

Comparison of Novel SPME Arrow with Traditional SPME Fiber for the Trace-level Analysis of Taste and Odor Compounds in Drinking Water

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1. Introduction

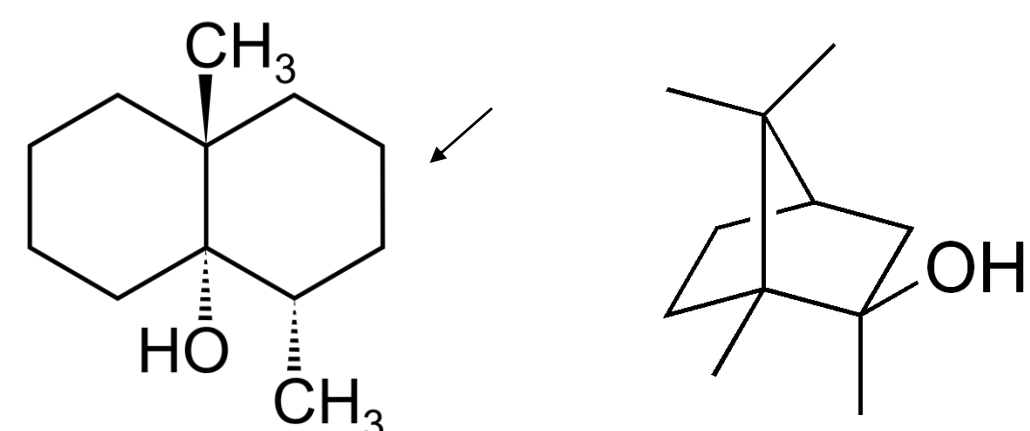


Figure 1. Molecular structures of geosmin (left) and 2-methylisoborneol (right)

Drinking water sources are sometimes contaminated by dying algae blooms which release “earthy” and “musty” odor compounds (2-methylisoborneol, or MIB, and geosmin). This odor is a major source of public complaints about unpleasant tasting drinking water. Although odor is only regulated by a secondary maximum contaminant level, 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).

Solid Phase Microextraction (SPME) coupled with GCMS detection is a common analysis technique for these compounds; however, use of SPME Arrow in this application, which is more sensitive and robust than conventional SPME, has been limited. In this study, Standard Method 6040D was implemented for the analysis of MIB and geosmin employing SPME, and multi-point calibration curve, methodological detection limits (MDLs), and reproducibility experiments were conducted. The SPME Arrow device was run with the same method to compare limits of detection and throughput between the two extraction techniques. 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

Table 1 summarizes the instrument conditions used on the Shimadzu GCMS-QP2020 NX equipped with an AOC-6000 autosampler throughout this work. 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 IBMP (10 ng/L) and surrogate IPMP (10 ng/L). Calibration curves were constructed over a range from 0.5 ng/L to 100 ng/L for MIB and geosmin, comparing SPME results to the new SPME Arrow (both devices were PDMS/DVB/Carboxen phases).

GCMS-QP2020 NX with AOC-6000	
SPME/SPME Arrow	80um /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 (Bold-quantification Others-reference)	MIB – 95, 93 , 107, 108, 135 Geosmin – 112 , 126 IPMP – 137, 152, 124 IBMP – 124, 151, 94

Table 1. SPME Arrow, GC, and MS conditions

3. Results

All calibration curves showed good linearity with R²s of at least 0.99, though residual sum of squares (RSS) improved significantly with the use of SPME Arrow for both compounds. Limits of detection were calculated from the 0.5 ng/L calibration level; based on 3 x signal-to-noise (S:N) ratio. For MIB the limit of detection was 7.5 ng/L and for geosmin it was 0.08 ng/L using the traditional SPME fiber (Figure 1). Limits of detection for both MIB (LOD 0.4 ng/L) and geosmin (LOD 0.03 ng/L) with SPME Arrow (Figure 2) were improved significantly, down to 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. Figure 3 compares two representative chromatograms to demonstrate the improvement of the Arrow technique

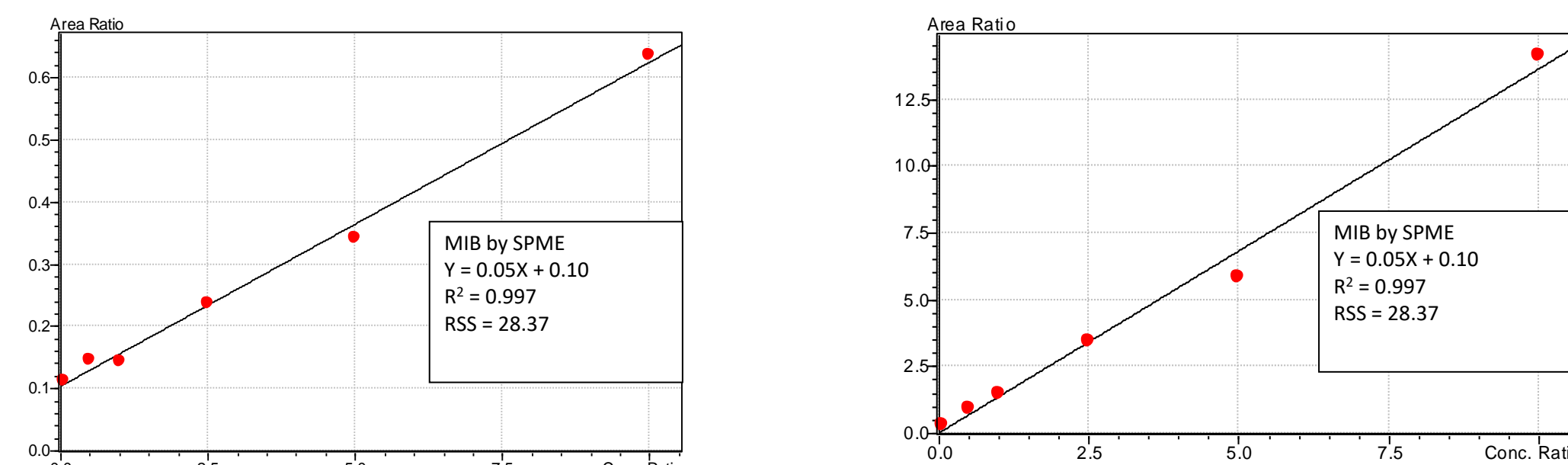


Figure 1. MIB (top) and geosmin (bottom) calibration curves with IBMP internal standard; by SPME.

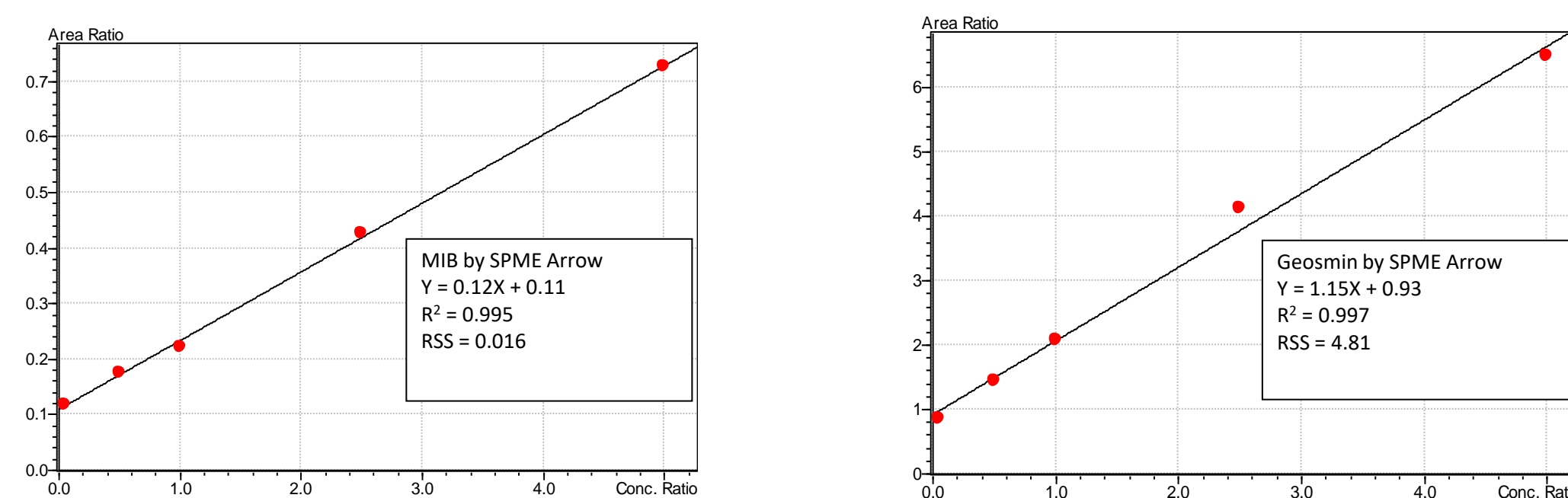


Figure 2. MIB (top) and geosmin (bottom) calibration curves with IBMP internal standard; by SPME Arrow.

The 10 ng/L calibration standard was measured 6 consecutive times to assess the reproducibility of the SPME Arrow method (Figures 4, 5, & 6). Precision was calculated from the internal standard: standard ratios, which was 3% RSD for MIB and 7% RSD for geosmin. At the lowest concentration level (0.5 ng/L) precision was 27% RSD for MIB and 22% RSD for geosmin.

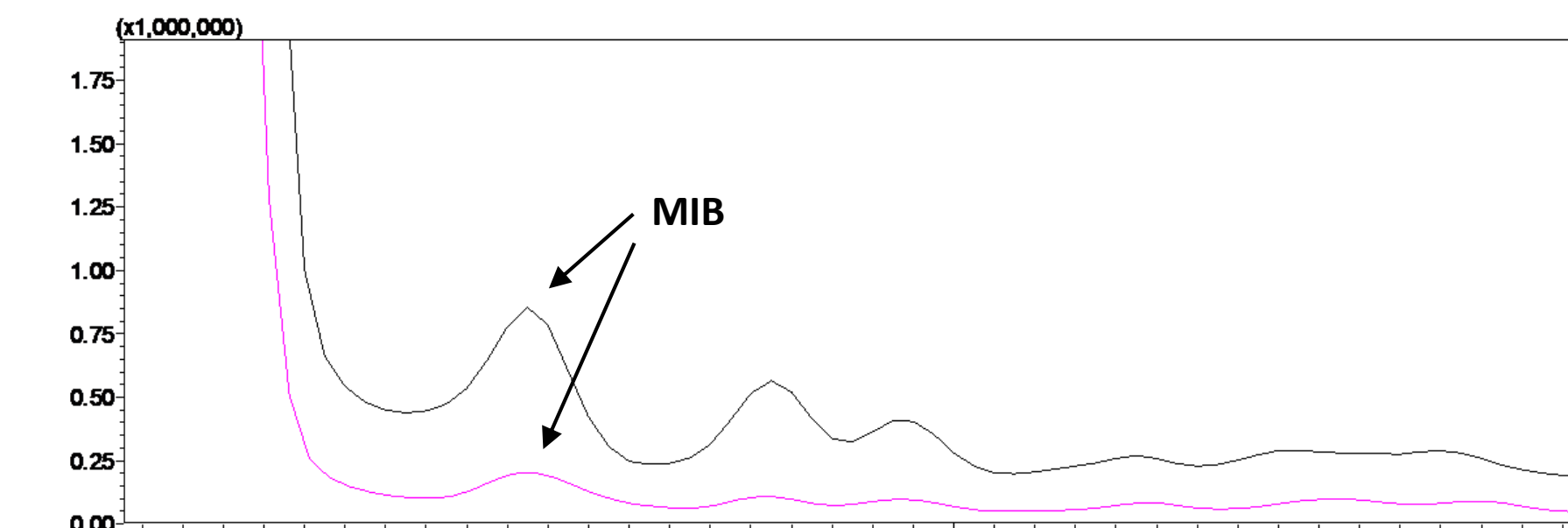


Figure 3. Representative chromatogram for 10 ng/L MIB standards run with SPME (pink trace) overlaid with SPME Arrow (black trace).

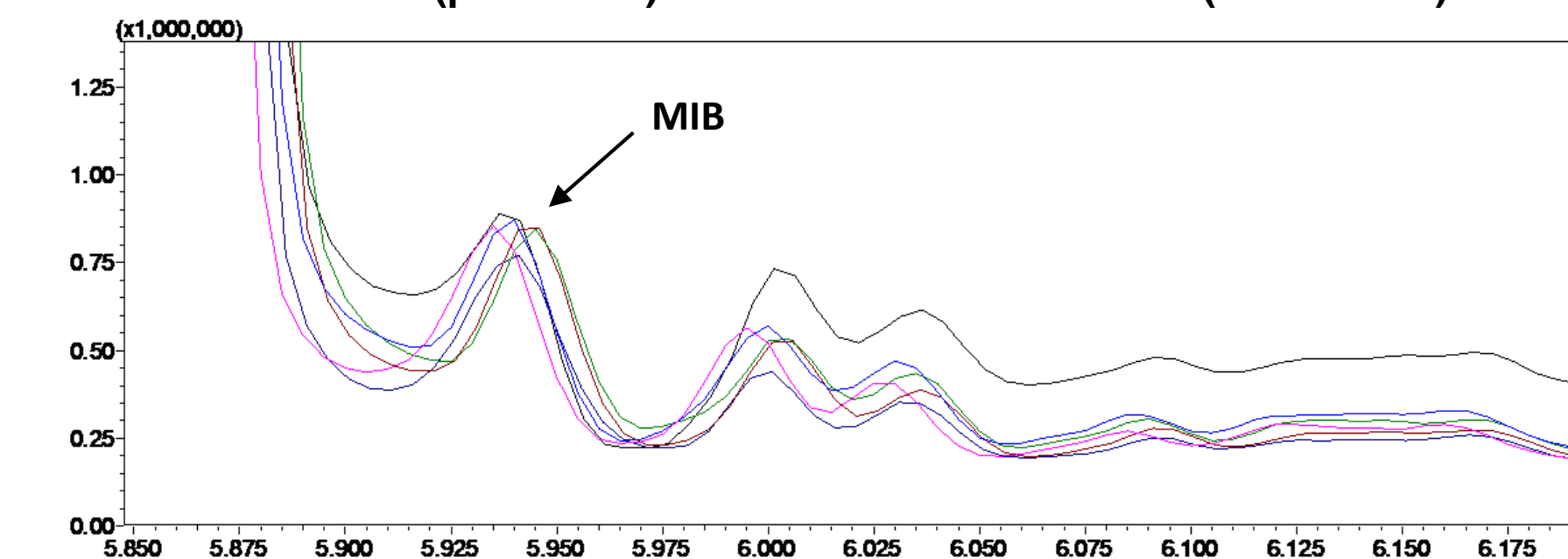


Figure 4. Overlaid chromatograms of reproducibility experiment at 10 ng/L for MIB (93 m/z) with SPME Arrow.

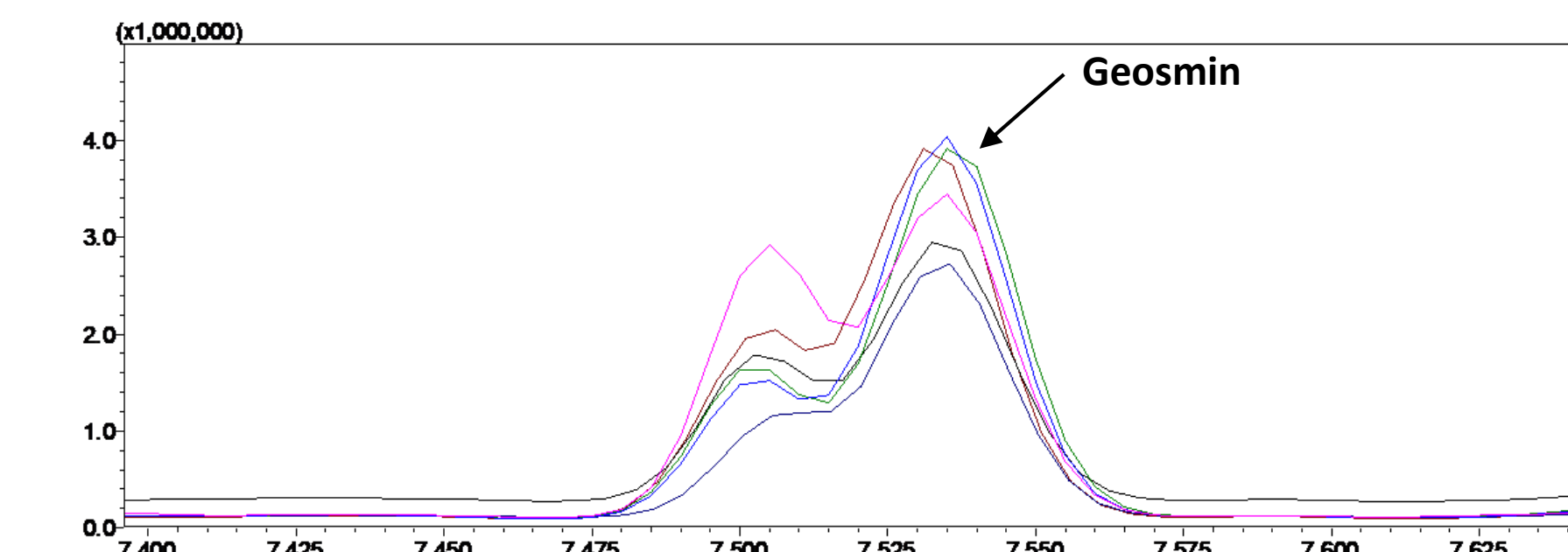


Figure 5. Overlaid chromatograms of reproducibility experiment at 10 ng/L for geosmin (112 m/z) with SPME Arrow.

4. Conclusion

The method reported in this work is fast (30 min per sample by overlapping autosampler extraction with GCMS analysis) and 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 improvement shown by using the SPME Arrow technique provides a significant advantage for this analysis.