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Implementation of novel SPME Arrow for the trace-level analysis of taste and odor compounds in drinking water

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1. Introduction

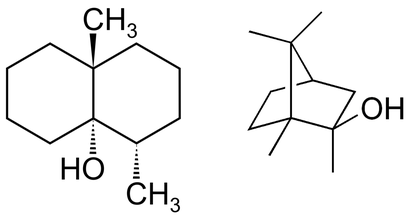

Figure 1. Molecular structures of geosmin (left) and 2-methylisoborneol (right)

Decaying algae blooms that occur in drinking water sources sometimes release “earthy” and “musty” odor compounds (2-methylisoborneol, or MIB, and geosmin – shown in Figure 1). This aroma is a major source of public complaints about unpleasant tasting drinking water. Although odor is only regulated by a secondary maximum contaminant level (a non-mandatory water quality standard), it is critical for utilities and environmental laboratories to accurately identify and quantify specific compounds potentially involved in Taste and Odor (T&O) events. Therefore, a highly sensitive, robust, accurate, and high-throughput technique is required for the analysis of MIB and geosmin at concentrations down to their odor threshold levels (low ng/L).

Standard Method 6040 details several sample introduction methods that can be used for trace-level analysis of MIB and geosmin in drinking water samples. Included are closed-loop stripping analysis, purge and trap, and solid phase microextraction (SPME). SPME is the most rapid method that is capable of achieving comparable sensitivity, when coupled with GCMS. The use of SPME Arrow, however, which is more sensitive and robust than conventional SPME fibers, has not been evaluated for use with this method.

In this work, we implemented Standard Method 6040D with SPME Arrow, rather than SPME fiber, for the analysis of MIB and geosmin at levels that would occur in T&O events. This workflow will help utilities and environmental labs in managing T&O events quickly and accurately.

Figure 2. Shimadzu GCMS QP 2020NX with AOC-6000 autosampler, featuring the SPME Arrow

2. Experimental Methods

Water samples were prepared as follows: 3 g of NaCl was weighed into 20 mL glass headspace vials containing 10 mL deionized water, prior to spiking in MIB and geosmin standards, plus internal standard isobutyl-methoxypyrazine (IBMP – at 10 ng/L) and surrogate standard isopropyl-methoxypyrazine (IPMP – at 10 ng/L).

Calibration curves were constructed over a range from 0.5 ng/L to 100 ng/L for MIB and geosmin, with extraction performed by SPME Arrow (PDMS/DVB/Carboxen).

Table 1 summarizes the instrument conditions used on a Shimadzu GCMS-QP2020 NX equipped with an AOC-6000 autosampler (shown in Figure 2) throughout this work.

Table 1. SPME Arrow, GC, and MS conditions

GCMS-QP2020 NX with AOC-6000	
SPME Arrow	1.1mm OD PDMS/DVB/Carboxen
Equilibration	65 °C, 10 min
Extraction	65 °C, 30 min
Desorption	250 °C, 10 min
Gas Chromatography	
Injection Port	250 °C splitless (1 min); split 20:1
Column	SH-Rxi-624 Sil MS column (30 m × 0.25 mm × 1.40 µm) He carrier gas; Constant Linear Velocity, 36.3 cm/s
Oven Temperature	50 °C > 195 °C (40 °C/sec) > 250 °C (15 °C/sec) - 2 min
Mass Spectrometry	
Interface Temperature	250 °C
Ion Source Temperature	200 °C
Detector Voltage	+0.5 kV (relative to tune result)
Event Time	0.3 sec
Ions for Quantification	MIB – 95, 93, 107, 108, 135 Geosmin – 112, 126 IPMP – 137, 152, 124 IBMP – 124, 151, 94

3. Results

3.1 Calibration curves for MIB and geosmin with SPME Arrow

Calibration curve levels were run in triplicate, with blanks run in between every sample. Internal standard calibration curves were built for both MIB or geosmin (internal standard: IBMP). Excellent linearity (R^2 = 0.99) were observed for both analytes, as shown in Figures 3 and 4.

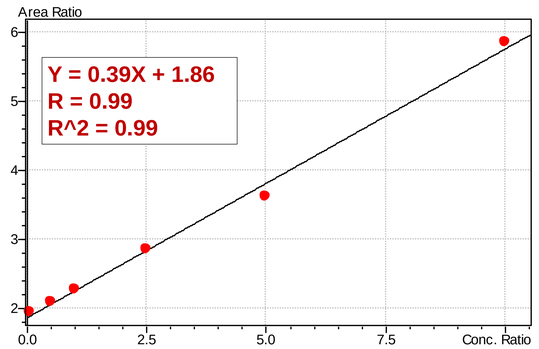

Figure 3. Calibration curve for MIB with IBMP internal standard by SPME Arrow

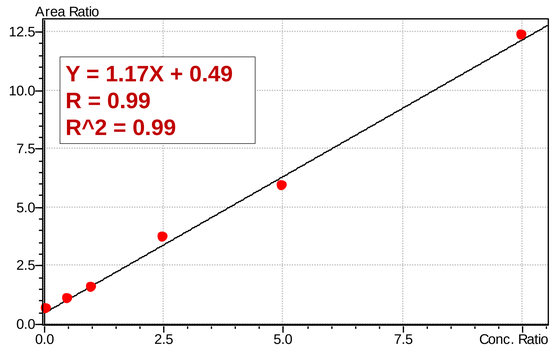

Figure 4. Calibration curve for geosmin with IBMP internal standard by SPME Arrow

3.2 Reproducibility

The 10 ng/L calibration standard was measured 8 consecutive times to asses the reproducibility of the SPME Arrow method. Precision was calculated from the internal standard: standard ratios, which was 15% RSD for MIB and 12% RSD for geosmin. At the lowest concentration level (0.5 ng/L) precision was 0.2% RSD for MIB and 5% RSD for geosmin. The corresponding chromatograms and results are shown in Figures 5, 6 and 7.

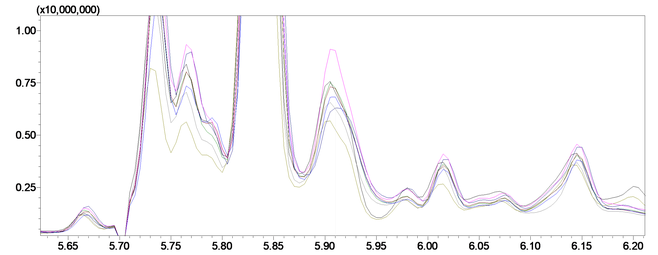

Figure 5. Overlaid chromatograms of reproducibility experiment (10 ng/L MIB)

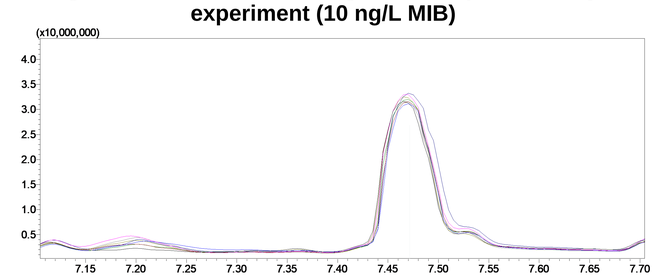

Figure 6. Overlaid chromatograms of reproducibility experiment (10 ng/L Geosmin)

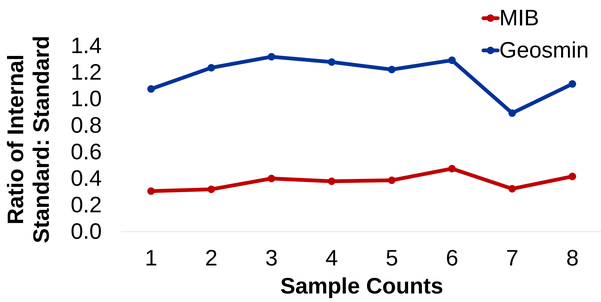

Figure 7. Reproducibility of 10 ng/L MIB and geosmin

3.3 Limits of detection

Limits of detection were calculated from the 0.5 ng/L calibration level; based on 3 x signal-to-noise (S:N) ratio. For both MIB and geosmin, the limit of detection for this method was 0.05 ng/L, roughly 2 orders of magnitude below their odor thresholds (approximately 0.02 µg/L MIB and 0.005 µg/L geosmin) in T&O events.

4. Conclusion

The method reported in this work is fast (30 min per sample by overlapping autosampler extraction with GCMS analysis) appropriate for trace-level detection of MIB and geosmin in drinking water for T&O events. Limits of detection are well below the odor thresholds for these compounds, and the reproducibility of the SPME Arrow technique is appropriate for this analysis.