

Sample Preparation Methods for Moldy Odor-Causing Substances in Water

N. Iwasa

User Benefits

- ◆ Multiple analytical techniques are available for moldy odor-causing substances in water, offering a variety of alternatives suited to the user's circumstances.
- ◆ Satisfactory measurement results can be obtained with all sample preparation methods.

Introduction

In recent years, consumers have shown heightened interest in the safety and security of foods. Off-flavor (moldy odor) has also become a problem in drinking water in some cases, and various analytical techniques for confirming the safety of water are available. The substances that cause moldy odor are 2-methylisoborneol (2-MIB) and geosmin, which are produced by blue-green algae or streptomyces bacteria. Because the human odor detection threshold for these compounds is a very low concentration on the level of several ng/L, sample preparation and high sensitivity measurement are required in analysis. The sample preparation methods used with moldy odor-causing substances are purge and trap gas chromatography mass spectrometry (PT-GC/MS), head space trap GC/MS (HS Trap-GC/MS), solid phase micro-extraction GC/MS (SPME-GC/MS), and solid phase extraction GC/MS (SPE-GC/MS). This article introduces the features of these sample preparation methods.

Sample Preparation Methods for Moldy Odor Compounds in Water

The features of the four sample preparation methods for moldy odor-causing compounds are outlined below. Fig.1 shows flowcharts of the respective methods, where manual preparation processes are shown in blue, and the processes executed under automatic control by an autosampler are shown in orange.

○ PT-GC/MS

This is a dynamic headspace method, in which purge gas is passed through the water sample, and the volatile analytes are forcibly expelled with the purge gas and trapped by an appropriate adsorbent. Sample preparation is comparatively easy, as the autosampler has an automatic internal standard addition function, and high sensitivity measurement is possible.

○ HS Trap-GC/MS

This method uses the static headspace method, in which the water sample is preheated to a certain temperature in the autosampler, and a set amount of the gas phase, which is in a gas-liquid equilibrium state, is introduced into the GC-MS. It is necessary to be measured in the trap mode for low-sensitivity moldy odors.

○ SPME-GC/MS

This is a type of thermal desorption method, as the water sample is preheated to a certain temperature and exposed to the SPME sampling needle (fiber coating) in the gas phase, and the target analytes are extracted and concentrated and then injected into the GC-MS. The entire process from solid phase micro-extraction through injection into the GC-MS can be controlled automatically by using the Shimadzu AOC™-6000 Plus multifunctional autosampler.

○ SPE-GC/MS

In the solid phase extraction method, the sample solution for injection into the GC-MS is prepared by adsorbing the target analytes in the water sample in a solid phase column, eluting the adsorbed analytes with dichloromethane and the concentrating the analytes. High sensitivity measurement is possible by concentrating the target analytes from a large volume of water sample in the sample preparation process.

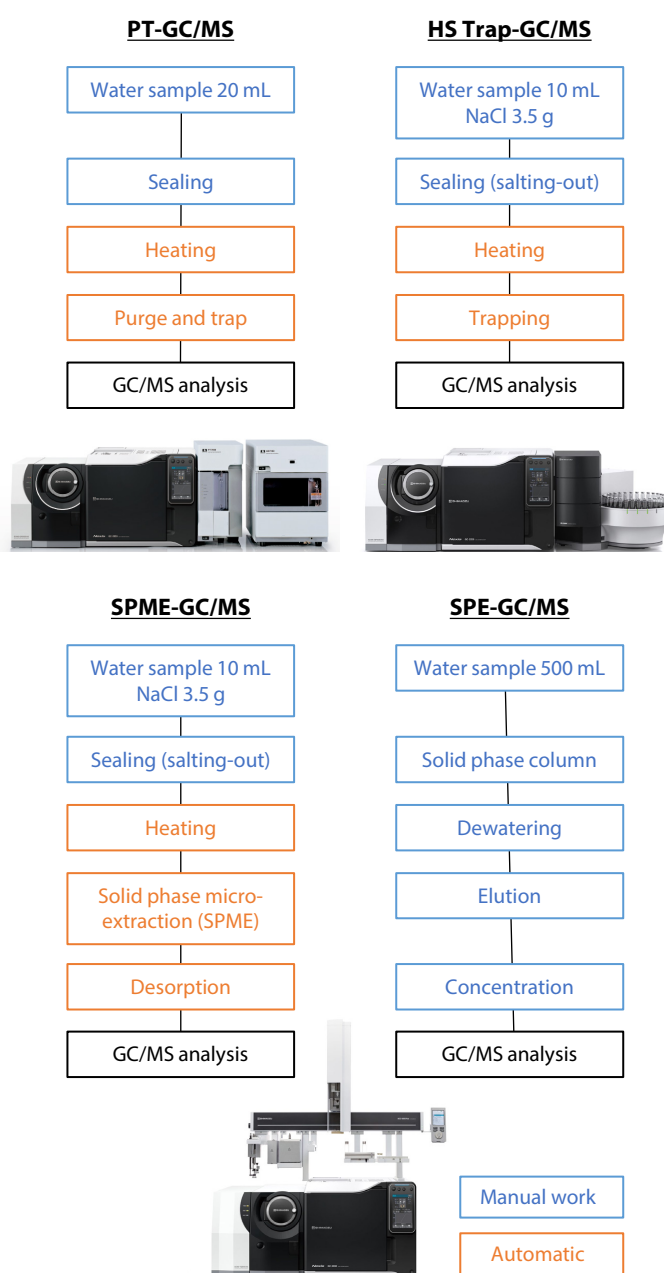


Fig. 1 Flowcharts of Sample Preparation Methods

As shown in Fig. 1, when using the SPE-GC/MS method, all of the sample preparation work must be done manually. With the other three sample preparation methods, after the analyst prepares the sample vial, all of the following processes can be carried out automatically by using an autosampler.

■ Measurement Conditions

Table 1 shows the instrument composition and analysis conditions which are common to the four sample preparation methods. Table 2 to Table 5 show the instrument compositions and analysis conditions used in each method.

Table 1 Common Instrument Composition and Analysis Conditions

Common instrument composition and analysis conditions	
Model	: GCMS-QP2020 NX
MS analysis conditions	
Ion source Temp.	: 200 °C
Interface Temp.	: 250 °C
Ionization method	: EI
Measurement mode	: SIM
SIM Ions m/z	: 2-MIB (Target: 95, Ident: 108) 2,4,6-Trichloroanisole-d3 (IS) (Target: 213, Ident: 215) Geosmin (Target: 112, Ident: 125)
Event Time	: 0.3 sec

Table 2 Instrument Compositions and Analysis Conditions (PT-GC/MS)

Instrument compositions	
Auto Sampler	: PT7000
Column	: InertCap® 5MS/Sil (30 m × 0.25 mm I.D., d.f. = 0.50 µm) (GL Sciences Inc.)
Analysis conditions	
PT	
Trap Tube	: AQUA TRAP-1
Sample Volume	: 20 mL
Sample Heater	: ON (60 °C)
Purge flow rate	: 60 mL/min
Purge Time	: 12 min
Dry purge Time	: 1 min
Desorb Temp.	: 220 °C
Desorb Time	: 3 min
Bake Temp.	: 230 °C
Bake Time	: 5 min
GC	
Injection Temperature	: 150 °C
Injection Mode	: Split (Split ratio 5)
Carrier Gas	: He
Carrier Gas Control	: Constant pressure (120 kPa)
Purge flow rate	: 2.5 mL/min
Column Temp.	: 60 °C (1min) – 4 °C/min – 120 °C – 10 °C/min – 170 °C – 20 °C/min – 220 °C (5min)

Table 3 Instrument Compositions and Analysis Conditions (HS Trap-GC/MS)

Instrument compositions	
Auto Sampler	: HS-20 NX
Column	: SH-5 MS (30 m × 0.25 mm I.D., d.f.= 0.25 µm)
Analysis conditions	
HS-20 NX Trap mode	
Vial Volume	: 20 mL
Sample Volume	: 10 mL (NaCl 3.5 g)
Oven Temperature	: 80 °C
Sample Line Temp.	: 150 °C
Transfer Line Temp.	: 150 °C
Vial Shaking Level	: 5
Multi injection	: 5
Vial Equivalating Time	: 30 min
Vial Pressurization Time	: 0.5 min
Vial Press. Equilib. Time	: 0.1 min
Loading Time	: 0.5 min
Load Equilib. Time	: 0.1 min
Vial Pressure	: 80 kPa
Dry purge Pressure	: 20 kPa
Dry purge Time	: 1 min
Trap Cooling Temp.	: 25 °C
Trap Heating Temp.	: 220 °C
Trap Standby Temp.	: 25 °C
Injection Time	: 5 min
Needle Flush Time	: 5 min
GC	
Injection Mode	: Split (Split ratio 3)
Carrier Gas	: He
Carrier Gas Control	: Constant linear velocity (57.7 cm/s)
Column Temp.	: 60 °C (3 min) – 25 °C/min – 150 °C – 5 °C/min – 160 °C – 25 °C/min – 250 °C (5 min)

Table 4 Instrument Compositions and Analysis Conditions (SPME-GC/MS)

Instrument compositions	
Auto Sampler	: AOC-6000 Plus
Column	: SH-5 MS (30 m × 0.25 mm I.D., d.f.= 0.25 µm)
Analysis conditions	
SPME	
Fiber	: 50/30 µm DVB/Carboxen/PDMS StableFlex Gas phase extraction
Sample	: 10 mL (NaCl 3.5 g)
Conditioning Temp.	: 270 °C
Pre Conditioning Time	: 0 min
Incubation Temp.	: 80 °C
Incubation Time	: 5 min
Agitator Speed	: 250 rpm
Sample Extract Time	: 30 min
Sample Desorb Time	: 2 min
GC	
Injection Temperature	: 250 °C
Injection Mode	: Splitless (Sampling time 2 min)
Carrier Gas	: He
Carrier Gas Control	: Constant linear velocity (52.9 cm/s)
Purge flow rate	: 7 mL/min
Column Temp.	: 40 °C (2 min) – 10 °C/min – 120 °C – 30 °C/min – 250 °C (5 min)

Table 5 Instrument Compositions and Analysis Conditions (SPE-GC/MS)

Instrument compositions	
Auto Injector	: AOC-20i Plus
Auto Sampler	: AOC-20s Plus
Column	: SH-I-5SIL MS (30 m × 0.25 mm I.D., d.f.= 0.25 µm)
Analysis conditions	
GC	
Injection Temperature	: 250 °C
Injection Mode	: Splitless (Sampling time 2 min)
Carrier Gas	: He
Carrier Gas Control	: Constant linear velocity (52.9 cm/s)
Column Temp.	: 40 °C (2 min) – 10 °C/min – 120 °C – 30 °C/min – 250 °C (5 min)
Injection Volume	: 1 µL

■ Measurement Results for Sample Preparation Methods

The measurement results (2-MIB and geosmin) obtained by using the four sample preparation methods in an analysis of moldy odor-causing substances in water were compared.

Fig. 2 shows the SIM chromatogram for the quantitation limit concentration (1 ng/L) and calibration curve. Satisfactory sensitivity was obtained with all sample preparation methods, and the correlation coefficient of the calibration curves was R = 0.999 or higher, indicating good linearity.

Table 6 shows the analysis results for a repeated analysis (n = 5) for the quantitation limit concentration (1 ng/L). Good results were obtained, as the recovery rate for the samples with addition of 1 ng/L was within ±20 % with all sample preparation methods, and the precision of repeated analyses (repeatability; RSD%) was within 5 %. Table 7 shows the S/N ratio. Measurement with high sensitivity was possible in the order of PT-GC/MS (highest sensitivity), followed by SPE-GC/MS, SPME-GC/MS, and HS Trap-GC/MS.

Note: In Fig. 2, Table 6, and Table 7, the order of sensitivity is arranged from the left (highest), divided into the cases where an autosampler was used in sample preparation (PT-GC/MS, SPME-GC/MS, and HS Trap-GC/MS) and where an autosampler was not used (SPE-GC/MS).

Table 6 Results of Repeated Analysis (n = 5)
for Quantitation Limit Concentration (1 ng/L)

Compound	Item	PT-GC/MS	SPME-GC/MS	HS Trap-GC/MS	SPE-GC/MS
2-MIB	Average concentration (ng/L)	0.939	1.065	1.011	1.018
	RSD%	5 % or less			
Geosmin	Average concentration (ng/L)	1.008	1.077	0.963	1.119
	RSD%	5 % or less			

Table 7 S/N Ratios *1 of Sample Preparation Methods

Compound	PT-GC/MS	SPME-GC/MS	HS Trap-GC/MS	SPE-GC/MS
2-MIB	55	24	11	45
Geosmin	133	31	17	75

*1 The S/N ratio was calculated by the peak to peak noise calculation method.

■ Conclusion

Good results were obtained with all sample preparation methods for analysis of moldy odor-causing substances in water. Table 8 shows a comparative table in which the sample preparation methods were evaluated in 3 levels (A, B, C). Since sensitivity, handling operation, and other features differed depending on the sample preparation method, the optimum sample preparation method should be selected based on an understanding of their respective characteristics.

Table 8 Comparison of Sample Preparation Methods for Moldy Odor Compounds in Water

Item	PT-GC/MS	SPME-GC/MS	HS Trap-GC/MS	SPE-GC/MS
Sensitivity	A	B	C	A
Quantitativity	A	A	A	A
Sample preparation	A Automatic internal standard addition function + No quantitative sampling	B Salting-out + Quantitative sampling of 10 mL sample	B Salting-out + Quantitative sampling of 10 mL sample	C Concentration using solid phase column
Maintainability	B	A	B	A

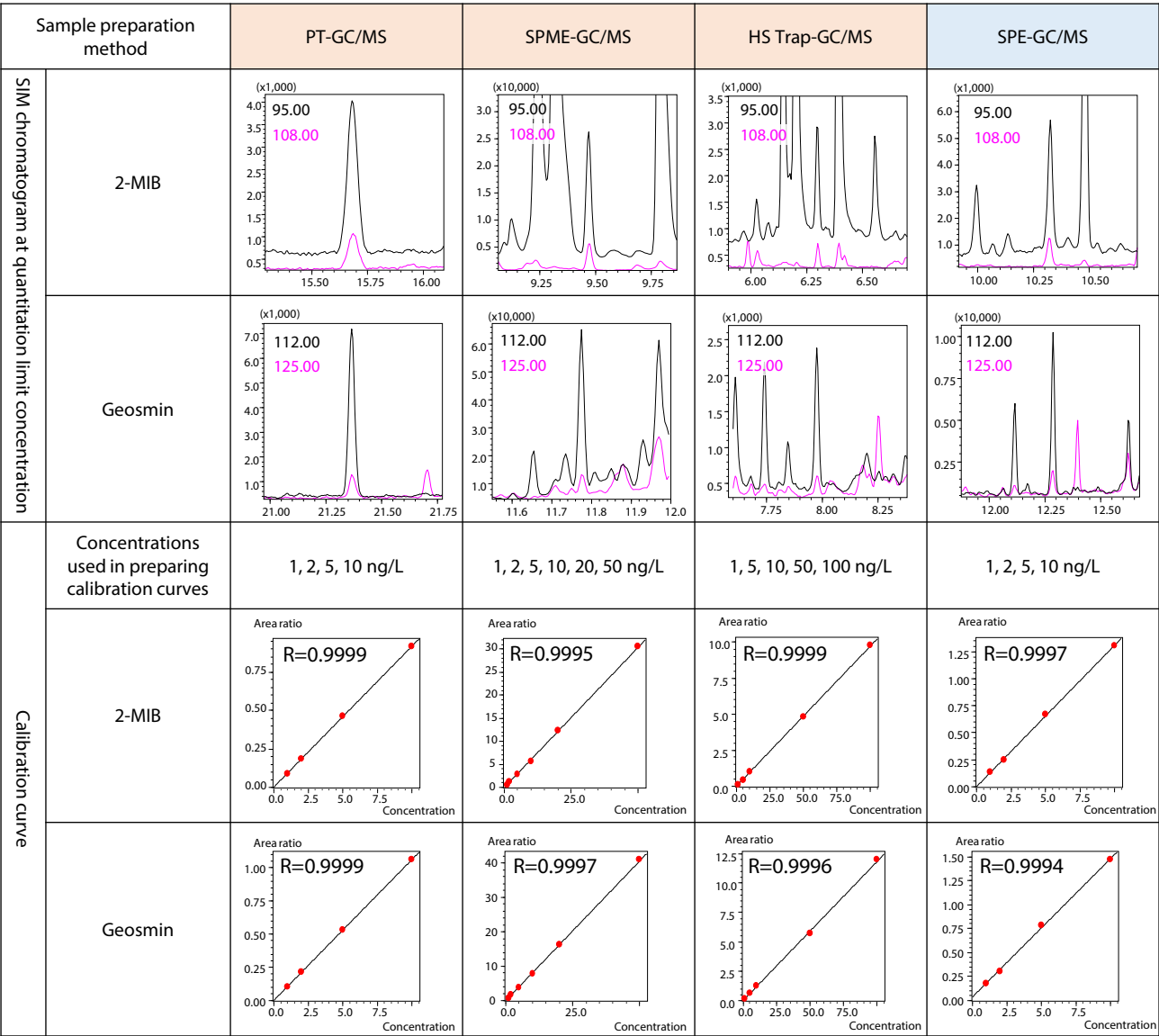


Fig. 2 SIM Chromatograms at Quantitation Limit Concentration (1 ng/L) and Calibration Curves for Sample Preparation Methods

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