provides sub-ppt MQLs for both geosmin and 2-MIB and a total extraction and analysis cycle time of less than 60 minutes per sample.

Acknowledgement

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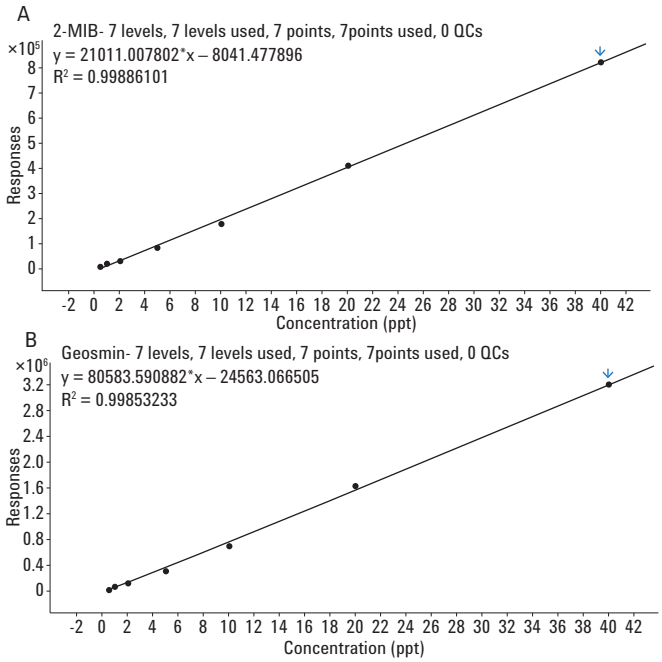

Figure 5. 2-MIB (A) and Geosmin (B) calibration curves from 0.5 ppt to 40 ppt.

Table 5. Determination of MDLs and MQLs

	2-MIB (ng/L)	Geosmin (ng/L)
sample1	5.2484	5.1347
sample2	5.2835	5.1061
sample3	5.2297	5.1906
sample4	5.1752	5.1276
sample5	5.2827	5.1435
Average	5.2439	5.1405
Standard deviation	0.044764	0.031235
MDL	0.134291	0.093704
MQL	0.402874	0.281112

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