US EPA Method 6040C Using the Teledyne Tekmar Atomx XYZ and Thermo Scientific™ TRACE™ 1310 GC and ISQ™ 7000 MS

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Abstract

US EPA Method 6040C was used to determine the concentration of taste and odor volatile organic compounds (VOCs) in drinking water. The Teledyne Tekmar Atomx XYZ purge and trap (P&T) system along with a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC) and ISQ™ 7000 Mass Spectrometer (MS) with an ExtractaBrite™ Source was used to create a working calibration curve, method detection limits (MDLs) and a mid-point verification study for accuracy and precision of target compounds. This study will demonstrate the ability of the Atomx XYZ's innovative moisture control system to remove water vapor transferred to the GC/MS and allow for detection as low as 2 ppt.

Introduction

Musty odors can be caused by the compounds 2-Methylisoborneol and Geosmin, both of which are by-products of the growth of blue-green algae and other microbes. These musty odors may lead drinking water consumers to believe their water is unsafe, if they are present. Because of this, water supplier quality control (QC) seeks to limit these compounds, even though they are not considered a hazard to public health. The human nose can detect 2-Methylisoborneol and Geosmin at very low concentrations, therefore extremely sensitive sample preparation and analytical techniques are necessary for their detection.

The Atomx XYZ is Teledyne Tekmar's most advanced P&T system and is based on the time-tested Atomx instrument platform. The concentrator's efficient trap cooling design reduces sample cycle time by as much as 14% over the previous model. Combined with its 84-position soil and water autosampler, the result is more samples tested per 12-hour period. An innovative moisture control system (MCS) improves water vapor removal by as much as 60%, thereby reducing peak interference and increasing GC column lifespan. In addition to other refinements, the Atomx XYZ incorporates a precision-machined valve manifold block to reduce potential leak sources and ensure the system is both reliable and robust.

Sample Preparation

Two working calibration standards, 10 parts per billion (ppb or µg/L) and 50 ppb, were prepared in methanol from a Restek® Geosmin and 2-Methylisoborneol Standard. In total, the standard contained two compounds.

A linear calibration curve was prepared from 2 part per trillion (ppt or ng/L) to 100 ppt for all compounds. The 2 ppt and 5 ppt calibration standards were prepared using the 10 ppb working calibration standard, while the 10 ppt to 100 ppt calibration standards were prepared using the 50 ppb standard. The relative response factor (RF) was calculated for each compound using one of the two internal standards: 2-Isobutyl-3-methoxypyrazine and 2,4,6-Trichloroanisole. Internal standards were prepared together in methanol from Restek standards at a concentration of 30 ppb, after which 20 µL was then mixed with each 20 mL sample for a resulting concentration of 30 ppt.

Ten 2 ppt standards were prepared for MDLs and precision calculations. Also, ten 50 ppt standards were prepared as a mid-point verification study for precision and accuracy calculations. All calibration, MDL and mid-point verification samples were analyzed with the Atomx XYZ conditions in Table I and the GC/MS conditions in Table II.

Experimental Instrument Conditions

Table I Teledyne Tekmar Atomx XYZ Water Method Conditions			
Standby	Variable	Purge	Variable
Valve Oven Temp	140 ºC	Dry Purge Flow	100 mL/min
Transfer Line Temp	140 ºC	Dry Purge Temp	20 ºC
Sample Mount Temp	60 ºC	Desorb	Variable
Water Heater Temp	90 ºC	Water Needle Rinse Volume	7.00 mL
Sample Vial Temp	20 ºC	Sweep Needle Time	0.25 min
Soil Valve Temp	50 ºC	Desorb Preheat Temp	245 ºC
Standby Flow	10 mL/min	Desorb Time	2.00 min
Purge Ready Temp	40 ºC	Drain Flow	300 mL/min
Purge	Variable	Desorb Temp	250 ºC
Sample Equilibrate Time	0.00 min	Methanol Needle Rinse	Off
Pre-sweep Time	0.25 min	GC Start Signal	Begin Desorb
Prime Sample Fill Volume	3.00 mL	**Bake**	**Variable**
Sample Volume	20.00 mL	Methanol Glass Rinse	Off
Sweep Sample Time	0.25 min	Water Bake Rinses	1
Sweep Sample Flow	100 mL/min	Water Bake Rinse Volume	22.00 mL
Sparge Vessel Heater	On	Bake Rinse Sweep Time	0.25 min
Sparge Vessel Temp	60 ºC	Bake Rinse Sweep Flow	100 mL/min
Pre-purge Time	0.00 min	Bake Rinse Drain Time	0.40 min
Pre-purge Flow	0 mL/min	Bake Time	20.00 min
Purge Time	11.00 min	Bake Flow	200 mL/min
Purge Flow	40 mL/min	Bake Temp	260 ºC
Purge Temp	20 ºC	Condensate Bake Temp	180 ºC
Condensate Purge Temp	20 ºC	Trap	K
Dry Purge Time	2.00 min	Purge Gas	Nitrogen

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Table II Thermo Scientific TRACE 1310 GC and ISQ 7000 MS System Conditions	
Thermo Scientific TRACE 1310 GC Conditions	
Column	TG VMS, 20 m x 0.18 mm, 1 µm Film, Helium – 0.8 mL/min
Oven Profile	35 ºC, 2 min, 10 ºC/min to 225 ºC, 3 min Hold, Run Time 24 min
Inlet	200 ºC, 20:1 Split, Purge Flow 0.5 mL/min
Thermo Scientific ISQ 7000 MS Conditions	
Temp	Transfer Line 230 ºC; Ion Source 280 ºC
SIM Ions	2-Isobutyl-3-methoxypyrazine: 124, 151, 2-Methylisoborneol: 95, 107, 108, 2,4,6-Trichloroanisole: 195, 197, 210, Geosmin: 111, 112, 125, Scan Window (min): 2.00, Total Scan Time: 0.300 sec, SIM Time: 0.300 sec, Lowest Dwell Time: 0.03343 sec
Current	Emission Current 50 µA, Gain 4.00E+006

Results

The relative standard deviation (%RSD) of the RFs for the calibration curve, MDL, precision and mid-point verification data are shown in Table III. Figure 1 displays a 50 ppt 2-Methylisoborneol standard, indicating excellent peak resolution and calibration linearity with minimal water inference. Figure 2 displays a 50 ppt Geosmin standard, also indicating excelled peak resolution and calibration linearity with minimal water interference.

Table III US EPA Method 6040C Water Calibration, Accuracy and Precision Data

Compound	Calibration				Method Detection Limit (n=10, 2 ppt)		Mid-Point Verification (n=10, 50 ppt)	
	Retention Time	Quant Ion	Linearity (r^2>0.99)	Average RF	MDL (ppt)	Precision (≤20%)	Accuracy (70-130%)	Precision (≤20% RSD)
2-Isobutyl-3-methoxypyrazine (IS)	13.87	124						
2-Methylisoborneol	14.70	107	0.996	0.111	0.37	8.5	94	6.4
2,4,6-Trichloroanisole (IS)	16.58	195						
Geosmin	17.73	125	0.998	0.171	0.33	12.9	104	7.0

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Figure 1 Thermo Scientific™ Chromeleon™ Software Results Showing Extracted Ion Chromatograms for 2-Methylisoborneol in the 50 ppt VOC Drinking Water Standard, Quantitation Ion with Two Confirming Ions (A) and a Linear Calibration over a Concentration Range of 2 ppt to 100 ppt (B).

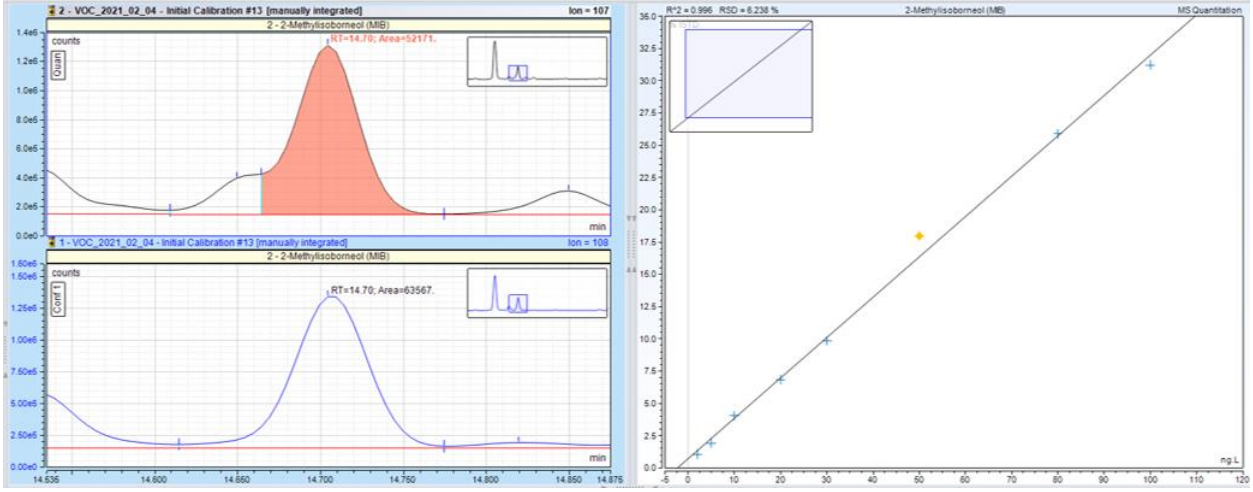
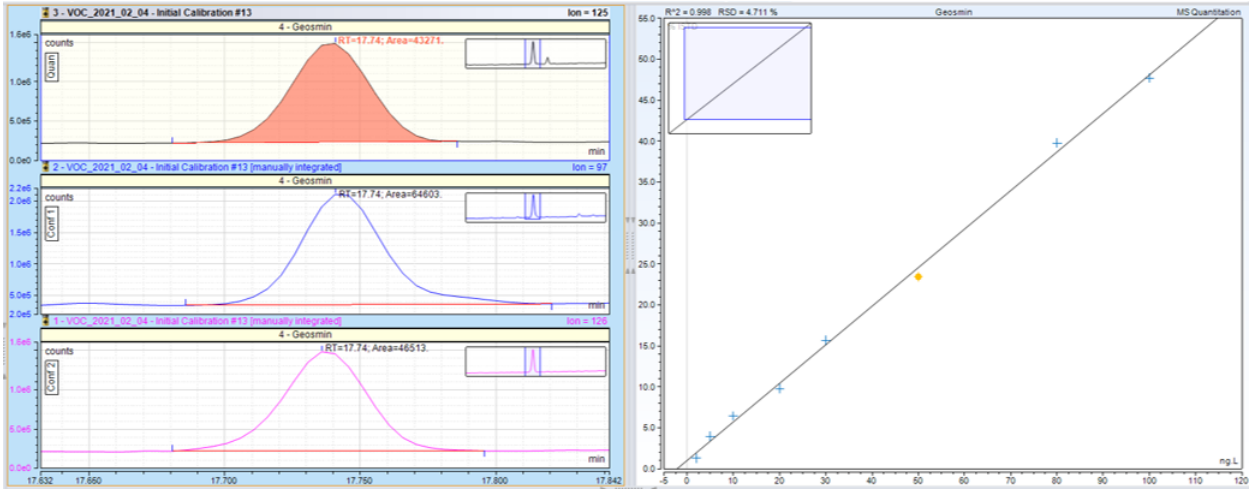


Figure 2 Thermo Scientific™ Chromeleon™ Software Results Showing Extracted Ion Chromatograms for Geosmin in the 50 ppt VOC Drinking Water Standard, Quantitation Ion with Two Confirming Ions (A) and a Linear Calibration over a Concentration Range of 2 ppt to 100 ppt (B).



Conclusion

This study demonstrates the capability of the Teledyne Tekmar Atomx XYZ P&T system to process taste and odor causing VOCs in drinking water samples following US EPA Method 6040C with detection by a Thermo Scientific TRACE 1310 GC and ISQ 7000 MS with an ExtractaBrite Source. The r^2 of the calibration curve was ≥0.996 for both compounds and passed all method requirements with minimal interference from excessive water. Furthermore, MDL, precision and mid-point verification for standards as low as 2 ppt displayed minimal interference from excessive water.

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