Application Note: 10213

Determination of Geosmin and 2-MIB in Drinking Water by SPME-PTV-GC/MS

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Key Words

- DSQ II GC/MS
- TriPlus Autosampler
- 2-MIB
- Geosmin
- SPME
- Taste and Odor Compounds

Introduction

Geosmin (1,2,7,7-tetramethyl-2-norborneol) and 2-MIB (2-methylisoborneol) are compounds mainly produced by blue-green algae (cyanobacteria) and actinomycete bacteria that cause musty, earthy odors in public water supply reservoirs. Although these compounds have not been shown to be a health concern in public water supplies, their odors require removal and thus concentrations of geosmin and 2-MIB are monitored routinely in areas where they occur. The odor threshold for these compounds is very low and humans can typically detect them in drinking water at 30 and 10 ng/L (ppt) for geosmin and 2-MIB, respectively.[1,2] Past analytical techniques to determine concentrations of these compounds have included closed-loop stripping, purge-and-trap with gas chromatography/mass spectrometry (GC/MS)), headspace with GC/MS, and solid phase microextraction (SPME) with GC/MS.[3,4,5,6,7] These methods were able to detect geosmin and 2-MIB to around 1.0 ppt, using selected ion monitoring with a single quadrupole mass spectrometer.

This note describes a technique for the analysis of these two compounds using automated headspace/SPME sampling in conjunction with the Thermo Scientific TRACE GC Ultra™ and Thermo Scientific DSQ™ II single quadrupole mass spectrometer, with linearity and sensitivity between 1 and 1000 ppt (ng/L).

Experimental

Materials and Sample Preparation

Calibration and internal standards were obtained as a Drinking Water Odor Standards Kit, # 47529-U from Supelco (Bellefonte, PA). Analytes in the standard solution kit were geosmin (CAS 23333-91-7), 2-MIB (CAS 2371-42-8) and 2-isopropyl-3-methoxypyrazine (IPMP, CAS 25773-40-4), used as the internal standard (Figure 1). All standard solutions were diluted in methanol. ACS grade sodium chloride was obtained from Fisher Scientific. Each calibration level (1, 10, 50, 100, 200, 500 and 1000 ppt) was prepared from stock solution in a 100 mL volumetric flask. Variable amounts of stock solution and 300 ppt of the internal standard were added to the volumetric flasks, resulting in the proper concentration of the standards. Care was taken to add the same concentration of methanol to all calibrators and samples at the time of sample preparation, since proper sorption onto the SPME fibers was dependent on methanol concentration in the sample. A 10 mL aliquot was transferred to a 20 mL headspace vial along with 3 g of sodium chloride prior to placement on the autosampler. All standards were run in duplicate.

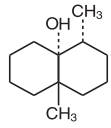
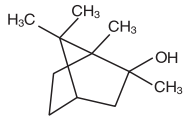
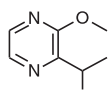
Compound Name	Molecular Structure	Formula	Molecular Weight
Geosmin		$C_{12}H_{22}O$	182.3
2-MIB		$C_{11}H_{20}O$	168.3
IPMP, internal standard		$C_8H_{12}N_2O$	152.2

Figure 1: Name, molecular structure, formula, and molecular weight of the compounds used in this application

Analysis

A Thermo Scientific TriPlus™ Duo autosampler equipped with a SPME* attachment was used. The injector contained a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30 µm thick fiber (part number 57329-U, Supelco, Bellefonte, PA) that was preconditioned prior to analyses. Samples contained in sealed 20 mL headspace vials with sodium chloride were incubated in the TriPlus oven at 60 °C for 30 minutes before desorption for 4 minutes in the GC inlet.

A Thermo Scientific TRACE GC Ultra with a Programmable Temperature Vaporizing (PTV) inlet was used with a 5% phenyl 95% methyl silicone 30 m x 0.25 mm ID x 0.25 µm film thickness fused silica capillary column. The GC was coupled to a Thermo Scientific DSQ II single quadrupole MS. The DSQ II MS used a closed-exit EI ion volume for enhanced sensitivity. Instrument conditions for the MS, GC and autosampler are shown in Table 1. Data were acquired and processed with Xcalibur™ 1.4 software and the Thermo Scientific EnviroLab™ Forms 2.0 data review and analysis package.

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Instrument Parameters

DSQ II Mass Spectrometer	
Lens 1:	-25.0 volts
Lens 2:	-5.40 volts
Lens 3:	-25.0 volts
Pre-filter Offset:	-8.70
Electron Lens:	15.0
Electron Energy:	-70 eV
Emission Current:	50 µA
Acquisition Time:	GC Run Time
Acquisition Threshold:	0
Source Temperature:	230 °C
Segment 1:	
Start Time:	7.00 minutes
Detector Gain:	3 x 10^5 (1224 volts)
Scan Event 1:	SIM
Mass 1:	137.00
Mass 2:	152.00
Width:	1.00
Dwell Time:	100 ms
Segment 2:	
Start Time:	8.00 minutes
Detector Gain:	3 x 10^5 (1224 volts)
Scan Event 1:	SIM
Mass 1:	95.00
Mass 2:	107.00
Width:	1.00
Dwell Time:	100 ms
Segment 3:	
Start Time:	10.00 minutes
Detector Gain:	3 x 10^5 (1224 volts)
Scan Event 1:	SIM
Mass 1:	112.00
Mass 2:	149.00
Width:	1.00
Dwell Time:	100 ms
Segment 4:	
Start Time:	11.00 minutes
Detector Gain:	3 x 10^5 (1224 volts)
Scan Event 1:	full scan, Scan Rate 500 amu/sec
First Mass:	50
Last Mass:	650

TRACE GC Ultra	
Oven:	60 °C, 4.00 min; 20 °C/min, 250 °C, hold 1.50 min (Split Flow: 15 mL/min)
Carrier Gas:	1.50 mL/min, constant flow
PTV Inlet:	60 °C, PTV Split Mode, Inject Time 0.1 min., Transfer Rate 14.5 deg/sec, Transfer Temp 250 °C, Transfer Time 4.0 min

TriPlus Duo Autosampler	
Incubation:	Constant at 60 °C
Agitator on time:	10 sec
Agitator off time:	10 sec
Incubation Time:	30 minutes
Standard Sampling Depth in Vial	
Injection Depth 20 mm	
No pre- or post-injection delay	
Synchronization Start:	Normal
Needle Speed in Vial:	20 mm/sec
SPME Extraction Time:	30 min
SPME Desorption Time:	4.0 min
Fiber Conditioning Station Time:	10.0 min
Fiber Conditioning Port Temp:	250 °C

Table 1: Instrument parameters used for geosmin/2-MIB analysis

Results and Discussion

Excellent linearity was obtained for both geosmin and 2-MIB, with r^2 values of 0.9994 and 0.9995, respectively, over a range of concentrations from 1 to 1000 ppt (Figures 2 and 3). Seven replicates were analyzed for method detection limits according to 40 CFR Part 136, Appendix B and showed the MDLs to be 0.191 and 0.358 ng/L for geosmin and 2-MIB (Figure 4). Average RSDs of the replicate injections were 0.56% for geosmin and 1.6% for 2-MIB. These detection limits were run as 1:10 split injections, thus lower detection limits are possible with splitless injections. Excellent sensitivity and chromatographic performance was demonstrated across the calibration range for both MIB and geosmin (Figure 5).

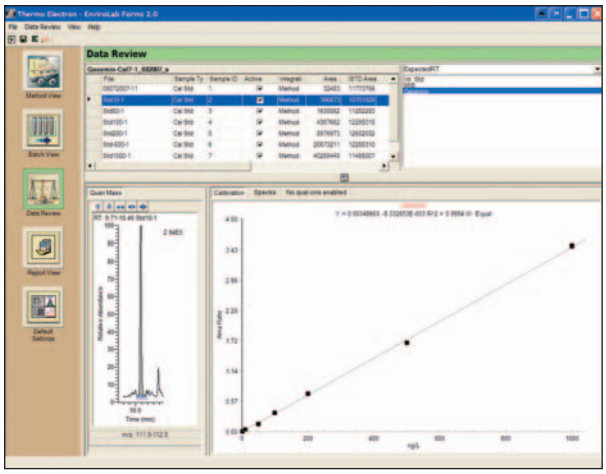

Figure 2: Calibration curve for geosmin for concentrations including 1, 10, 50, 100, 200, 500, and 1000 ppt

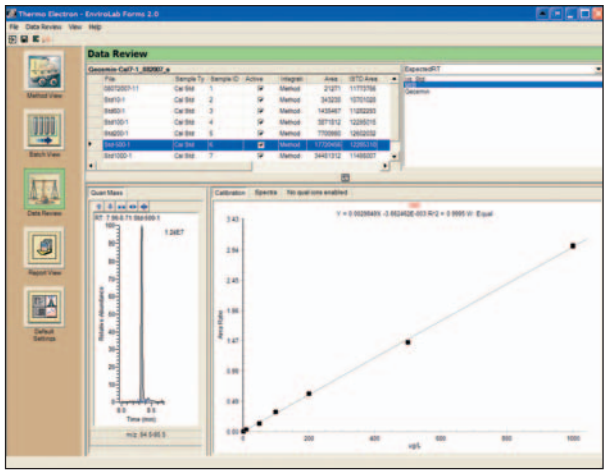

Figure 3: Calibration curve for 2-MIB for concentrations including 1, 10, 50, 100, 200, 500, and 1000 ppt

Method Detection Limit Report

LabName:	Thermo Scientific Laboratory		Page 1 of 3
InstID:	Thermo Scientific GC-MS	**Method:**	Geosmin-Cal7-1-MDL_882007_b.mext (Geosmin-MIB-1)
OperatorID:	User		
Batch:	Geosmin-Cal7-1-MDL_882007_b	**Cali File:**	Geosmin-Cal7-1_882007_a.cxml

Method Detection Limit Summary

Component	Avg Conc	Std Dev	TSTAT	%RSD	MDL
Int_Std	11140241	449528			
MIB	1.900	0.114	3.143	6.003	0.359
Geosmin	3.182	0.061	3.143	1.916	0.192

Figure 4: Method Detection Limit Report for geosmin and 2-MIB using EnviroLab reporting software. MDLs are in ng/L (ppt)

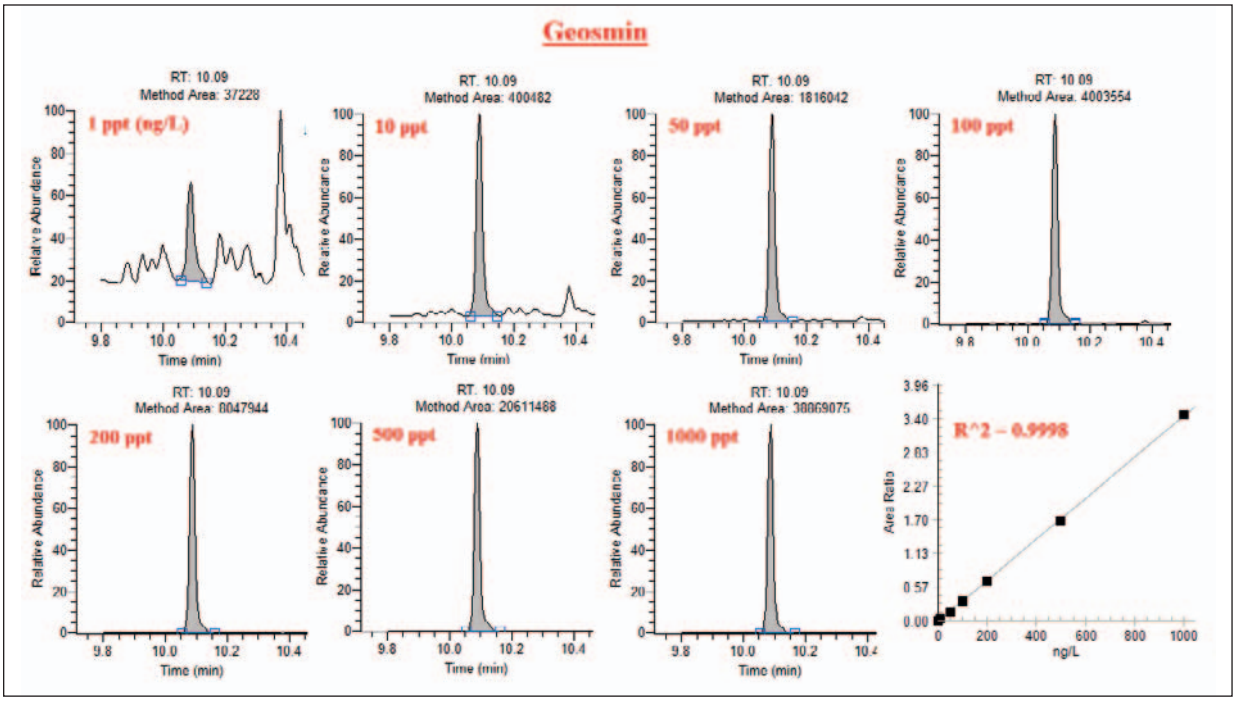

Figure 5: Geosmin chromatograms, demonstrating excellent peak shape, linearity and sensitivity from 1.0 – 1000 ppt

Conclusion

The technique of SPME configured on the TriPlus Duo, together with the TRACE GC Ultra gas chromatograph and DSQ II single quad MS, offers an easy method for the analysis of trace levels of odorants in drinking water samples. The sensitivity and wide linear dynamic range of the DSQ II GC/MS working in SIM mode permits target compounds to be accurately quantified over a concentration range of at least three decades. Method detection limits for geosmin and 2-MIB were less than 0.3 ppt – less than the concentrations typically detected by humans. The optimized incubation geometry of the TriPlus SPME accessory ensures optimal fiber lifetime while ensuring precise operation and efficient extractions. Ease of data processing is enhanced with the use of EnviroLab reporting, which offers rapid data review and standard forms for quality control and high sample throughput.

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