Comparativa del análisis del mal olor en agua mediante las técnicas de Purga y Trampa (PTC) y Micro extracción en fase sólida (SPME)

Aplicación 001

Resumen

El olor y el sabor del agua son importantes para los usuarios de agua potable. Los dos compuestos responsables de muchos de los problemas asociados al sabor y olor del agua son geosmin y el 2-metil-isoborneol. Ambos compuestos son de origen microbiano y presentan una muy baja resolución de parte a olor**. Este es el motivo de que muchos de los laboratorios de aguas potables requieren niveles de detección inferiores a** 10ppt**.** El análisis de estos compuestos se hace mediante microextraction (SPME). Esta nota aplicativa compara el análisis de estos compuestos que aportan mal olor mediante las técnicas de Purga y Trampa asociada a GC/MS frente a la técnica SPME y GC/MS. Las diferencias analíticas como los tiempos del ciclo analítico, linealidad, exactitud y precisión se revisaran para ambos.

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, it is necessary to be able to detect these compounds at extremely low levels.

Mold odor analysis is commonly performed by solid-phase microextraction (SPME). Samples are prepared and a coated fiber is placed inside the sample for about 30 to 60 minutes to extract the analytes.   These short fibers are essentially inside out gas chromatography columns, which are fragile and at times indiscriminant. The compounds are absorbed onto the fiber and desorbed directly in the heated injection port of the gas chromatograph. This fiber must be conditioned prior to analysis and after each subsequent sample. SPME fiber performance is also sensitive to changes in solvent concentrations when preparing calibration standards and samples. Sampling also requires specialized consumables like fiber assemblies and injection liners designed specifically for SPME. Autosamplers are also available to

automate the process, but different analyses can require different fibers, which must be switched out prior to extraction.

For this study, a Stratum Purge and Trap Concentrator (PTC) was used in conjunction with an AQUATek 100 Waters-only Autosampler. This set-up allows for complete automation of sample preparation for the analysis of liquid samples for purge and trap. Samples are loaded into the 100-position carousel and prepared for extraction in either 5mL or 25mL aliquots. Analytes are purged out of the sample onto a sorbent trap. The trap is then heated and analytes are desorbed to the GC/MS for analysis. Utilizing an Agilent 7890A/5975 GC/MS in Selective Ion Monitoring (SIM) mode, a linear calibration was performed and percent relative standard deviation (%RSD), method detection limits (MDLs), and percent carryover were determined for all compounds. An example of a SIM scan for the mold odor analysis can be found in Figure 1. In addition, mold odor samples were evaluated in conjunction with samples run by USEPA Method 524.2[1] to demonstrate capability and identify possible matrix effects of the salted samples over time.
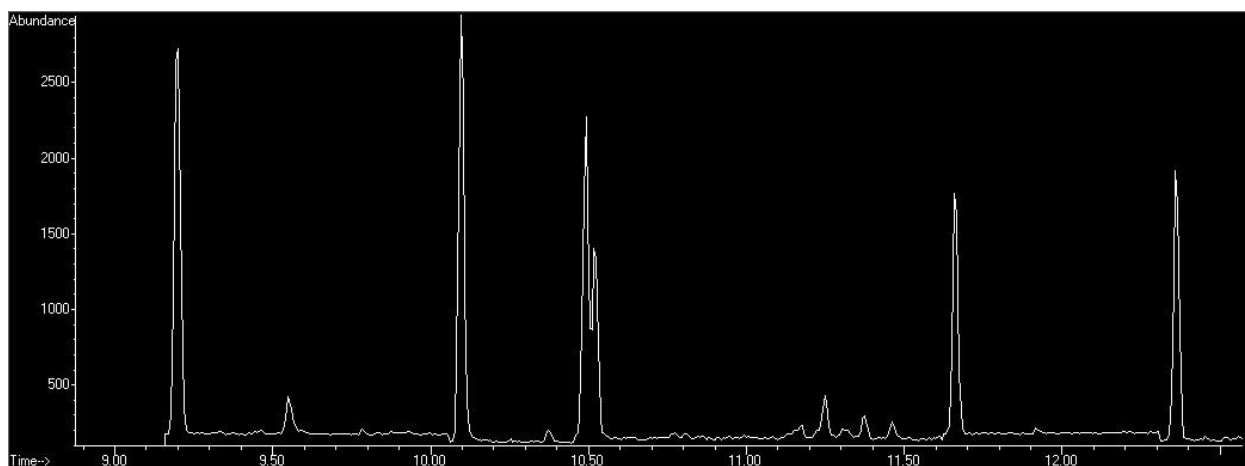

Figure 1: Selective Ion Monitoring (SIM) Scan of 10ppt Mold Standard

Experimental-Instrument Conditions

The Stratum PTC and AQUATek 100 Autosampler were coupled to an Agilent 7890/5975 GC/MS for analysis. Teledyne Tekmar's proprietary #9 trap was the analytical trap of choice. The GC was configured with a Restek Rtx-624 20m x 0.18mm x 1.0μm column. The GC/MS parameters are outlined in Tables 1 and 2. Table 3 outlines the P&T and autosampler conditions.

GC Parameters	
GC:	Agilent 7890A
Column:	Restek Rtx-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
Source:	230° C
Quad:	150°C
Solvent Delay:	2.0 min
SIM Ions:	95, 107, 112, 124, 125, 137, 151, 152, 195, 197, 212
Dwell Time:	100 msec per ion
MS Transfer Line Temp:	230°

| Stratum PTC and AQUATek 100 Parameters			
Variable	**Value**	**Variable**	**Value**
Pressurize Time	0.85 min	Purge Time	10.00
Sample Transfer Time	1.25 min	Purge Temp	20°C
Rinse Loop Time	0.85 min	Purge Flow	100mL/min
Sweep Needle Time	0.30 min	Dry Purge Time	5.00 min
Bake Rinse	On	Dry Purge Temp	20°C
Bake Rinse Cycles	3	Dry Purge Flow	45mL/min
Bake Rinse Drain Time	1.50 min	GC Start	Start of Desorb
Presweep Time	0.35 min	Desorb Preheat Temp	245°C
Water Temp	90° C	Desorb Drain	On
Valve Oven Temp	175°C	Desorb Time	2.00 min
Transfer Line Temp	175°C	Desorb Temp	250°C
Sample Mount Temp	60°C	Desorb Flow	300mL/min
Purge ready Temp	40°C	Bake Time	5.00 min
Condenser Ready Temp	40°C	Bake Temp	260°C
Condenser Purge Temp	20°C	Bake Flow	250mL/min
Standby Flow	45mL/min	Condenser Bake Temp	200°C
Pre-Purge Time	0.00 min		
Pre-Purge Flow	0mL/min		
Sample Heater	On		
Sample Preheat Time	0.01 min		
Sample Temp	40°C		

Table 3: Stratum PTC and AQUATek 100 Parameters (Stratum PTC Parameters are in Blue)

Calibration Data

A 50ppb stock mold odor standard was prepared in methanol containing isobutylmethoxypyrazine (IBMP), 2,4,6-trichloroanisole, 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 1ppt to 100ppt. Samples were transferred to headspace free 40mL VOA vials for analysis. The Internal Standard (IS), isopropylmethoxypyrazine (IPMP), was prepared in methanol at a 50ppb concentration. After transferring to the standard vessel on the AQUATek 100, the IS was added in 5µL aliquots to each sample, bringing the final concentration of 10ppt, factoring in the 25mL 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 2ppt. MDL results for all compounds were below 1ppt. Percent carryover for each compound was determined by running blank samples after a 100ppt mold odor standard.

Compound Name	Average RRF	%RSD	r²	Minimum Detection Limit	% Carryover
Isopropylmethoxypyrazine (IPMP) (IS)	1.000	N/A	N/A	N/A	N/A
Isobutylmethoxypyrazine (IBMP)	1.225	1.13	1.0000	0.04	0.25
Methylisoborneol (MIB)	0.861	0.71	1.0000	0.04	0.07
Geosmin	0.340	6.43	0.9998	0.05	0.43
2,4,6-Trichloroanisole	0.787	1.37	1.0000	0.03	0.45

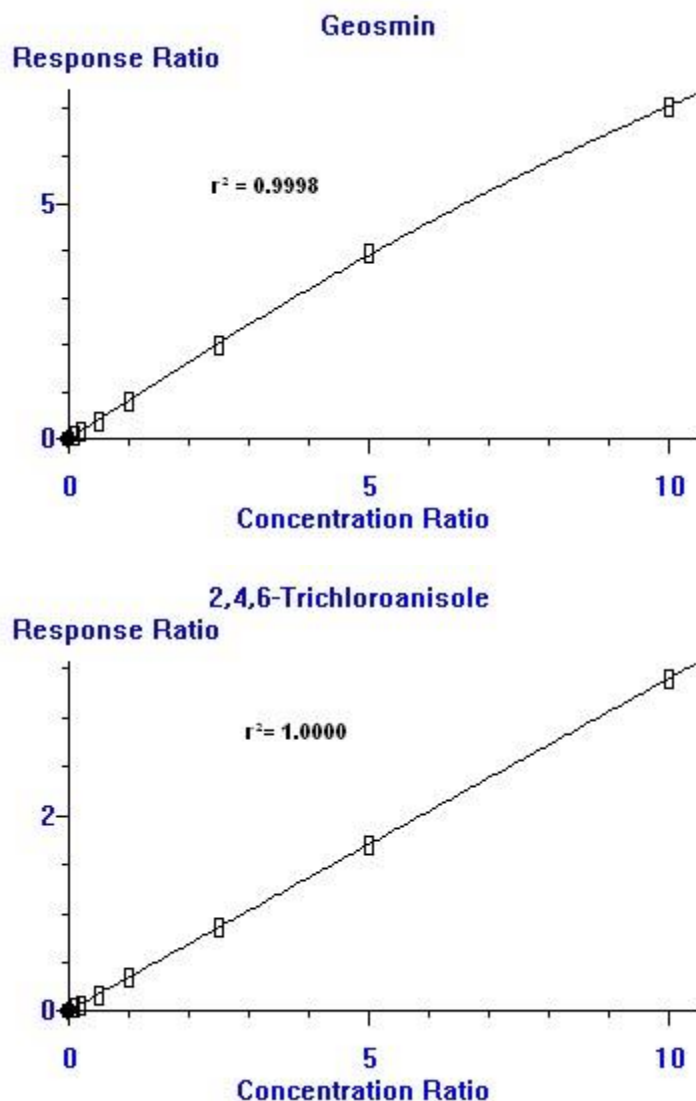*Table 4: Calibration, MDL, and % Carryover Data for Mold Odor Analysis*
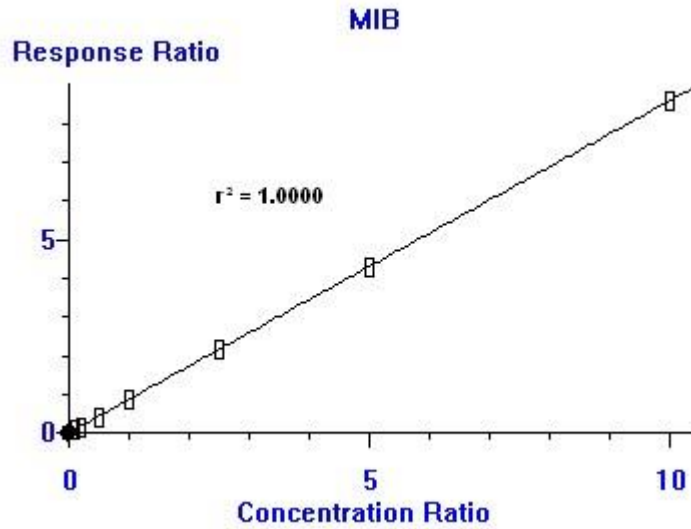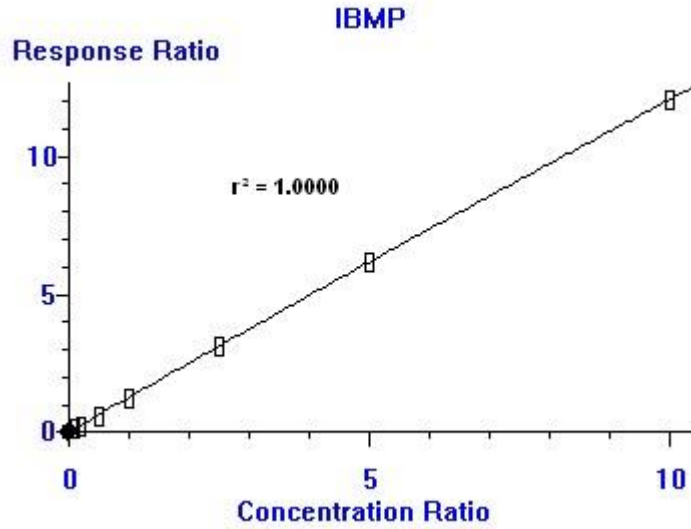
Figure 2: Calibration Curves (1 to 100ppt) for Mold Odor Compounds

In addition to a mold odor calibration, an USEPA Method 524.2 calibration curve was established in the same run to demonstrate the flexibility of the Stratum PTC equipped with a #9 trap. All performance criteria for Method 524.2 were met and the calibration data can be found in Table 5. A 24-hour continuing calibration verification (CCV) study was also run to determine possible effects of the 10% salt solution on both mold odor and 524.2 analyses over time. All CCVs passed with percent recoveries for all compounds above 80% over 24 hours for both analyses.

Compound Name	Linearity (r²)	Compound Name	Linearity (r²)
Dichlorodifluoromethane	1	4-Methyl-2-Pentanone	1
Chloromethane	1	1,1-Dichloropropanone	1
Vinyl Chloride	0.9999	Toluene	0.9997
Bromomethane	0.9999	trans-1,3-Dichloropropene	0.9996

Chloroethane	1	1,1,2-Trichloroethane	1
Trichlorofluoromethane	0.9998	Tetrachloroethene	0.9999
Diethyl Ether	0.9999	2-Hexanone	1
1,1-Dichloroethene	0.9998	1,3-Dichloropropane	0.9999
Acetone	0.9999	Dibromochloromethane	0.9998
Iodomethane	0.9999	1,2-Dibromoethane	0.9999
Carbon Disulfide	0.9995	Chlorobenzene	0.9995
Allyl Chloride	0.9999	1,1,1,2-Tetrachloroethane	0.9995
Methylene Chloride	0.9999	Ethylbenzene	0.9991
trans-1,2-Dichloroethene	0.9995	m,p-Xylene	0.9966
MTBE	0.9999	o-Xylene	0.9999
Acryl Nitrile	1	Styrene	0.9999
1,1-Dichloroethane	0.9999	Bromoform	0.9999
2-Butanone	1	Isopropylbenzene	0.9999
2,2-Dichloropropane	0.9999	Bromobenzene	1
cis-1,2-dichloroethene	0.9998	1,1,2,2-Tetrachloroethane	0.9993
Methyl Acrylate	1	trans-1,4-Dichloro-2-butene	0.9999
Propionitrile	1	1,2,3-Trichloropropane	1
Methacrylonitrile	0.9998	n-Propylbenzene	0.9999
Bromochloromethane	0.9997	2-Chlorotoluene	1
Tetrahydrofuran	0.9999	4-Chlorotoluene	0.9999
Chloroform	0.9997	1,3,5-Trimethylbenzene	1
1,1,1-Trichloroethane	0.9998	tert-Butylbenzene	1
Carbon Tetrachloride	0.9997	1,2,4-Trimethylbenzene	1
1-Chlorobutane	0.9999	sec-Butylbenzene	1
1,1-Dichloropropene	0.9995	1,3-Dichlorobenzene	1
Benzene	0.9996	p-Isopropyltoluene	0.9999
1,2-Dichloroethane	0.9999	1,4-Dichlorobenzene	1
Trichloroethene	1	1,2-Dichlorobenzene	1
Methyl Methacrylate	0.9996	n-Butylbenzene	0.9998
1,2-Dichloropropane	0.9999	Hexachloroethane	0.9998
Dibromomethane	0.9998	1,2-Dibromo-3-chloropropane	0.9994
Ethyl Methacrylate	0.9999	Nitrobenzene	0.9973
2-Nitropropane	0.9994	1,2,4-Trichlorobenzene	0.9997

Bromodichloromethane	0.9998	Hexachlorobutadiene	0.9997
Chloroacetonitrile	0.9999	Naphthalene	0.9999
cis-1,3-Dichloropropene	0.9997	1,2,3-Trichlorobenzene	0.9998

Table 5: Calibration Data for Method 524.2

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 Stratum PTC and AQUATek 100 Autosampler, 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.
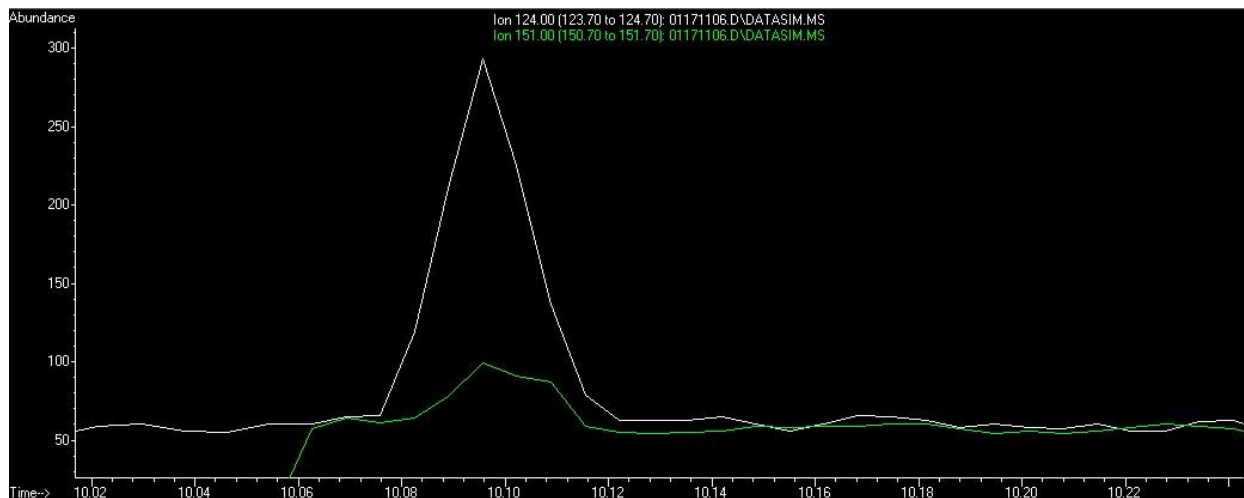

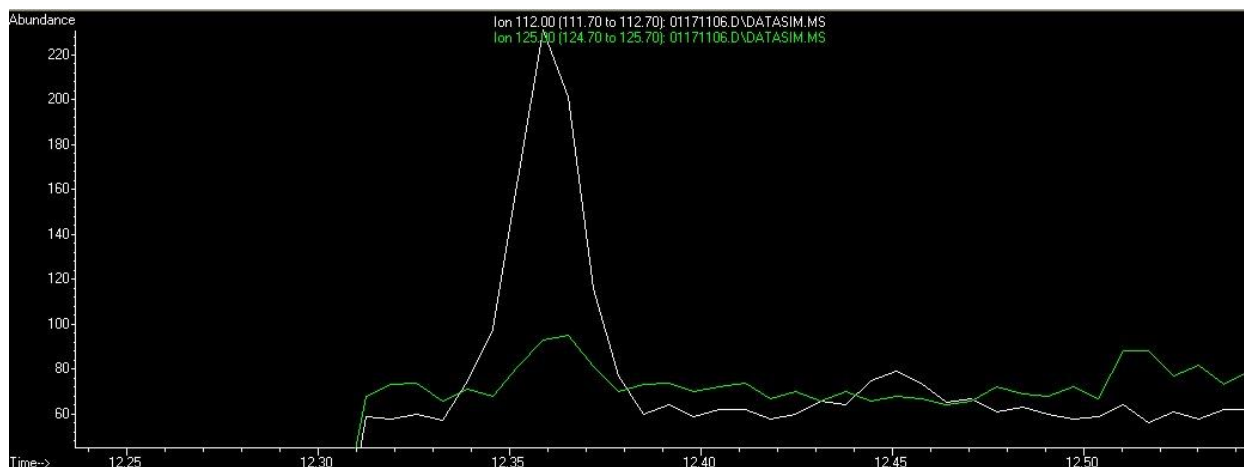*Figure 3: Extracted Ion Chromatogram of 1ppt IBMP Standard*

Figure 4: Extracted Ion Chromatogram of 1ppt Geosmin Standard

When comparing the two sample preparation techniques, the AQUATek 100 and Stratum PTC offer a multitude of added benefits while meeting, and in most cases exceeding, SPME performance[2,3], with none of the drawbacks. Sampling and analysis do not require any specialized consumables and are completely automated, increasing efficiency. Separate sampling and extraction devices are unnecessary and samples are continuously run rather than waiting on long extraction and conditioning times. The "allin-one" set up also transitions between analyses seamlessly for greater throughput.

The flexibility provided by the AQUATek 100 and Stratum PTC, equipped with a #9 trap is unmatched by other sampling methods.   Multiple analyses are possible on a single Purge and Trap simply by changing the autosampler and GC/MS acquisition methods, allotting VOC analyses to be run side-by-side with mold odor samples. USEPA Methods can be run right alongside other, more specialized analyses. Also, by utilizing an Agilent 7890/5975 GC/MS which allows for both total ion and SIM chromatograms to be saved for each run, samples can be analyzed for mold odor compounds as well as volatile organics. And by completely automating the sample preparation, without compromising sensitivity, efficiency and throughput can be greatly increased while saving time and money.

References

1) USEPA Method 524.2, "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS)," Revision 4.1, 1995.

2) Supelco, "Solid-Phase Microextraction of Odors in Drinking Water, for Analysis by GC/MS," 2002.
3) Thermo Scientific, "Determination of Geosmin and 2-MIB in Drinking Water by SPME-PTVGC/MS," 2007.