Analysis of Trace Odorants in Drinking Water by Headspace-Solid Phase Microextraction-Gas Chromatography-Time of Flight Mass Spectrometry

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1. Introduction

Odor-causing compounds can find their way into drinking water from a number of sources. Odors with a "musty" character are often attributed to chemical byproducts from several classes of microbes. One of the most common compounds causing a "musty" or "earthy" smell is geosmin which is released when microbes such as blue-green algae and actinobacteria die. Other well known odor causing compounds that originate from natural sources include 2-methylisoborneol and methoxypyrazines. Many of these compounds are of interest since they have very low odor thresholds. Many people are able to detect them at concentrations as low as 10 parts per trillion (ppt). Since these odorants have sensory thresholds in the ppt range, it is important to have an analytical method capable of detecting them at trace levels. This application note highlights a modified method 6040D showing an automated Headspace-Solid Phase Microextraction (HS-SPME) sampling approach. This sampling approach coupled to GC-TOFMS provides sensitivity required for detection of targeted odorants. GC-TOFMS also allows detection and identification of non-targeted odorant compounds.

Odorants can also originate from packaging materials such as plastic bottles. These compounds are often oxidation products such as aldehydes. Odorants which originate from packaging materials will not be discussed in this application note, but may be part of future studies, since bottled water is an $8 billion industry in the US alone.

2. Experimental Conditions

Samples

Water odorant standards containing 2-isopropyl-3-methoxypyrazine (IPMP), 2-isobutyl-3-methoxypyrazine (IBMP), 2-methylisoborneol (MIB), and geosmin at concentrations ranging from 2.5 to 100 ppt were prepared using water odorant standards purchased from Supelco (Bellefonte, PA). An internal standard 2,4,6-trichloroanisole (2,4,6-TCA) was used in each water standard at a concentration of 10 ppt. A 10 mL aliquot of each water standard was placed in respective 20 mL headspace autosampler vials which contained 2.5 grams of NaCl.

The addition of NaCl is a "salting out" procedure which was used to lower the partition coefficient (K) of the analytes. This forces the analytes of interest out of the liquid phase and into the gas phase where they are collected by the SPME fiber. This improves the overall sensitivity of the sampling method. See the illustration in Figure 1 showing the effects of salt addition. These standards were analyzed by HS-SPME-GC-TOFMS using a LECO TruTOF® HT Benchtop GC-TOFMS system. The conditions used are detailed below.

Gerstel MPS2 Autosampler w/SPME Option
SPME Fiber: 2 cm, DVB/Carboxen/PDMS
Incubation Temp: 65°C
Incubation Time: 30 minutes, with fiber exposure
Agitator Speed: 100 rpm (10 second duration, every 60 seconds)
Desorb Time: 3 minutes @ 260°C

GC: Agilent 6890 Gas Chromatograph
Injection: SPME, Splitless (60 second Purge Time) @ 260°C
Carrier Gas: He @ 1.5 mL/minute
Column: Rxi-5ms; 20 m x 0.18 mm x 0.18 µm
GC Oven: 60°C (2 minute hold), programmed @ 30°C/minute to 250°C (10 minute hold)
MS Transfer Line: 280°C

MS: LECO TruTOF
Ionization: 70eV EI
Mass Range: 45-300 m/z
Acquisition Rate: 20 spectra/second
Source Temp: 300°C

3. Results

HS-SPME-GC-TOFMS exhibited the ability to detect odorant compounds in water at low ppt levels. A major benefit of TOFMS for this application is the ability to reach these levels of detection while acquiring across a mass range of 45 to 300 m/z without sacrificing speed or sensitivity. This allows the analyst to confirm analyte identity using the deconvoluted full range mass spectrum,
and to detect non-targeted compounds that may also be contributing to the aroma profile of the water sample. Quadrupole MS systems operating in selected ion monitoring (SIM) mode could not accomplish either of these functions. Figure 2 shows the Caliper (raw), Peak True (deconvoluted), and NIST library spectral match for the compound 2-isopropyl-3-methoxypyrazine as generated by the LECO TruTOF GC-TOFMS system with ChromaTOF® software. These spectra were generated from the analysis of water odorant standards at 2.5 ppt. This demonstrates the ability of TOFMS and the advanced peak find algorithms of the ChromaTOF software to detect trace level components within the chromatographic background. The deconvoluted mass spectrum received a mass spectral similarity of 735 out of a possible 1000.

Figure 2. Caliper (raw), Peak True (deconvoluted), and NIST library spectra for 2-isopropyl-3-methoxypyrazine.

Figure 3 shows the extracted ion chromatogram for IPMP, IBMP, MIB, 2,4,6-TCA, and geosmin.

Figure 3. Extracted ion chromatogram (EIC) showing the quantitation masses for IPMP (A), IBMP (B), MIB (C), 2,4,6-TCA (D) and geosmin (E).

This HS-SPME-GC-TOFMS method was able to demonstrate linearity across a calibration range of 2.5 to 100 ppt. The low ends of these calibrations are below the reported odor threshold of the human nose for these compounds. The calibration curves for all four compounds are shown in Figure 4.

The GC-TOFMS tabular data for the calibration curves are shown in Table I. Notice how the results shown in the "Calculated Concentration" columns correlate well with the "Certified Concentration" columns. These show the accuracy of the calculated concentration for each individual standard based on the slope of the curve. The "% Difference Concentration" columns show that the error between the certified and calculated concentration is <10% for most standards.

Table I. Tabular data for water odorant calibrations.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>2-isopropyl-3-methoxypyrazine @ 2.5 ppt</td>
<td>205287</td>
<td>0.33</td>
<td>0.34</td>
<td>0.2%</td>
<td>1000</td>
<td></td>
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<tr>
<td>2-isopropyl-3-methoxypyrazine @ 10 ppt</td>
<td>670125</td>
<td>3.33</td>
<td>3.34</td>
<td>0.3%</td>
<td>997</td>
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<tr>
<td>3-chloro-3-methoxypyrazine @ 2.5 ppt</td>
<td>610341</td>
<td>1.5</td>
<td>1.5</td>
<td>0.0%</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>3-chloro-3-methoxypyrazine @ 10 ppt</td>
<td>1370783</td>
<td>10</td>
<td>10</td>
<td>0.0%</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>1-methyl-4-isoxazoline @ 2.5 ppt</td>
<td>1257687</td>
<td>10</td>
<td>10</td>
<td>0.0%</td>
<td>1000</td>
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<tr>
<td>1-methyl-4-isoxazoline @ 10 ppt</td>
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<td>10</td>
<td>0.0%</td>
<td>1000</td>
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</tr>
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<td>3,5-dimethyl-3-isoxazoline @ 2.5 ppt</td>
<td>610341</td>
<td>1.5</td>
<td>1.5</td>
<td>0.0%</td>
<td>1000</td>
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<td>3,5-dimethyl-3-isoxazoline @ 10 ppt</td>
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<td>10</td>
<td>10</td>
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<tr>
<td>Geosmin @ 2.5 ppt</td>
<td>1220522</td>
<td>10</td>
<td>10</td>
<td>0.0%</td>
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<tr>
<td>Geosmin @ 10 ppt</td>
<td>1371135</td>
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<td>10</td>
<td>0.0%</td>
<td>1000</td>
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<td>10</td>
<td>0.0%</td>
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<tr>
<td>Geosmin @ 100 ppt</td>
<td>1371135</td>
<td>10</td>
<td>10</td>
<td>0.0%</td>
<td>1000</td>
<td></td>
</tr>
</tbody>
</table>
4. Conclusions
The experiments described in this application note demonstrate the use of the LECO TruTOF (GC-TOFMS) for the analysis of odorant components in drinking water per a variation of American Water Works Association (AWWA) method 6040D. This procedure varied from 6040D in two aspects. First, it required less water than the original method. Method 6040D requires 45 mL while this procedure requires 10 mL. The ability to use 10 mL of water instead of 45 mL allows for ease of automation through the use of the Gerstel MPS2 autosampler which utilized 20 mL headspace vials for these analyses. Second, the SPME extracts were analyzed using a GC-TOFMS system capable of trace level detection of the odorant compounds while collecting across a mass range of 45 to 300 m/z. This allows a more powerful confirmation of targeted analyte identity than SIM and provides the ability to detect and identify non-targeted compounds that may also be contributing to the aroma profile of the water sample.

5. References
1Method 6040D, Developed by the American Water Works Association (AWWA)