Determination of Algae Compounds in Drinking Water

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EST Analytical

Overview

- Purge and Trap Sampling
- SPME Sampling
- Observations
- Conclusions
- Q&A

Abstract

It has been found that the presence of blue green algae in water sources produces 2-Methylisoborneol (2-MIB) and Geosmin. Both Geosmin and 2-MIB are malodorous compounds that emit a musty earthy aroma. When the algae generates an abundance of these compounds in a drinking water reservoir, there are resulting taste and odor problems.

Abstract

Drinking waters are tested in order to determine water quality for prospective consumers. Two of the major complaints that water suppliers need to address are issues with taste and odor. Geosmin and 2-MIB, although non-toxic, both have very strong odors and can be detected at levels below 10ppt.

Purge and Trap Advantages

1. Exhaustive sampling technique
2. Completely automated sampling

Purge and Trap Disadvantages

1. Water
2. Poor purge efficiency
3. Long desorb time

Purge and Trap Products

CENTURION
PURGE AND TRAP AUTOSAMPLER

The most reliable VOC autosampler on the market today

- IS 3% RSD
- No vial movement for water samples
- No lost vial, syringe or elevator errors
- Separate processing area for water and soil samples
- Rugged X, Y, Z engineering design

EPA Methods

502.1	524.2	601	624	5035	8010	8240
502.2	524.3	602		5030	8015	8260
	524.4	603			8020	
					8021	
					8030	

EVOLUTION
PURGE AND TRAP CONCENTRATOR

The most reliable VOC concentrator on the market today

- Superior moisture control (patented feature)
- Low carryover (patented feature)
- Easy maintenance & diagnostics
- Best in-class service & support
- 3 year warranty on electronic boards

EPA Methods

502.1	524.2	601	624	5035	8010	8240
502.2	524.3	602		5030	8015	8260
	524.4	603			8020	
					8021	
					8030	

Standard Preparation

To Make a 2-Methylisoborneol/Geosmin Standard at 50ppb Diluted in P&T Methanol

Amount	Supelco Part #	Standard	Concentration	Final Vol.
5µl	47525-U	2-MIB/Geosmin	100µg/ml	10.0ml

Use 10ml volumetric flask and dilute standards to 10.0ml in purge and trap methanol

To Make the BFB Internal Standard at 50ppm Diluted in P&T Methanol

Amount	AccuStd Part #	Standard	Concentration	Final Vol.
100µl	CLP-004-100X	BFB	2.5mg/ml	5.0ml

Use 5ml volumetric flask and dilute standards to 5.0ml in purge and trap methanol

To Make the Final BFB Internal Standard at 12.5ppb Diluted in P&T Methanol

Amount	AccuStd Part #	Standard	Concentration	Final Vol.
2.5µl	N/A	BFB dilution	50µg/ml	10.0ml

Use 10ml volumetric flask and dilute standards to 10.0ml in purge and trap methanol

Calibration Curve Preparation

To Prepare a 2-Methylisoborneol/Geosmin Curve Diluted in DI Water			
Concentration	**Standard**	**Standard Amount**	**Final Vol.**
1ppt	50ppb	2µl	100ml
5ppt	50ppb	10µl	100ml
10ppt	50ppb	20µl	100ml
20ppt	50ppb	40µl	100ml
50ppt	50ppb	100µl	100ml
100ppt	50ppb	200µl	100ml

Water Standards

Fill 40ml Vial with final standard leaving no headspace in the vial.

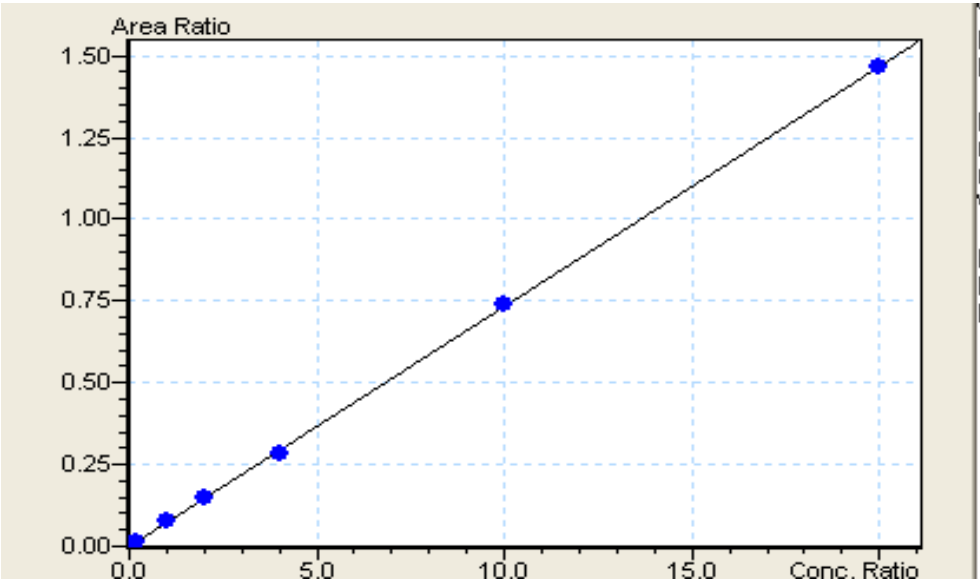
GCMS Parameters

GC/MS	Shimadzu QP2010S
Flow Control mode	Linear Velocity
Pressure	29.2 kPa
Total Flow	43.0ml/min
Column Flow	2.0ml/min
Linear Velocity	51.0 cm/sec
Purge Flow	1.0 ml/min
Column	Rxi-1MS 30m x 0.32mm I.D. x 0.5µm film thickness
Oven Temp. Program	40ºC hold for 2 min, ramp 16ºC/min to 160ºC, hold for 0.0 min, ramp 20ºC/min to 240ºC hold for 3 min
Ion Source Temp.	185ºC
Interface Temp.	180ºC
Solvent Cut Time	3.0 min
Event Time	0.30 sec
ACQ Mode	SIM
SIM ions 174 and 75	3.0 to 8.0 min
SIM ions 95, 107 and 108	8.0 to 9.5min
SIM ions 112, 125 and 126	9.5 to 16.5 min

Purge and Trap Parameters

Purge and Trap Concentrator	EST Encon Evolution
Trap Type	A
Valve Oven Temp.	150ºC
Transfer Line Temp.	150ºC
Trap Temp.	35ºC
Moisture Reduction Trap (MoRT) Temp.	39ºC
Purge Time	12 min
Purge Flow	45mL/min
Dry Purge Temp.	ambient
Dry Purge Flow	50mL/min
Dry Purge Time	3.0 min
Desorb Pressure Control	On
Desorb Pressure	5psi
Desorb Time	6.0 min
Desorb Preheat Delay	0 sec.
Desorb Temp.	230ºC
Moisture Reduction Trap (MoRT) Bake Temp.	210ºC
Bake Temp	230ºC
Sparge Vessel Bake Temp.	130ºC
Bake Time	10
Bake Flow	40mL/min
Purge and Trap Auto-Sampler	**EST Centurion WS**
Sample Type	Water
Sample Fill Mode	Syringe
Sample Volume	25mL
Syringe Rinse	On/25mL
Number of Syringe Rinses	2
Sample Loop Rinse	On/25 sec
Sample Loop Sweep Time	40 sec
Number of Sparge Rinses	Syringe/2
Rinse Volume	25mL
Water Heater Temp.	85°C
Internal Standard Vol.	10µl

2-MIB Purge and Trap Calibration

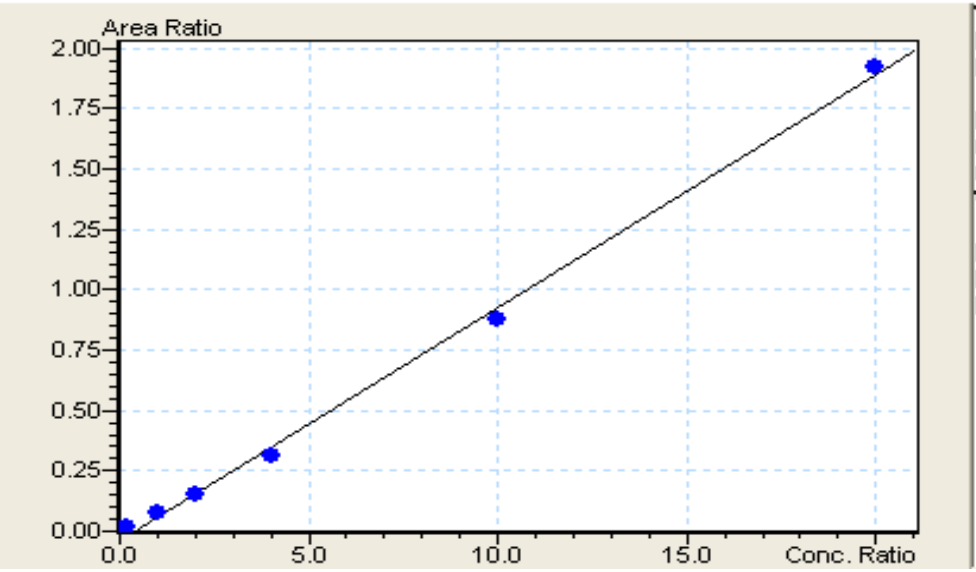


Y = 7.335935e-002X - 8.879833e-00
R^2 = 0.999846
R = 0.999923

Internal Standard
Curve: Linear
Origin: Not Forced
Weighting Method: None

Mean RF : 7.417055e-002
RF SD : 0.0022947
RF %RSD : 3.093797

Geosmin Purge and Trap Calibration



Y = 9.641053e-002X - 3.823746e-00
R^2 = 0.9975745
R = 0.9987865

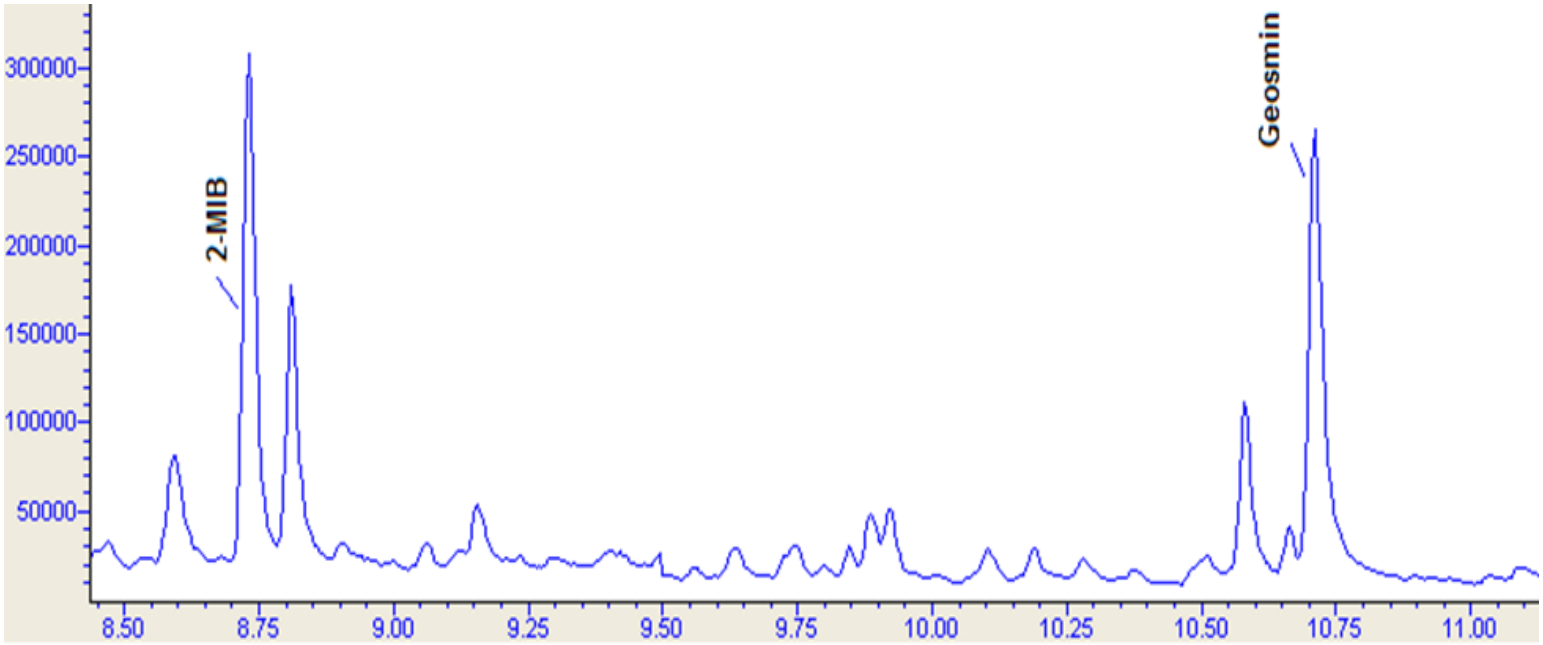
Internal Standard
Curve: Linear
Origin: Not Forced
Weighting Method: None

Mean RF : 8.339139e-002
RF SD : 0.0073433
RF %RSD : 8.805783

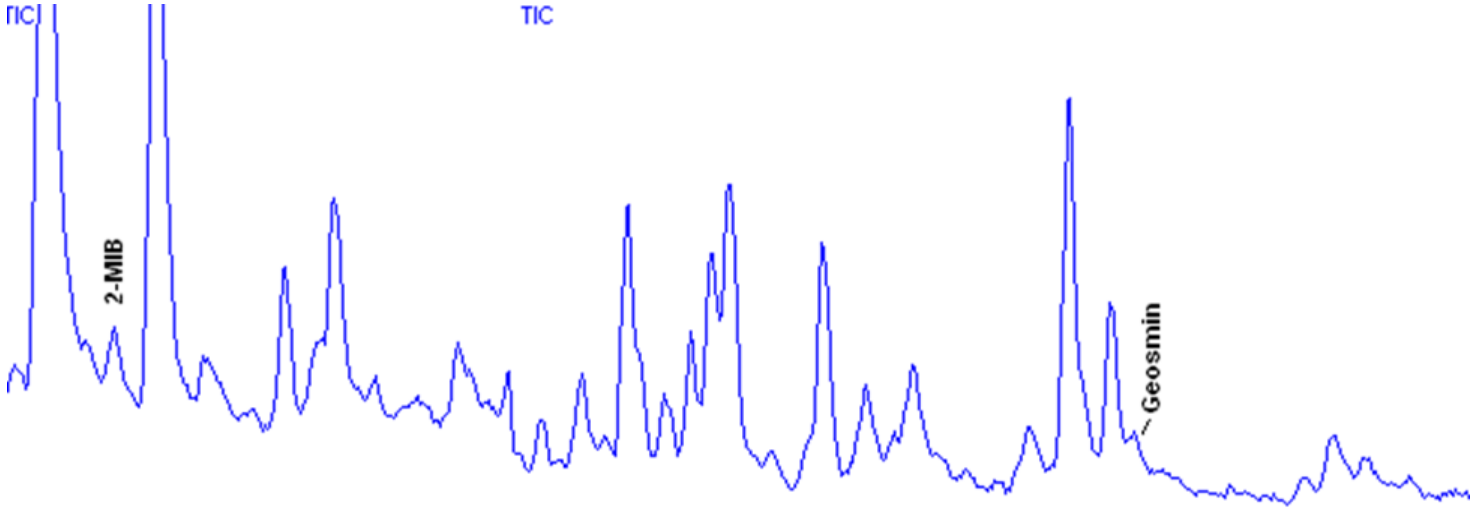
Results Summary

Compound	Curve %RSD	Curve R^2	MDL (1ppt)	Precision, %RSD (1ppt)	Accuracy %Recovery (1ppt)	Precision %RSD (50ppt)	Accuracy %Recovery (50ppt)
Methylisoborneol	3.09	1.000	0.34	12.60	85.70	3.67	88.03
Geosmin	8.81	0.998	0.35	13.34	83.87	1.89	113.28

50ppt Chromatogram



1ppt Chromatogram



SPME Advantages

- No problems with water
- Easily automated

SPME Disadvantages

- Longevity of SPME fiber
- Not as sensitive
- Non-exhaustive sampling technique

Method 6040d

- Standards Method 6040d describes the determination of 2-MIB and Geosmin by Solid Phase Micro Extraction (SPME)

- The method calls for the analysis to be done by Gas Chromatography/Mass Spectrometry (GC/MS) in Selective Ion Monitoring (SIM) Mode

Sampling

- FLEX Robotic Sampling Platform
- 50/30µm DVB/CAR/PDMS

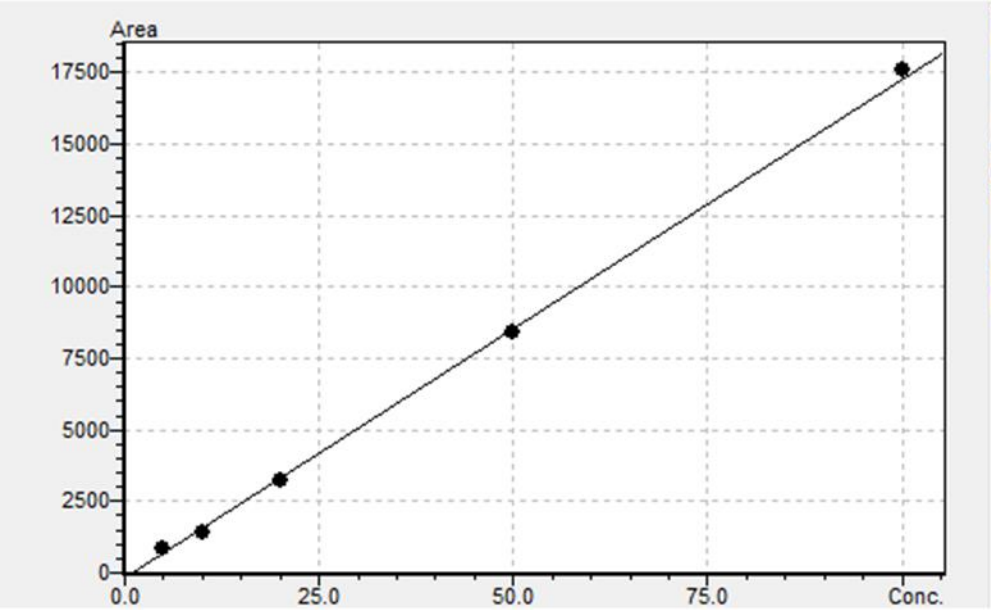
Sampling Parameters

Autosampler	FLEX
General	
Method Type	SPME
GC Ready	Continue
GC Cycle Time	21min
Constant Heat Mode	Yes/Continue
Sample Incubate Agitate	
Incubation Temp.	65ºC
Incubation Time	1.0min
Extraction	
Fiber Guide Depth	45%
Sample Vial Fiber Depth	1cm
Extraction Time	30.1min
Fiber Extraction Agitate	Yes
Agitation Type	Oscillate
Agitation Delay	0.1min
Agitation Duration	30.0min
Wait	
Wait on Input	Yes
Wait Input	GC Ready
Desorbtion	
Injection Port	A
Fiber Guide Speed	40%
Fiber Guide Depth	50%
Fiber Insertion Speed	75%
Fiber Insertion Depth	1cm
Fiber Desorbtion Time	3min
Injection Start Output	Start

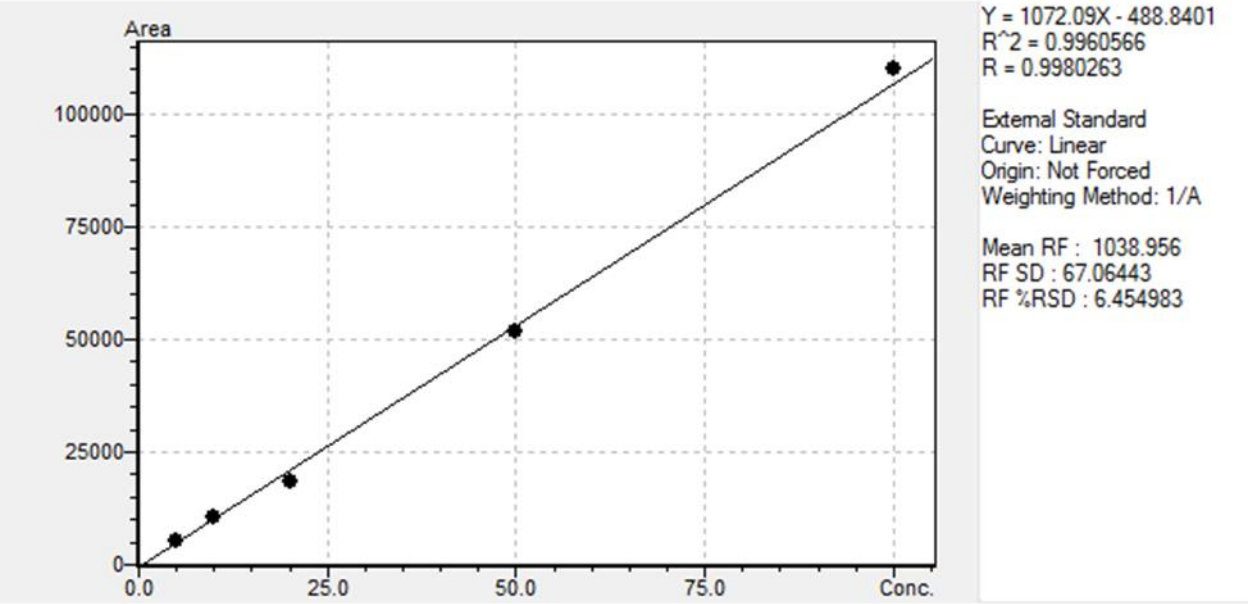
GCMS Parameters

GC/MS	Shimadzu QP 2010 SE
Inlet	Split/Splitless
Inlet Temp.	270ºC
Inlet Head Pressure	40.7kPa
Mode	Splitless
Injection Pulse Pressure	50kPa for 2.0 min
Carrier Gas Split Ratio	2:1
Desorption	3.0min at 270°C
Column	Rxi-5 Sil MS 30.0m X 0.25mm X 0.25µm
Oven Temp. Program	60ºC hold for 2.0 min., ramp 8ºC/min to 200ºC, hold for 0.5min, 20min run time
Column Flow Rate	0.8ml/min
Gas	Helium
Linear Velocity	32.6ml/min
Source Temp.	220ºC
MS Transfer Line Temp.	300ºC
Acquisition Mode	SIM
SIM Ions 3.01 to 12.50min	95, 107, 108
SIM Ions 12.51 to 20.00min	112, 125, 126
Event Time	0.30sec
Solvent Cut Time	3.0min

2-MIB SPME Calibration



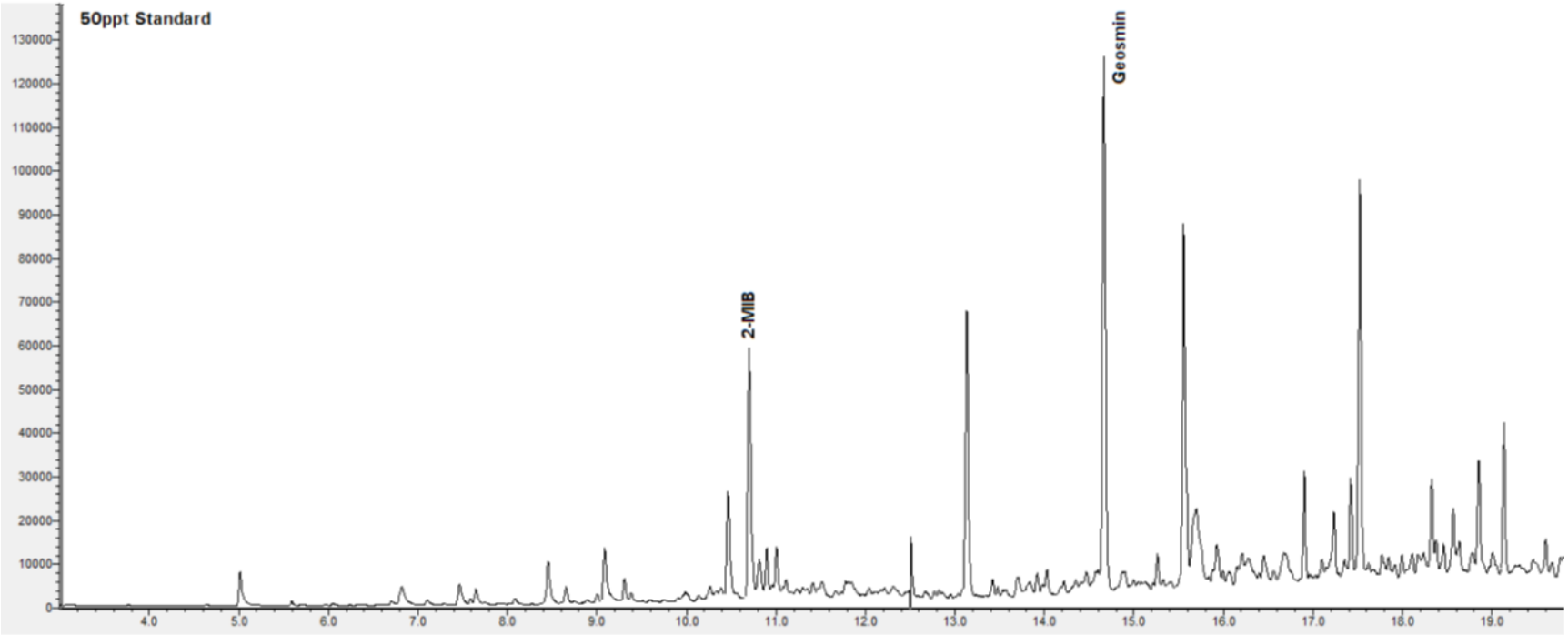
Geosmin SPME Calibration



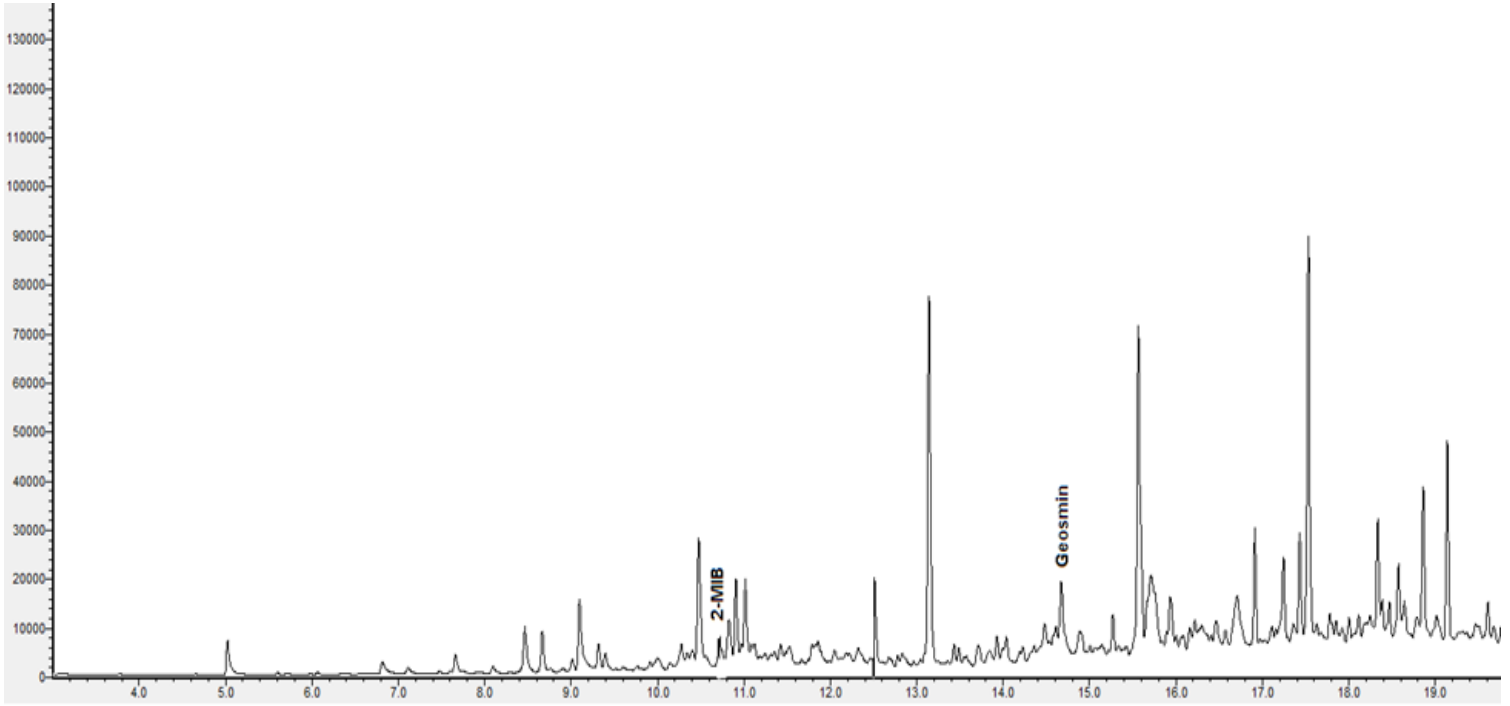
Results Summary

Compound	Curve %RSD	Curve R^2	MDL (5ppt)	Precision (5ppt) %RSD	Accuracy (5ppt) %Recovery	Precision (50ppt) %RSD	Accuracy (50ppt) %Recovery
Methylisoborneol	8.77	0.997	2.00	12.27	103.51	11.85	94.10
Geosmin	6.45	0.996	1.95	11.92	104.06	12.57	91.05

50ppt Chromatogram



5ppt Chromatogram



Calibration Curve and MDL Comparison

Compound	Curve %RSD		Curve R^2		MDL	
	P&T	SPME	P&T	SPME	P&T	SPME
2-MIB	3.09	12.36	1.000	0.999	0.34	2.14
Geosmin	8.81	11.46	0.998	1.000	0.35	1.06

Precision and Accuracy Comparison

Compound	Precision MDL %RSD		Accuracy MDL %Recovery		Precision %RSD		Accuracy %Recovery	
	P&T (1ppt)	SPME (5ppt)	P&T (1ppt)	SPME (5ppt)	P&T (50ppt)	SPME (50ppt)	P&T (50ppt)	SPME (50ppt)
2-MIB	12.60	16.22	85.70	83.94	3.67	10.39	88.03	95.03
Geosmin	13.34	7.07	83.87	95.22	1.89	5.40	113.28	101.85

Conclusions

- The SPME fiber was good for about 150 injections, and when a new fiber was installed, a new calibration was needed
- The purge and trap Tenax trap did not need to be replaced through the course of the study and no longevity study was done

Conclusions

- Purge and trap sampling is an exhaustive sampling technique as compared to SPME, so the linear range was better for purge and trap
- Purge and trap also had better detection limits
- Both techniques had great linearity, precision and accuracy.

Conclusions

- Purge and trap required a 25ml sample and a 6 minute desorb due to the poor purge efficiency of MIB and Geosmin, these parameters couple with a slightly higher purge flow and purge time caused a lot of water problems in the system
- Salt is sometimes used in order to increase purge efficiency, although not used here

Conclusions

- SPME is less hard on the GCMS system than Purge and Trap due to water exposure.
- The preferred technique would be dependent more on lab instrumentation and customer requirements.

References

- Standard Method 6040d Constituent Concentration by Gas Extract, Solid Phase Microextraction, Approved by Standard Methods Committee, 2011
- Pawliszyn, Janusz, *Handbook of Solid Phase Microextraction*, Chemical Industry Press, 2009

Questions

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