

### Application Note

#### Abstract

Taste and odor are widely associated with drinking water quality. Musty odors, caused by compounds such as geosmin and 2-methylisoborneol (MIB), may lead consumers to believe their water is unsafe. These compounds are byproducts of the growth of blue-green algae and other microbes. Since consumers rely on taste and odor as primary indicators for water safety, water suppliers take steps to limit these compounds, even though they are not considered a public health hazard. The low odor thresholds of many of these compounds, some below 10 parts-per-trillion, necessitate extremely sensitive sample preparation and analytical techniques for their determination.

This application note will demonstrate a new purge and trap method for analyzing drinking water samples for these mold odor compounds at the part-per-trillion (ppt) level. A Teledyne Tekmar Atomx multimatrix autosampler will be used in conjunction with a GC/MS system employing selective ion monitoring (SIM) to achieve the low levels required by this analysis.



#### Introduction

Taste has become an increasingly important factor of water quality. Musty odors, caused by compounds like geosmin and 2-methylisoborneol (MIB), lead consumers to believe their water may be unsafe. These compounds are byproducts of the growth of blue-green algae and other microbes. Since consumers rely on taste and odor as primary indicators for water safety, water suppliers take steps to limit these compounds, even though they are not considered a public health hazard. With odor thresholds for some mold contaminants below 10 parts per trillion (ppt), it is necessary to be able to detect these compounds at extremely low levels.

This application note utilizes an Atomx multimatrix autosampler integrated with a purge and trap concentrator. This set-up allows for complete automation of sample preparation for the analysis of liquid, soil and methanol extracted samples for purge and trap. For this study, samples were loaded into the 80-position tray and prepared for extraction. 25 mL samples containing 10% w/v sodium chloride are transferred to the sparging tube and purge onto a sorbent trap using helium. Due to their poor purge efficiency, these mold odor compounds often require heat and/or matrix modification. The trap is then heated and analytes are desorbed to the GC/MS for analysis. Utilizing an Agilent 7890A/5975 GC/MS, a linear calibration was performed and percent relative standard deviation (%RSD), method detection limits (MDLs), and percent carryover were determined. An overlay chromatogram showing a blank and the 50 ppt mold odor standard can be found in Figure 1.

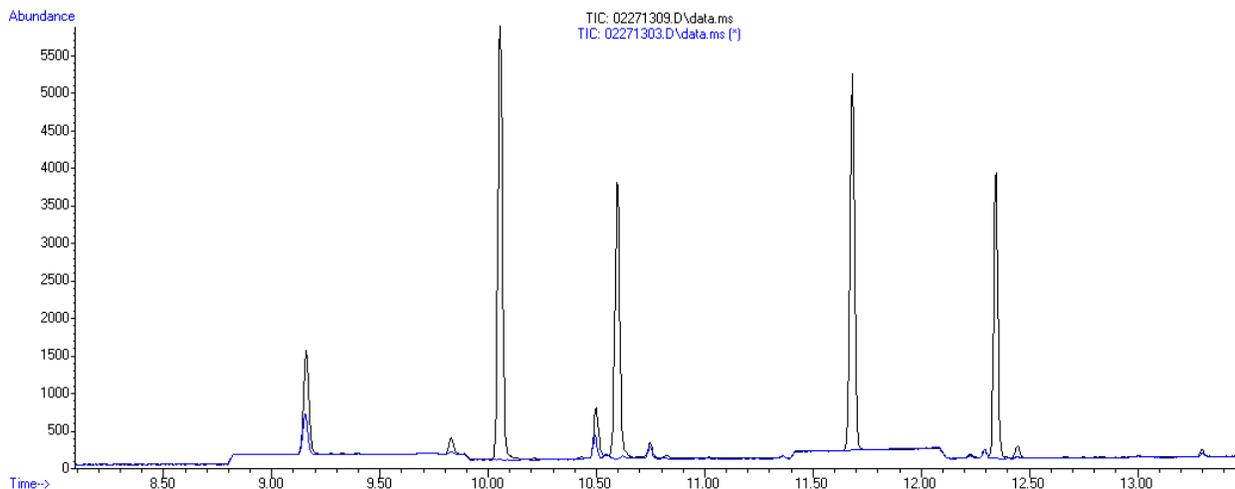


Figure 1: Overlay SIM Chromatogram showing the difference between a blank (blue) and 50ppt standard (black). RTs for mold compounds: IBMP – 10.05 min, MIB – 10.59 min, 2,4,6-TCA – 11.69 min, Geosmin – 12.34 min.

## Experimental-Instrument Conditions

The Atomx Automated VOC Sample Prep System was coupled to an Agilent 7890/5975 GC/MS for this analysis. A Tenax trap (1A) was the analytical trap of choice. The GC was configured with a J&W DB-624 20m x 0.18mm x 1.0µm column. The GC/MS parameters are outlined in Tables 1 and 2. Table 3 outlines the Atomx conditions.

GC Parameters	
GC:	Agilent 7890A
Column:	J&W DB-624 20m x 0.18mm x 1.0µm
Oven Program:	40 °C for 2 min, to 160 °C at 16 °C/min, for 0 min, to 240 °C at 20 °C/min
Inlet:	220 °C
Column Flow:	0.9 mL/min
Gas:	Helium
Pressure:	21.542 psi
Split Ratio:	10:1

MS Parameters	
MSD:	Agilent 5975C TAD
Source:	250 °C
Quad:	200 °C
Solvent Delay:	5.0 min
SIM Ions:	95, 107, 112, 124, 125, 137, 151, 152, 195, 197, 212
Dwell Time:	100 msec per ion
MS Transfer Line Temp:	250 °C

Tables 1 &amp; 2: GC and MSD Parameters

Atomx Water Parameters			
Variable	Value	Variable	Value
Valve oven Temp	175 °C	Dry Purge Flow	45 mL/min
Transfer Line Temp	175 °C	Dry Purge Temp	20 °C
Sample Mount Temp	60 °C	Methanol Needle Rinse	Off
Water Heater Temp	90 °C	Methanol Needle Rinse Volume	3.0 mL
Sample Vial Temp	20 °C	Water Needle Rinse Volume	25.0 mL
Sample Equilibrate Time	0.00 min	Sweep Needle Time	0.25 min
Soil Valve Temp	100 °C	Desorbs Preheat Time	220 °C
Standby Flow	45mL/min	GC Start Signal	Start of Desorb
Purge Ready Temp	40 °C	Desorbs Time	4.00 min
Condensate Ready Temp	45 °C	Drain Flow	300 mL/min
Presweep Time	0.25 min	Desorbs Temp	225 °C
Prime Sample Fill Volume	3.0 mL	Methanol Glass rinse	Off
Sample Volume	25.0 mL	Number of Methanol Glass Rinses	1
Sweep Sample Time	0.25 min	Methanol Glass Rinse Volume	3.0 mL
Sweep Sample Flow	100 mL/min	Number of Bake Rinses	3
Spurge Vessel Heater	On	Water Bake Rinse Volume	27.0 mL
Spurge Vessel Temp	40 °C	Bake Rinse Sweep Time	0.25 min
Prepurge Time	0.00 min	Bake Rinse Sweep Flow	100 mL/min
Prepurge Flow	0 mL/min	Bake Rinse Drain Time	0.40 min
Purge Time	10.00 min	Bake Time	5.00 min
Purge Flow	100 mL/min	Bake Flow	250 mL/min
Purge Temp	20 °C	Bake Temp	230 °C
Condensate Purge Temp	20 °C	Condensate Bake Temp	200 °C
Dry Purge Time	5.00 min		

Table 3: Atomx Parameters (items in yellow were not used)

## Calibration and Results

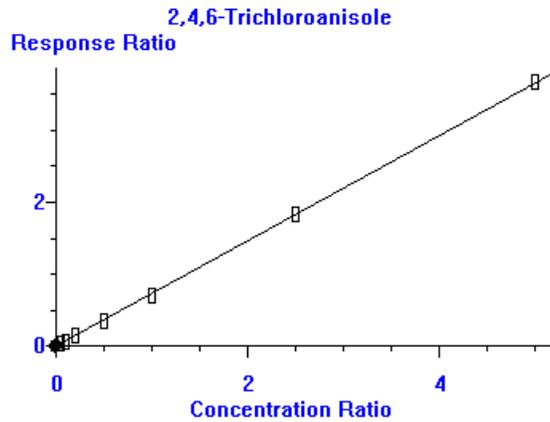
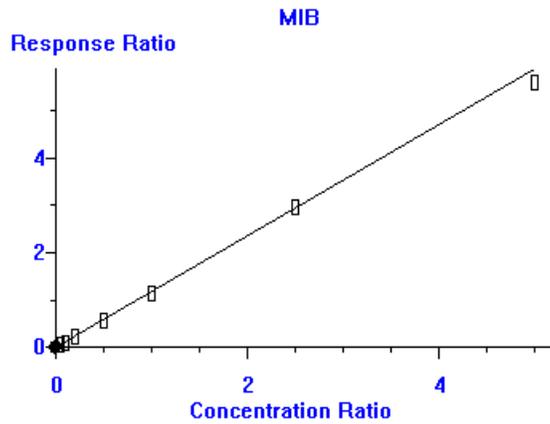
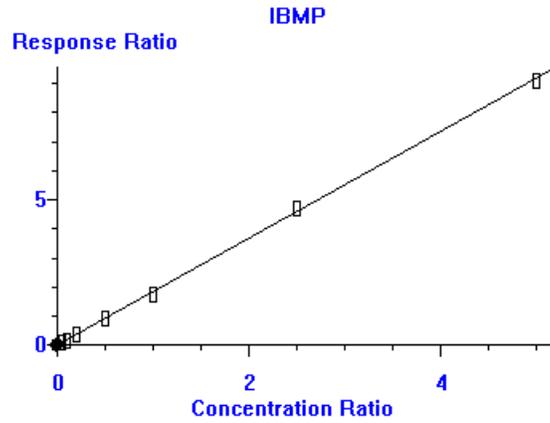
A 50 ppb stock mold odor standard was prepared in methanol containing isobutylmethoxypyrazine (IBMP), 2,4,6-trichloroanisole (2,4,6-TCA), geosmin, and 2-methylisoborneol (MIB). Calibration standards were prepared in volumetric flasks filled with 10% (w/v) sodium chloride de-ionized water over a range of 1 ppt to 100 ppt. Samples were transferred to headspace free 40 mL VOA vials for analysis.

The Internal Standard (IS), isopropylmethoxypyrazine (IPMP), was prepared in methanol at a 100 ppb concentration. After transferring to the standard vessel on the Atomx, the IS was added in 5 µL aliquots to each sample, bringing the final concentration of 20 ppt, factoring in the 25 mL purge volume. Agilent Chemstation software was used to process the calibration data.

Relative response factors for mold odor compounds were evaluated for %RSD and coefficient of determination ( $r^2$ ) with results for all compounds listed in Table 4. Calibration curves can be found in Figure 2. Method detection limits (MDL) were also established for all compounds by analyzing seven replicates at a concentration of 1 ppt. MDL results for all compounds were all well below 1 ppt. Percent carryover for each compound was determined by running blank samples after a 100 ppt mold odor standard.

Compound Name	Average RRF	%RSD	r <sup>2</sup>	Minimum Detection Limit	% Carryover
Isobutylmethoxypyrazine (IBMP)	1.831	2.19	1.000	0.06	0.12
Methylisoborneol (MIB)	1.170	4.23	0.999	0.12	0.09
Geosmin	1.214	2.01	1.000	0.07	0.17
2,4,6-Trichloroanisole	0.728	1.74	1.000	0.04	0.31

Table 4: Mold Odor Calibration Data



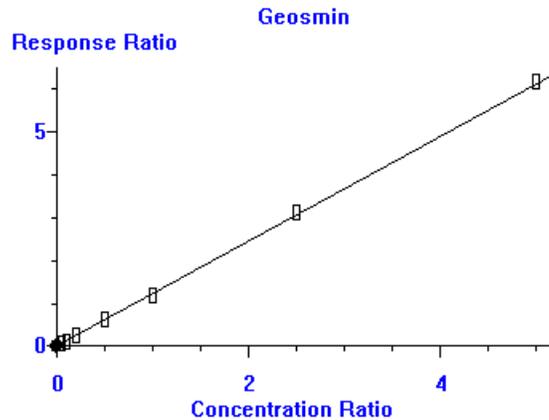


Figure 2: Calibration Curves for IBMP, MIB, 2,4,6-TCA, and Geosmin. %RSD and  $r^2$  values can be found in Table 4.

## Conclusions

With taste becoming an increasingly important aspect of water quality, detecting and eliminating mold odor compounds is critical to water suppliers. Through the method developed for mold odor analysis using the Atomx, detection limits were established well below human sensory thresholds. Even with complete automation, the precision and accuracy required to detect the mold odor compounds at the part-per-trillion level was not sacrificed. Extracted ion chromatograms for 1ppt standards of IBMP and geosmin can be found in Figures 3 and 4.

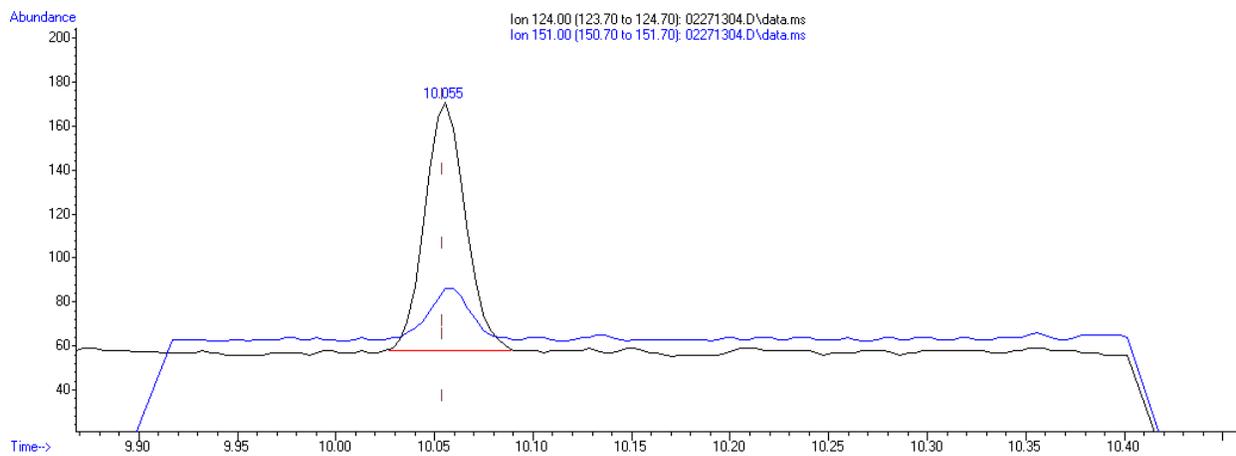


Figure 3: Extracted Ion Chromatograms (124 m/z and 151 m/z) of 1ppt IBMP Standard

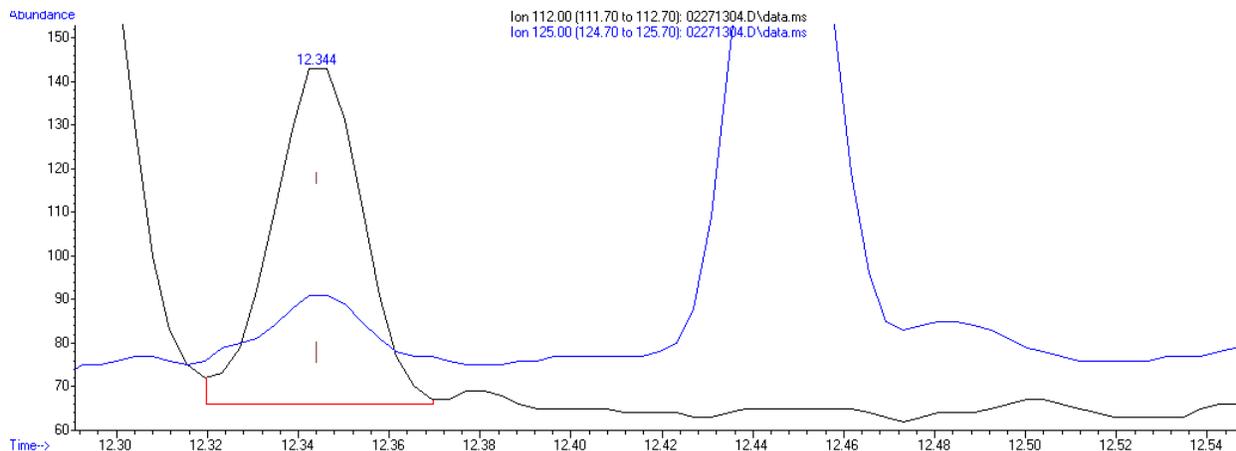


Figure 4: Extracted Ion Chromatograms (112 m/z and 125 m/z) of 1ppt Geosmin Standard

The flexibility provided by the Atomx, with the ability to run waters, soils, and automated methanol extractions, is unmatched by other sampling methods. Multiple analyses are possible in one run simply by changing the autosampler and GC/MS run methods, allotting VOC analyses of multiple matrices to be performed in one run. USEPA Methods can be run right alongside other, more specialized analyses. Utilizing an Agilent 7890/5975 GC/MS in SIM mode allows for the necessary sensitivity to run these low-level analyses. And by completely automating the sample preparation, without compromising sensitivity, efficiency and throughput can be greatly increased while saving time and money.