



# **Determination of Algae Compounds in Drinking Water**

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# 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 |
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|       | 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    | 2 $\mu$ l       | 100ml      |
| 5ppt          | 50ppb    | 10 $\mu$ l      | 100ml      |
| 10ppt         | 50ppb    | 20 $\mu$ l      | 100ml      |
| 20ppt         | 50ppb    | 40 $\mu$ l      | 100ml      |
| 50ppt         | 50ppb    | 100 $\mu$ l     | 100ml      |
| 100ppt        | 50ppb    | 200 $\mu$ l     | 100ml      |

### Water Standards

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

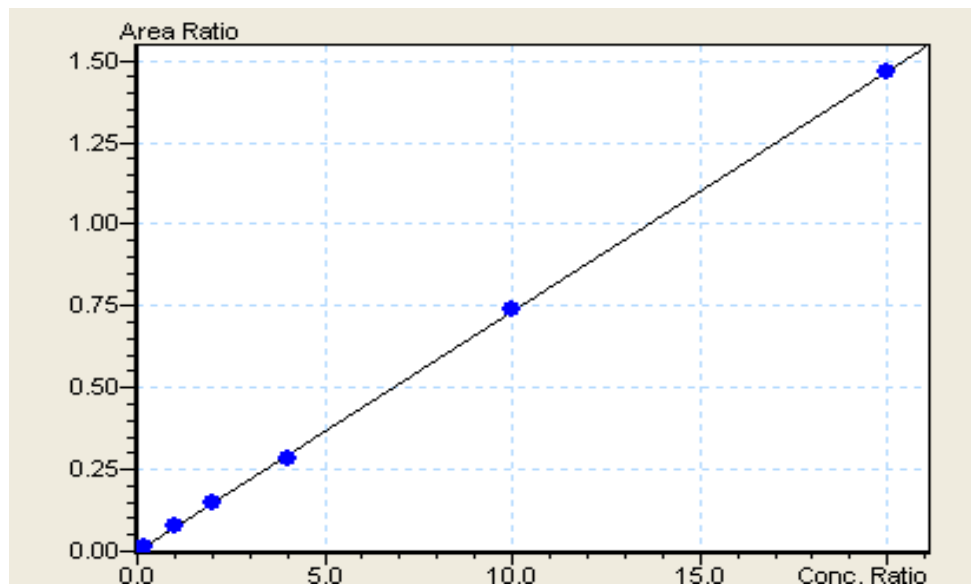
# GCMS Parameters

| 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        | 40°C hold for 2 min, ramp 16°C/min to 160°C, hold for 0.0 min, ramp 20°C/min to 240°C hold for 3 min |
| Ion Source Temp.          | 185°C  |
| Interface Temp.           | 180°C  |
| 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.                          | 150°C               |
| Transfer Line Temp.                       | 150°C               |
| Trap Temp.                                | 35°C                |
| Moisture Reduction Trap (MoRT) Temp.      | 39°C                |
| 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.                              | 230°C               |
| Moisture Reduction Trap (MoRT) Bake Temp. | 210°C               |
| Bake Temp                                 | 230°C               |
| Sparge Vessel Bake Temp.                  | 130°C               |
| 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

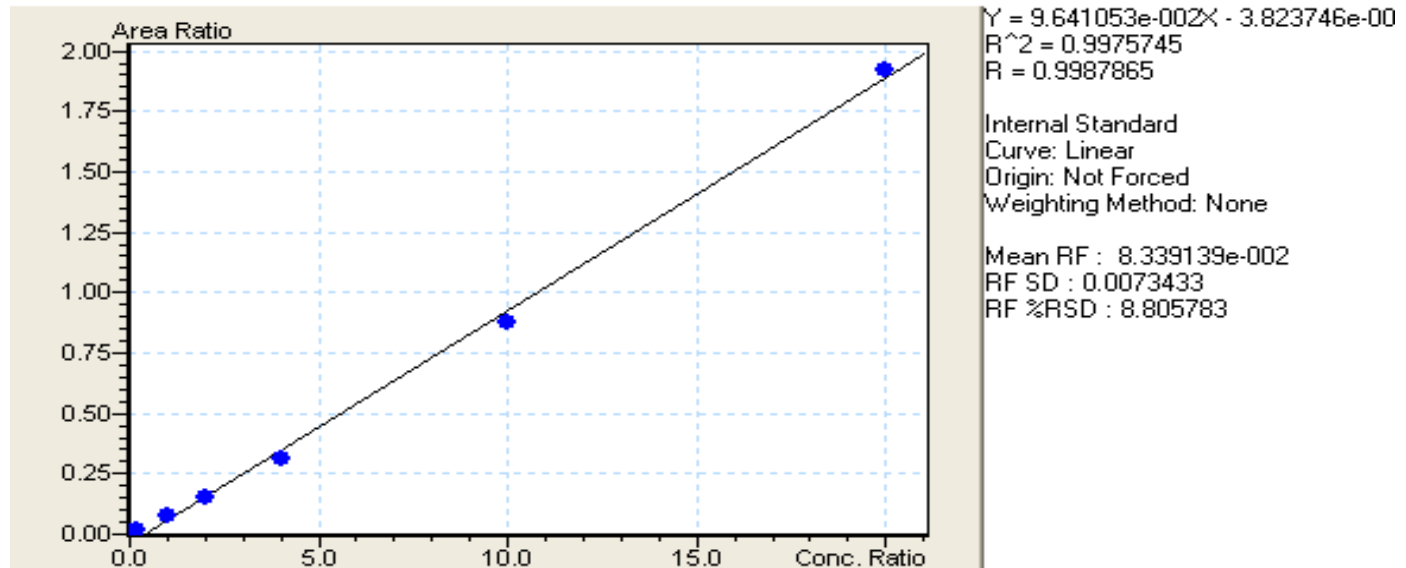


$Y = 7.335935e-002X - 8.879833e-00$   
 $R^2 = 0.999846$   
 $R = 0.999923$

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

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

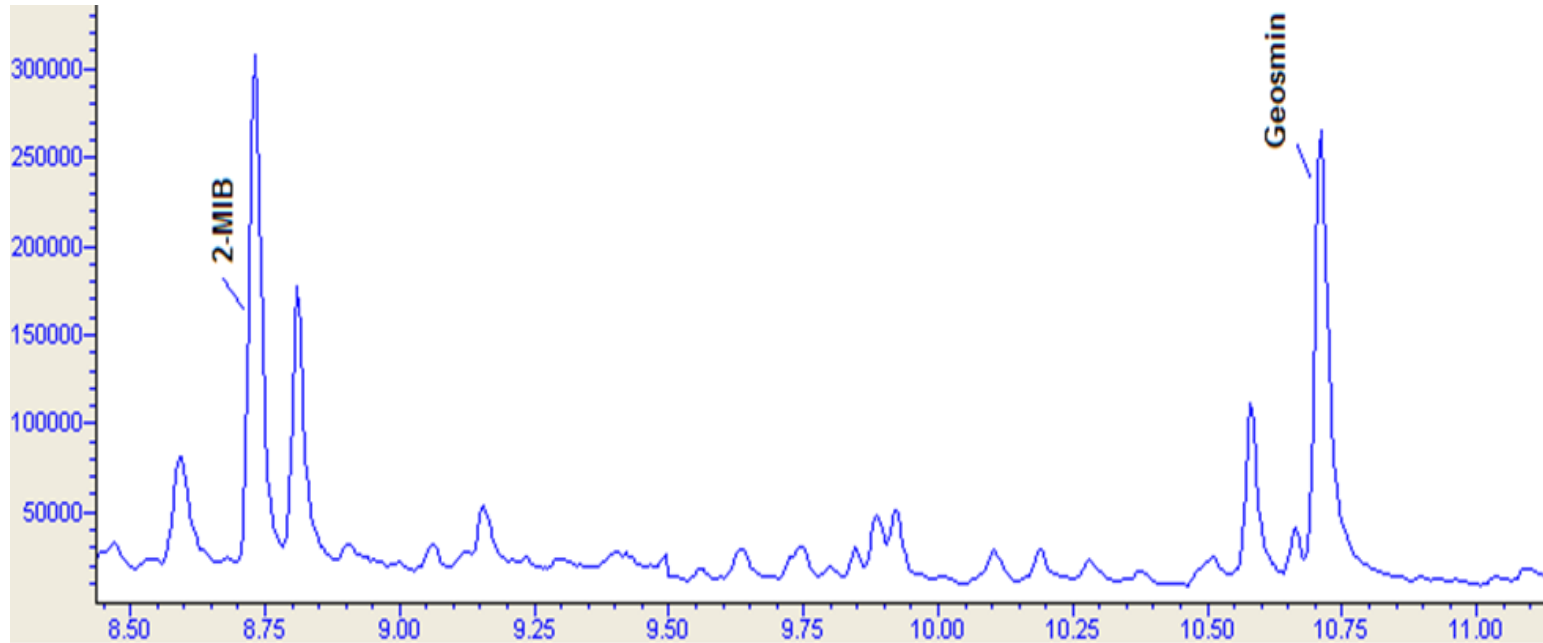
# Geosmin Purge and Trap Calibration



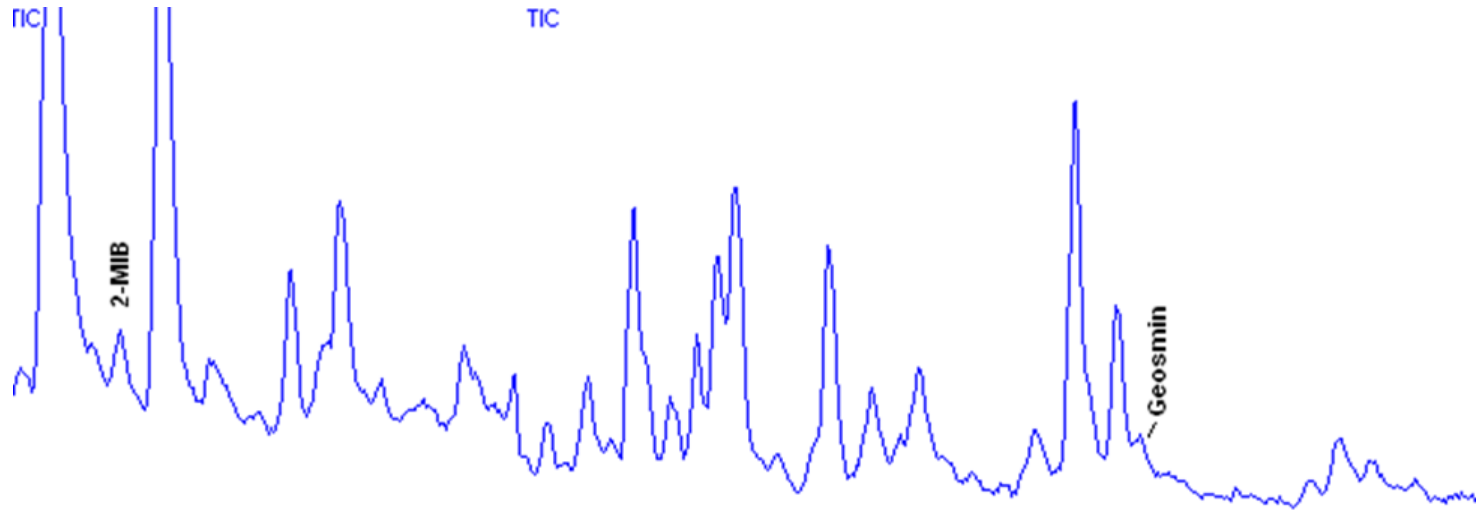
# Results Summary

| Compound         | Curve %RSD | Curve R <sup>2</sup> | 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
- 50/30 $\mu$ m DVB/CAR/PDMS



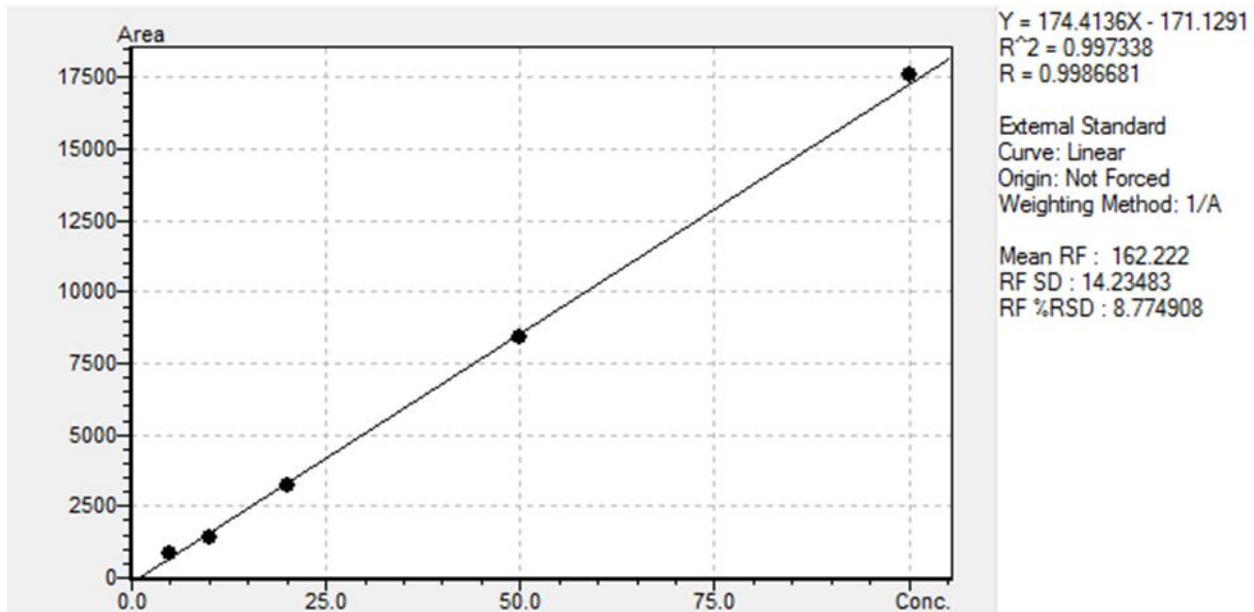
# Sampling Parameters

| Autosampler                    | FLEX         |
|--------------------------------|--------------|
| <b>General</b>                 |              |
| Method Type                    | SPME         |
| GC Ready                       | Continue     |
| GC Cycle Time                  | 21min        |
| Constant Heat Mode             | Yes/Continue |
| <b>Sample Incubate Agitate</b> |              |
| Incubation Temp.               | 65°C         |
| Incubation Time                | 1.0min       |
| <b>Extraction</b>              |              |
| 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      |
| <b>Wait</b>                    |              |
| Wait on Input                  | Yes          |
| Wait Input                     | GC Ready     |
| <b>Desorbtion</b>              |              |
| 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        |

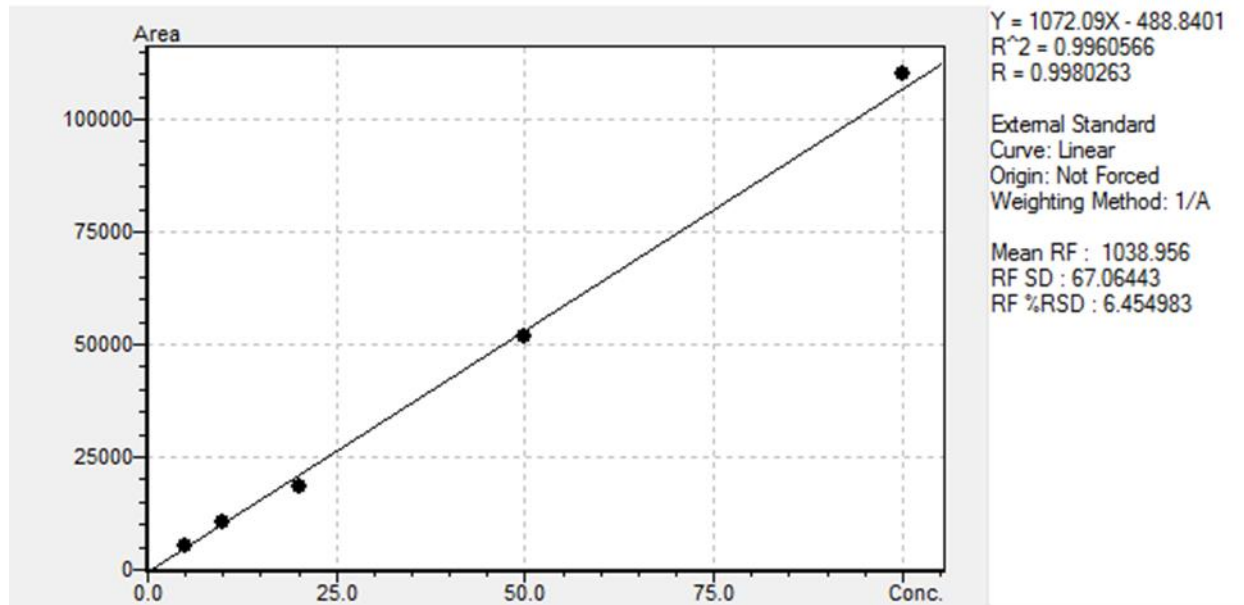
# GCMS Parameters

| GC/MS                      | Shimadzu QP 2010 SE  |
|----------------------------|--|
| Inlet                      | Split/Splitless  |
| Inlet Temp.                | 270°C  |
| 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         | 60°C hold for 2.0 min., ramp 8°C/min to 200°C, hold for 0.5min, 20min run time |
| Column Flow Rate           | 0.8ml/min  |
| Gas                        | Helium   |
| Linear Velocity            | 32.6ml/min   |
| Source Temp.               | 220°C  |
| MS Transfer Line Temp.     | 300°C  |
| 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

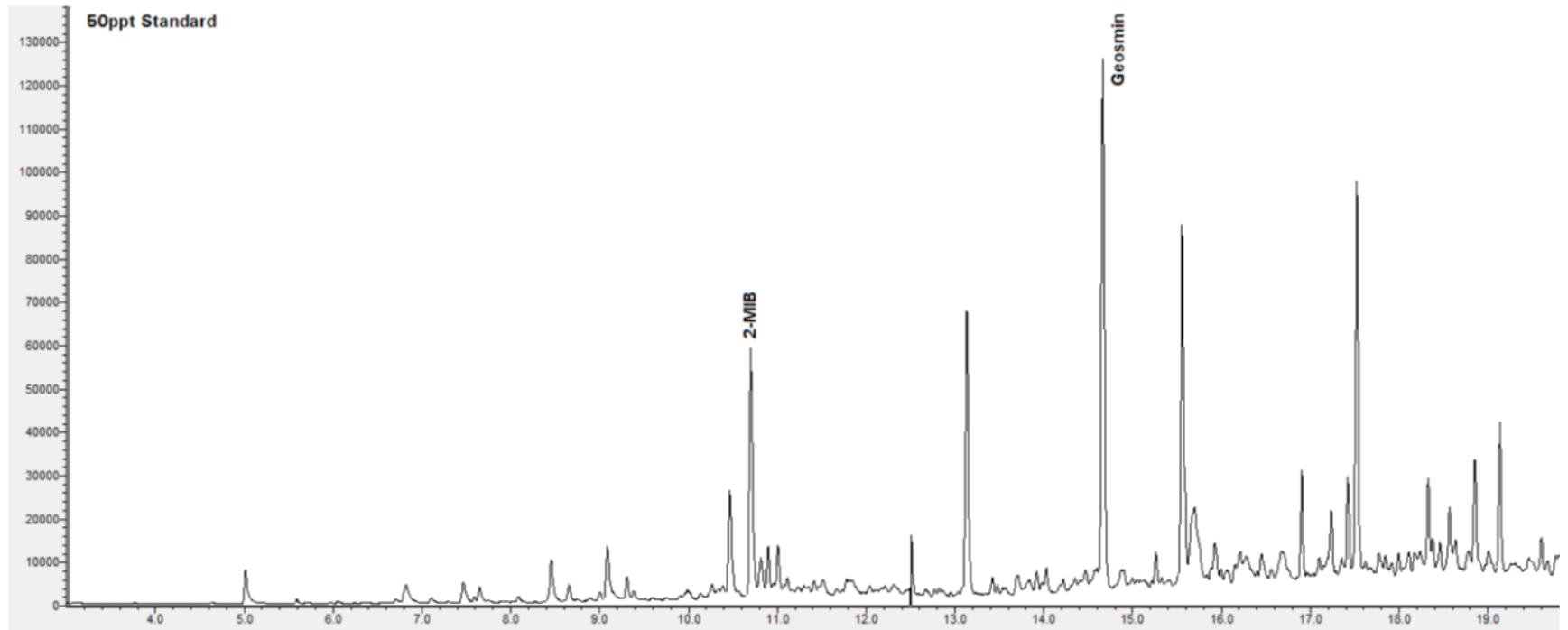




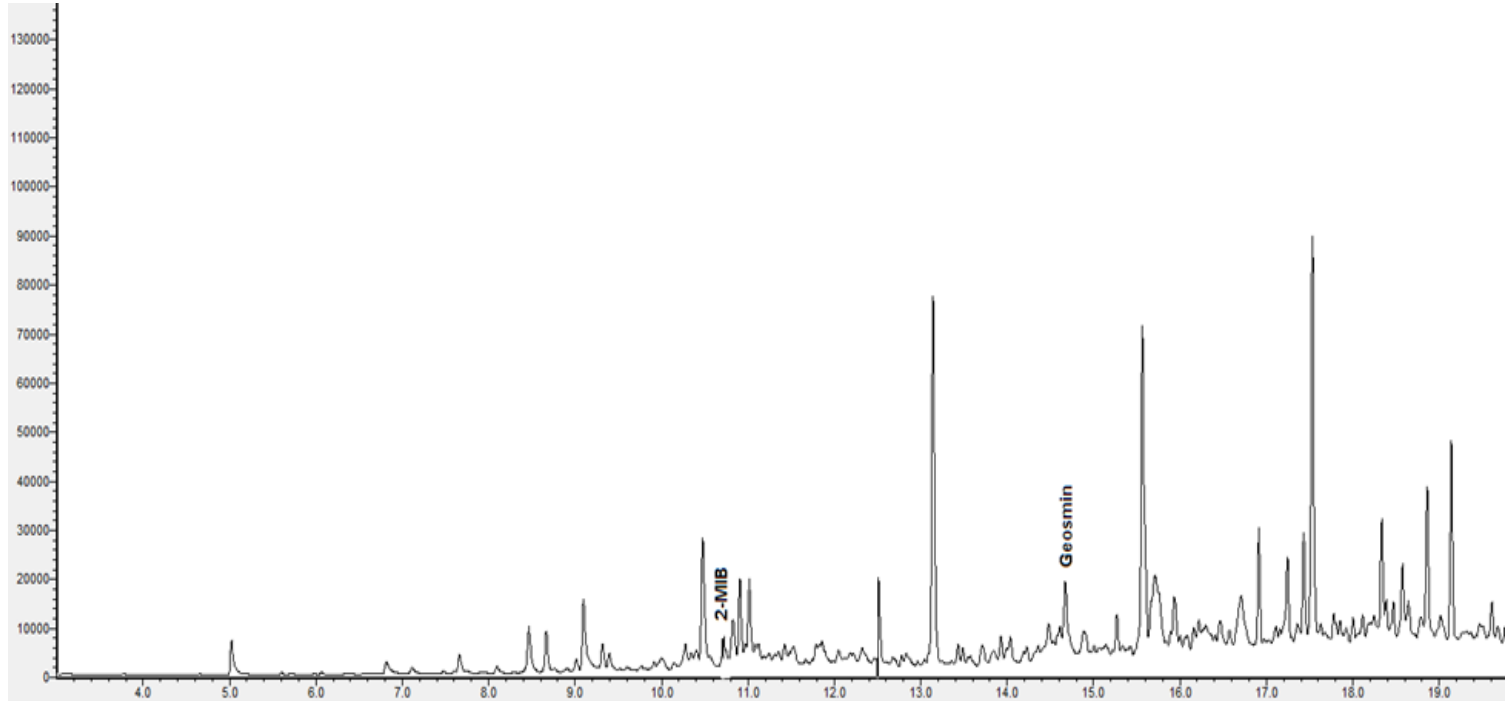
# Results Summary

| Compound         | Curve %RSD | Curve R <sup>2</sup> | 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 <sup>2</sup> |       | 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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