High Sensitive Analysis of Musty Odor Compounds in Drinking Water by Purge and Trap-Gas Chromatography - Mass Spectrometry (PT-GC-MS)

Takumi Kunieda*, Tatsuya Shimofuji, Kazuyuki Ishii, Noriyuki Baba, Hiroshi Hayashida, GL Sciences Inc. Tokyo, Japan

Introduction

Geosmin and 2-methylisoborneol are compounds produced by algae and bacteria in surface water, known to cause taste and odor issues in drinking water. In Japan, the regulatory standards for drinking water quality set the acceptable concentrations of these compounds under 10 ng/L each. Consequently, high sensitivity and accuracy are required for the analytical instruments used to detect these substances. GC-MS is commonly used as the analytical method, and sample preparation techniques include solid-phase extraction (SPE), solid-phase microextraction (SPME), and headspace (HS). However, these methods require the measurement of sample water volumes during preparation, and both SPME and HS methods necessitate salting-out operations to enhance sensitivity, making the procedures cumbersome. Therefore, the authors optimized the method using P&T-GC-MS, the simplest method for VOC analysis, and report obtaining satisfactory results.

GCMS - QP2020 NX　PT7000 Purge and Trap　AS7100 Vial Autosampler

Method

The purge and trap device PT7000 (GL Sciences Inc.) and GC-MS, GCMS-QP2020 NX (Shimadzu Corporation) were used. To detect highly adsorptive musty odor compounds with high sensitivity, the PT7000 was equipped with stainless steel tubes with advanced inert treatment along the sample path. Standard samples were prepared to achieve concentrations of 1 ng/L, 2 ng/L, 5 ng/L, and 10 ng/L for both 2-methylisoborneol (2-MIB) and geosmin. Samples were collected in 40 mL pre-cleaned vials and set in an autosampler without adding salt. The sample loop size for automatic measurement was set to 20 mL. For the analytical column, a moderately polar capillary column, InertCap 5MS/Sil, with a liquid phase of 5% diphenyl and 95% dimethylpolysilphenylene siloxane, was used. To prevent water from entering the detector, an AQUA TRAP 1 packed with hydrophobic polymers, Tenax TA (poly-2,6-diphenyl-p-phenylene oxide) and Tenax GR, was selected as the trap tube. Internal standards, 2,4,6-trichloroanisole-d3 and geosmin-d3, were prepared at concentrations of 20 ng/L and 5 ng/L, respectively, in 20 mL samples using the autosampler's automatic addition function.

Table 1 P&T Method Conditions

Standby		Bake	
Valve oven temp.	150 ℃	Bake time	5 min
Transfer line temp.	150 ℃	Bake temp.	220 ℃
Mount temp.	60 ℃	MCS bake temp.	bypass
Purge ready temp.	35 ℃	Bake flow rate	80 mL/min
MCS temp.	bypass	Bake sparger time	5 min
Standby flow rate	40 mL/min	After bake time	1 min
B.O.T temp.	150 ℃	After bake flow rate	100 mL/min
Purge MCS temp.	40 ℃	Autosampler	
Dry purge MCS temp.	bypass	Sampling time	0.60 min
Purge		I.S. addition	ON
Prepurge time	0 min	Fill I.S. time	0.20 min
Prepurge flow rate	0 mL/min	Transfer time	0.70 min
Sample temp.	60 ℃	Loop wash time	0.60 min
Preheat time	0.01 min	Loop purge time	0.60 min
Purge time	12 min	Rinse frequency	3
Purge temp.	40 ℃	Bake fill time	0.60 min
Purge flow rate	60 mL/min	Bake transfer time	0.70 min
Dry purge time	1 min	Bake drain time	0.70 min
Dry purge temp.	40 ℃	Bake drain flow rate	200 mL/min
Dry purge flow rate	60 mL/min	Note	
Desorb		Sparger	20 mL
GC start	Start of desorb	Trap	AQUATrap-1 (Tenax TA / Tenax GR)
Desorb Preheat temp.	20 ℃	Sample loop	5 mL
Drain	ON	Chiller Tray	ON
Desorb time	3 min	Purge Gas	Nitrogen
Desorb temp.	220 ℃		
Desorb flow rate	100 mL/min		

Table 2 GC - MS Method Conditions

GC-MS	GCMS - QP2020 NX (Shimadzu Corporation)
Column	InertCap 5MS/Sil 0.25 mmI.D. x 30 m , df = 0.5 µm (GL Sciences Inc.)
Split ratio	1: 5
Oven Temp.	60 ℃(hold 1.0 min) - 4 ℃/min - 120 ℃ - 10 ℃/min - 170 ℃ - 20 ℃/min - 220 ℃ (hold 5 min)
Carrier gas	He, 120 kPa
Detection	MS , SIM Time(min) m/z 14.00 - 17.00 min : 95,107,108,135 17.00 - 19.85 min : 213,215,217,195,197 19.85 - 21.50 min : 112,125,111,126,115,128,114,129

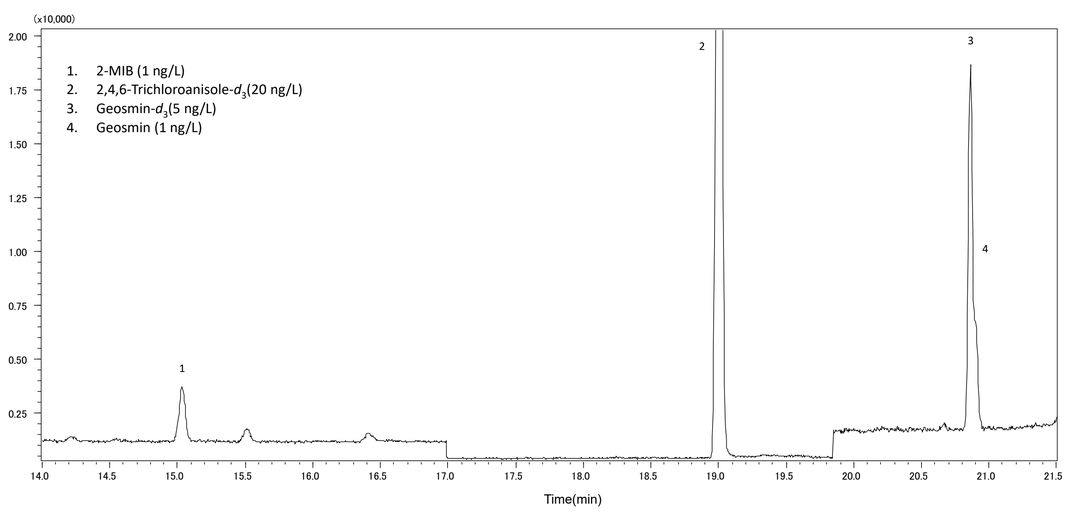

Fig.1 Total Ion Current Chromatogram (TICC)

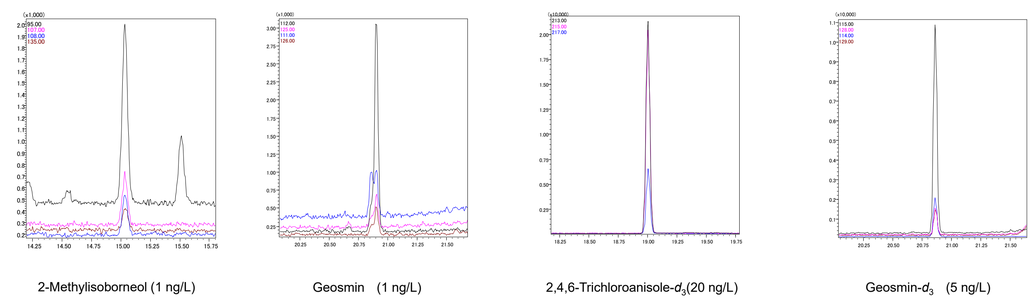

Fig.2 Chromatogram of 2-Methylisoborneol, Geosmin, 2,4,6-Trichloroanisole-d_3 and Geosmin-d_3

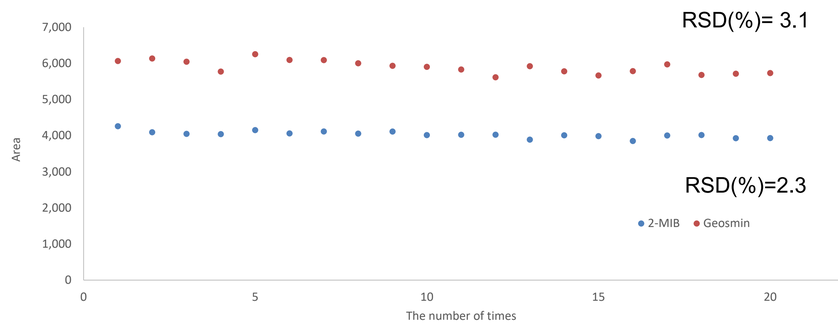

Fig.3 Repeatability of peak area (1 ng/L, n=20)

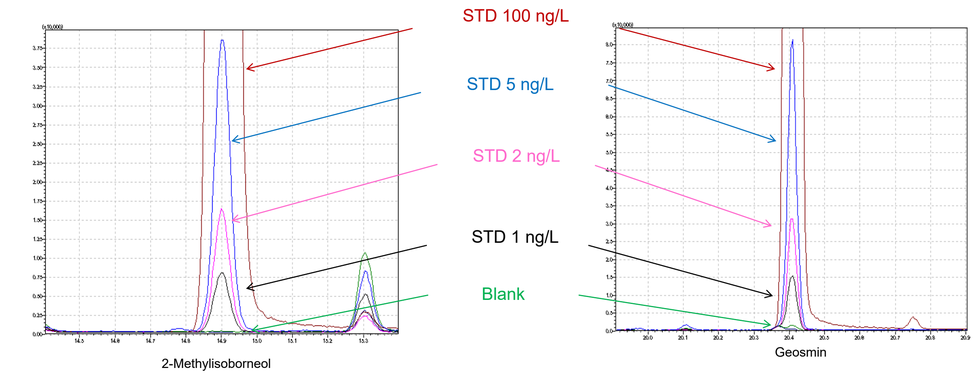

Fig.4 Carry over

Table 3 Calibration and Repeatability in parallel tests.

	Compounds	Calibration 1-10 ng/L		Repeatability (n=7, 1 ng/L)			
		R.T. (min)	Linearity (r2)	Ave.Conc. (ng/L)	MDL (ng/L)	Accuracy (±20%)	Precision (≦20%)
1	2-Methylisoborneol	14.983	0.9995	1.1	0.069	9.2	1.9
2	Geosmin	20.874	0.9990	1.1	0.092	5.3	2.4
3	2,4,6-Trichloroanisole-d_3	18.969	-	-	-	-	-
4	Geosmin-d_3	20.834	-	-	-	-	-

Results

Figure 1 and Figure 2 show the chromatogram of the standard substance at 1 ng/L. In these chromatograms, the separation from the blank was sufficient, and the S/N ratios for 2-MIB and geosmin were 36 and 95, respectively. Figure 3 shows the precision of the area values of 2-MIB and geosmin (n=20). The repeatability was good, 2.3% for 2-MIB and 3.1% for geosmin. Figure 4 shows the blank chromatogram after measuring 100 ng/L of mold odor substances. The chromatogram of musty odor compounds at 100 ng/L is brown, the blank is green, and the chromatograms of 1, 2, and 5 ng/L are also shown for comparison. Carryover of 2-MIB was below the detection limit, while for geosmin, it was approximately 0.2%. Table 3 shows the calibration curves and repeatability in parallel tests. Calibration from 1 to 10 ng/L was good linearity. The method detection limits (MDLs) calculated from the repeatability of 1 ng/L were 0.069 ng/L for 2-MIB and 0.092 ng/L for geosmin.

Conclusion

The system combining the PT7000 purge and trap enrichment device with the GCMS-QP2020 NX gas chromatograph mass spectrometer demonstrated stable analysis of geosmin and 2-methylisoborneol in tap water. The use of stainless steel tubes with advanced inert treatment and the selection of an appropriate trap tube significantly contributed to the method's performance. Additionally, the elimination of the need for salting-out operations and the simplicity of the P&T-GC-MS method make it a practical alternative to other more cumbersome techniques.

References

1. Standard test method in water, Ministry of Health, Labor and Welfare, Japan
2. Water supply test method, 2020 Edition, Japan Water Works Association