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Application Note
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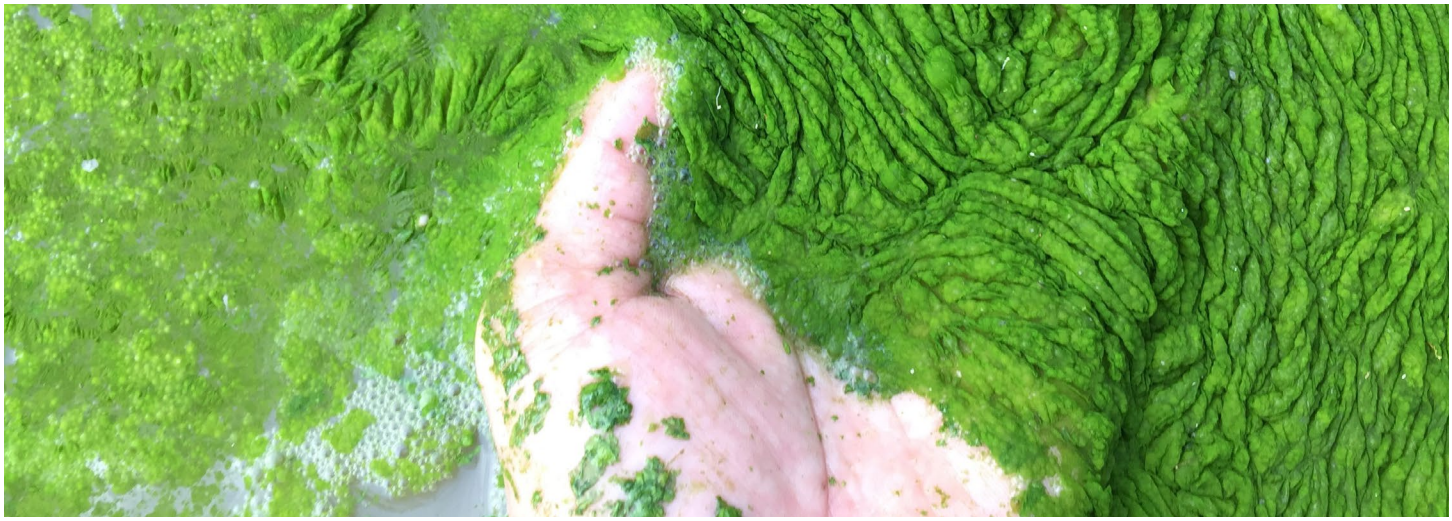
Highly Sensitive Detection of Geosmin and MIB by Purge and Trap (P&T) with Gas Chromatography/Mass Spectrometry (GC/MS) to Support Management of Harmful Algal Blooms

ENVIRONMENTAL SERIES



Introduction

Harmful Algal Blooms (HABs) caused by cyanobacteria bring a number of challenges for drinking water treatment. HAB management strategies often prioritize the removal of potentially harmful toxins, which is readily achieved by conventional treatment methods. One of the most insidious impacts of HABs on drinking water quality is the taste and odor compounds cyanobacteria produce which have a tendency to persist throughout treatment.

In many instances consumer complaints about taste and odor may be attributed to Geosmin (trans-1,10-Dimethyl-trans-9-decalol) and MIB (2-Methylisoborneol). 2-MIB causes a musty smell and taste and is produced throughout the life cycle of cyanobacteria. Geosmin causes an earthy smell and taste and is commonly trapped in a cell body and released in high concentrations when the cells die.

The presence of these compounds is a major concern because of their extremely low threshold concentration and persistence throughout conventional water treatment. The effects of taste and odor compounds on drinking water is purely aesthetic. However, these stubborn compounds may cause the perception that the water is not safe to drink, since consumers associate taste and odor with HABs, and there has been increasing awareness that HABs can pose a safety risk for drinking water.[1]

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A HAB management strategy should therefore include effective management of Geosmin and MIB. That requires the ability to accurately measure the concentrations in raw and finished water on a routine basis. Because the perception threshold is so low, 4-22 ppt, it is necessary to have an analysis that can detect the compounds at a lower level than the threshold.[2] This study will present an optimized method using purge and trap concentration with separation and detection by gas chromatography and mass spectrometry using selective ion monitoring (SIM) to achieve a reporting level of 1 ppt.

Instrumentation

Purge and trap (P&T) concentration was performed with an OI Analytical 4760 P&T with a 4100 Soil/Water Sample Processor. The 4100 has a standard addition module, LV20, for a programmed injection of Internal Standard (IS) and Surrogate Standard (SS). An Agilent 7890A/5975C GC/MS was used for chromatographic separation and detection. A column suitable for volatile organic analysis was utilized.

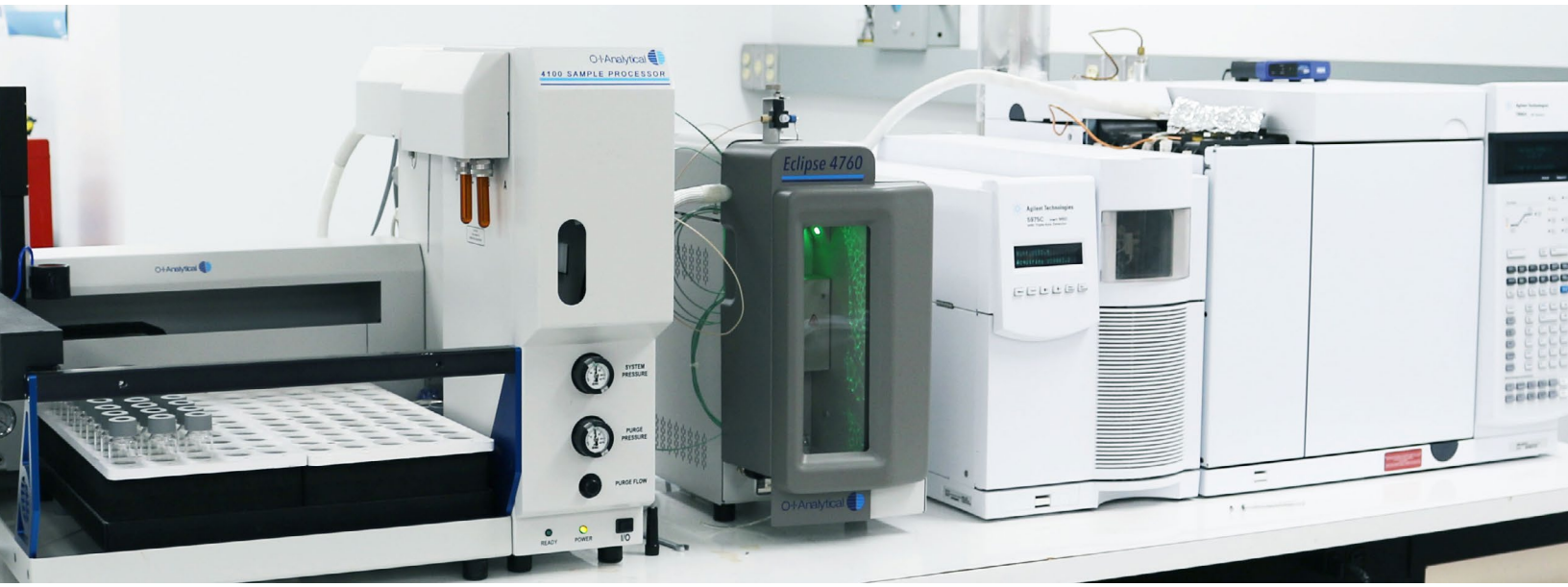


Figure 1. From left to right, the OIA 4100 Autosampler, OIA 4760 Eclipse Purge & Trap, and the GC/MS system.

Experimental

EPA Method 524.3 for volatile organic analysis was used as a guideline for this study.[3] The compounds of interest are saturated tertiary alcohols, so are hydrophilic in nature and are not easily purged from water. Low reporting levels require a modified method for successful analysis. Several factors affect this including maximizing purging efficiency, optimizing P&T parameters, and employing SIM. Purging efficiency can be increased by varying purge flow and temperature as well as increasing sample volume. For example several variations were employed including using purge flows of 40-50 mL/minute, purge temperatures from 45-80 ˚C, and 5, 10, and 25 mL purge volumes. Other P&T parameters were also varied including desorb time, dry purge time, and desorb pre-heat. A conservative approach was used for stability and consistency. For example heating at 80 ˚C increased response but not enough to justify the risk of more water being transferred to the GC/MS. A 10 mL purge gave almost twice the response of a 5 mL purge while the 25 mL purge did not give five times the response versus 5 mL. The purging efficiency of the 25 mL purge is not as good as the lower volumes because of the larger water column in the sparger. For this study 10 mL was purged.

A pulsed split injection was used to maximize efficient transfer of the analytes to the GC column. The pulsed injection increases the inlet pressure at the beginning of the run to boost carrier flow at desorption and sweeps the sample onto the column faster. This also minimizes the time in the inlet which can lead to decomposition of analytes. This can be a concern with 2-MIB which decomposes at high temperatures in the GC inlet. Please see Table 1 for instrument conditions.

Table 1. Instrument Configuration and Operating Conditions

Purge-and-Trap	Eclipse 4760 P&T Sample Concentrator
Trap	#7 trap; Tenax®
Purge Gas	Zero grade Helium at 40 mL/min
Purge Time	11 min
Sparge Mount Temperature	45 °C
Sample Temperature (purge)	60 °C
Sample Temperature (bake)	70 °C
Desorb Time	1.5 min
Bake Time	6 min
OI #7 Trap Temperature	Ambient during purge No desorb pre-heat 180 °C during desorb 200 °C during bake
Water Management	120 °C during purge Ambient during desorb 240 °C during bake
Transfer line Temperature	160 °C
Six-port Valve Temperture	160 °C

Autosampler	4100 Water/Soil Sample Processor
System Gas	Zero grade nitrogen
Purge Gas	Zero grade helium
LV20 Pressure	8.0 psi
Loop-based Time Settings	Default
Rinse Water	80 °C
Soil Sample Transfer	150 °C
Soil Oven	150 °C
Soil LIft Station	45 °C

Sample Type	Waters only
Needle Rinses	1
SAM A (µL)	5
SAM B (µL)	0
SAM C (µL)	0
SAM D (µL)	0
Purge Time (min)	11.0
Desorb Time (min)	1.5
P&T Rinses	3
Rinse Water	Hot
Water Stir Time (min)	0
Water Settle Time (sec)	5

Gas Chromatograph	Agilent 7890A
Column	Restek Rtx-VMS 30 meter, 0.25 mm ID, 1.4 µm film
Carrier Gas	Zero grade helium
Inlet Temperature	240 °C
Inlet Liner	Agilent Ultra Inert, 2 mm straight
Column Flow Rate	0.8 mL/min
Split Ratio	5 Pulsed split at 45 psi for 1 minute
Oven Program	Hold at 40 °C for 1 min 16 °C/minute to 180 °C 40 °C/minute to 220 °C Hold at 220 °C for 4 min Total GC Run is 17.25 min

Mass Spectrometer	Agilent 5975C	
Mode	SIM 100 msec dwell time	
SIM Compounds		
Group 1	1,4-Dichlorobenzene-d4 and 1,2-Dichlorobenzene-d4	m/z 115, 150, 152 Start 9.50 minutes
Group 2	2-MIB	m/z 95, 107, 135 Start 11.20 minutes
Group 3	Geosmin	m/z 112, 149 Start 12.00 minutes
Solvent Delay	9.5 min	
Transfer Line Temperature	240 °C	
Source Temperature	230 °C	
Quadrupole Temperature	150 °C	
Draw Out Plate	6 mm	

A 2000 ppm 524.3 Internal Standard-Surrogate Standard (P/N 30017) and a 100 ppm Geosmin and 2-MIB Standard (P/N 30608) were purchased from Restek. Both stock standards were in Methanol. Intermediate standards were diluted from these in Methanol. The Geosmin and 2-MIB standards were diluted in Methanol to make a 0.1 ppm standard. A calibration of 1, 2, 5, 10, 25, 50, 75, and 100 ppt Geosmin and 2-MIB was prepared by injecting µL amounts of 0.1µg/mL working standard in Methanol into water. The 4100 Water/Soil Sample Processor's LV20 Standard Addition Module was programmed to add 5 µL of 0.02 ppm IS-SS working standard for a final concentration of 10 ppt. Because the concentration of the working standards were so low they were made fresh daily.

4-Bromofluorobenzene was injected at the beginning of each sequence and method 524.3 acceptance criteria was met for tuning. Agilent ChemStation software was used to process data. Please see Table 2 for calibration results.

Table 2 Calibration Results

Analyte	Compound	Avg Response Factor	% RSD	Coef of Det
1	1,4-Dichlorobenzene-d4 (IS)	N/A	N/A	N/A
2	1,2-Dichlorobenzene-d4 (SS)	0.496	2.47	N/A
3	2-MIB	0.450	4.48	0.998
4	Geosmin	0.375	5.14	0.999

The calibration points must be re-quantitated as an unknown using the calibration curve and linear regression. The low level must be within +/- 50% of the true value and other points +/- 30% of the true value to meet calibration criteria.

After calibration the Minimum Reporting Level (MRL) must be established by running seven replicates of the low standard (1 ppt). The mean and standard deviation for the replicates are calculated and the Half Range for the Prediction of Interval Results is established (HR_{PIR}) as follows:

$$HR_{PIR} = 3.963 \times \text{Standard Deviation}$$

The Upper PIR Limit must be ≤150% recovery.

$$\frac{\text{Mean HR} + HR_{PIR}}{\text{Fortified Concentration}} \times 100$$

The Lower PIR Limit must be ≥50% recovery.

$$\frac{\text{Mean HR} - HR_{PIR}}{\text{Fortified Concentration}} \times 100$$

The Initial Demonstration of Capability (IDC) must also be run by analyzing seven replicates of a mid-level standard (25 ppt). The relative standard deviation (RSD) is calculated to demonstrate precision and the mean recovery is calculated to demonstrate accuracy. Both must be </= 20%.

Results

All Method 524.3 Quality Control criteria were easily met. Please see Tables 3, 4, and 5. Please see Figures 2, 3, and 4 for example chromatograms.

Table 3 Calibration Acceptance and Validation

Compound	1 ppt Std	1 ppt % Rec	2 ppt Std	2 ppt % Rec	5 ppt Std	5 ppt % Rec	10 ppt Std	10 ppt % Rec
1,2-Dichlorobenzene-d4 (SS)	9.81	98.1	9.83	98.3	9.99	99.9	9.57	95.7
2-MIB	1.03	103	2.41	121	6.02	120	10.6	106
Geosmin	1.13	113	2.03	102	5.25	105	9.65	97.0

Compound	25 ppt Std	25 ppt % Rec	50 ppt Std	50 ppt % Rec	75 ppt Std	75 ppt % Rec	100 ppt Std	100 ppt % Rec
1,2-Dichlorobenzene-d4 (SS)	10.2	102	10.15	102	10.31	103	10.16	102
2-MIB	25.4	102	51.8	104	77.3	103	97.2	97.2
Geosmin	24.5	98.0	50.1	100	76.8	102	98.7	98.7

Low Level % Recovery must be +/- 50%
Other levels must be +/- 30%

Table 4 Minimum Reporting Level (MRL) Confirmation

1 ppt	PIR 1	PIR 2	PIR 3	PIR 4	PIR5	PIR6	PIR7	Mean	STD Dev	HR PIR	(1.0 ppt = True Value) Upper PIR Limit <=150%	Lower PIR Limit >=50%
1,2-Dichlorobenzene-d4 (SS)	9.67	9.73	9.76	9.85	9.55	9.48	9.82	9.69	0.137	0.54	102	91.5
2-MIB	1.06	1.10	1.25	1.11	1.15	1.12	1.15	1.13	0.060	0.24	137	89.8
Geosmin	0.99	1.01	1.04	1.15	1.01	1.12	1.03	1.05	0.061	0.24	129	80.9

Table 5 Initial Demonstration of Capability

Results Signal 1	IDC1	IDC2	IDC3	IDC4	IDC5	IDC6	IDC7	Precision %RSD =20%	Accuracy % Recovery +/- 20%
1,2-Dichlorobenzene-d4 (SS)	9.94	9.98	9.87	10.04	9.55	9.60	9.89	1.92	98.4
2-MIB	25.6	28.1	27.5	28.8	26.8	27.0	27.2	3.73	109
Geosmin	25.1	26.8	27.1	27.8	25.7	25.8	26.5	3.46	106

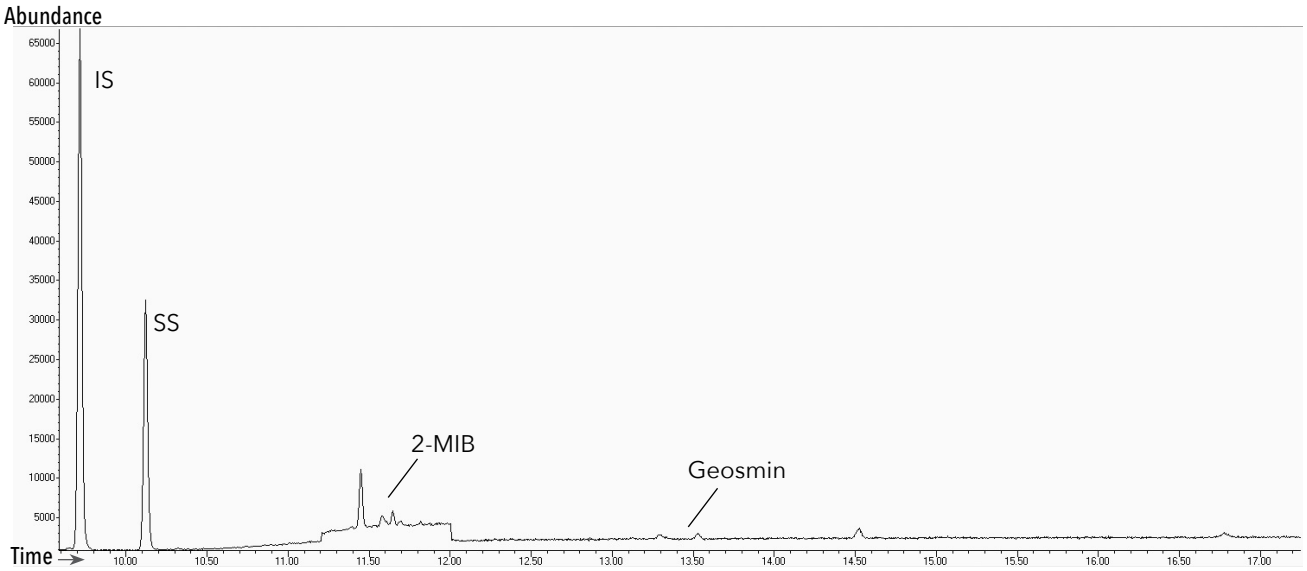


Figure 2. 1 ppt Standard

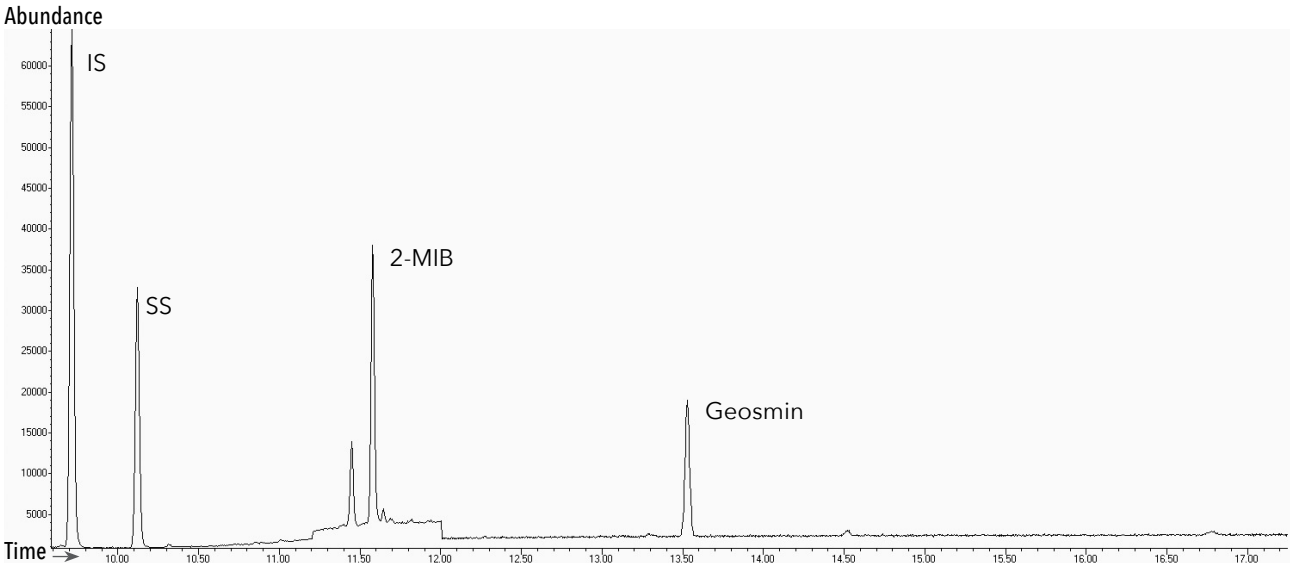
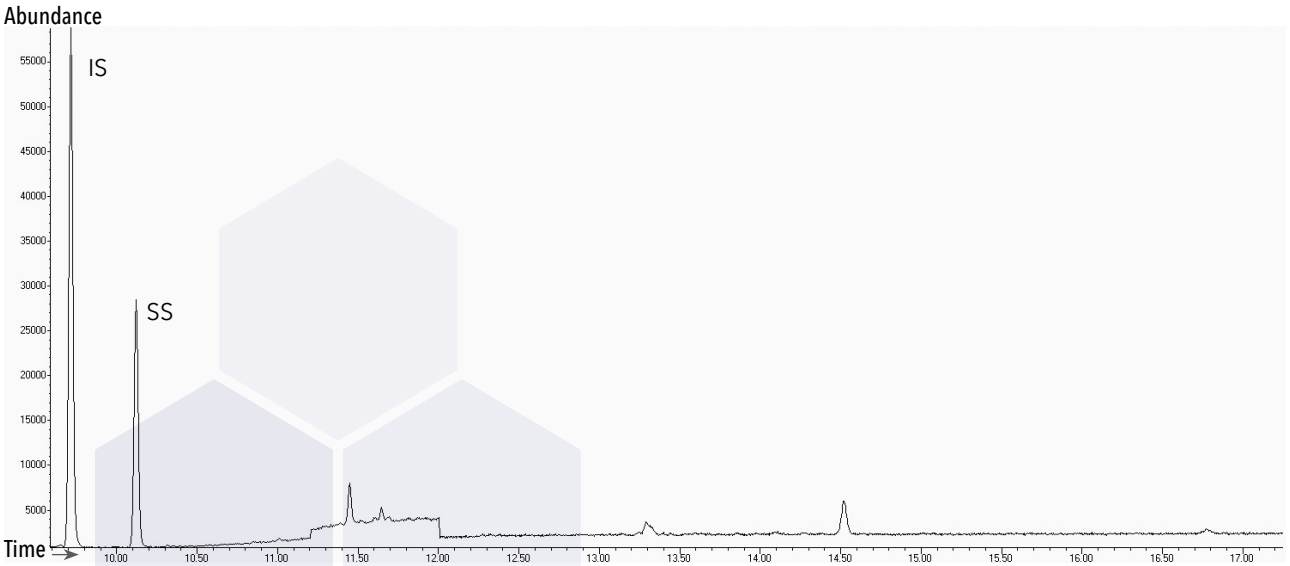


Figure 3. 25 ppt Standard



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Conclusions & Recommendations

The P&T and GC/MS operating conditions for Geosmin and 2-MIB were optimized to meet a very low reporting level and meet strict QC criteria. Since the column used is a volatile column the only change that would be needed to run full list, full scan volatiles would be a trap change with appropriate P&T parameters. Older methods for Geosmin and 2-MIB required "salting" samples, running a 25 mL purge volume, and heating the sample to 80 ˚C. Improvements on instrumentation over the years has made these steps unnecessary.

It is recommended that only drinking water type samples be run, and laboratories might even consider a dedicated setup for this procedure. Wastewater samples might eventually build up in the sample pathway and affect response.

For example, our first attempts at method development did not yield the expected results. The P&T sample pathway was replaced and the Mass Spec source was cleaned. After preventative maintenance the response increased significantly above background. Thus the system must be maintained very well, and the sample pathway and GC/MS must be kept scrupulously clean in order to achieve the low reporting levels demonstrated here.

References

1. EPA Drinking Water Contaminant - Standards and Regulations. EPA.GOV.2018.

2. Nerenberg et al. Ozone /Biofiltration for Removing MIB and Geosmin. Journal AWWA (Dec. 2000)

3. USEPA Method 524.3 Measurement of Purgeable Organic Compounds in Water b Capillary Column Gas Chromatography/Mass Spectrometry, Version 1.0 June 2009.

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