

Robust analysis of taste and odor compounds in drinking water using purge and trap and single quadrupole GC-MS

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Goal

To demonstrate the use of the Thermo Scientific™ TRACE™ 1310 gas chromatograph (GC) coupled to the Thermo Scientific™ ISQ™ 7000 mass spectrometer (MS) with NeverVent™ technology and the Teledyne Tekmar Atomx XYZ purge and trap (P&T) system for the analysis of geosmin and 2-methylisoborneol (2-MIB) in drinking water according to Standard Method 6040C.¹ Linearity, MDLs, accuracy, precision, and robustness will be assessed.



Introduction

Drinking water that has a strange taste or odor may lead consumers to think that the water is unsafe to drink. However, this is not always the case. Compounds such as geosmin and 2-MIB have earthy/musty tastes and odors with very low taste and odor thresholds and can be detected by humans at levels as low as 1.3 ng/L.² Although these compounds are not currently considered harmful to human health,³ it is still important for water companies to monitor the levels of these compounds to mitigate any potential complaints from consumers. There are several different sample preparation methods that can be used for the analysis, including liquid-liquid extraction (LLE) and solid phase extraction (SPE).⁴ These techniques are both labor intensive and require the use of large quantities of solvent (LLE) or expensive extraction cartridges (SPE). Valuable alternatives involve solventless extraction techniques through the enrichment of the water headspace, like dynamic headspace (ITEX)⁵, purge and trap (P&T) according to the Standard Method 6040C, and solid phase microextraction (SPME) according to the Standard

Method 6040D, followed by GC-MS analysis. These approaches offer the advantage to eliminate almost all the labor involved with sample preparation while still meeting the sensitivity requirements. Analysis according to Standard Method 6040C is described in this application note.

To perform Standard Method 6040C, initial demonstration of capability (IDC) testing must be performed. This includes criteria for linearity, method detection limit (MDL), precision, and accuracy. It is essential that analytical environmental testing laboratories produce results consistently day in and day out. As well as demonstrating the method could be performed, an extended run of samples was used to demonstrate the robustness of the instrumentation for the method. This was achieved by running a continuing calibration check regularly to ensure that the instrument response has not significantly changed since the initial calibration. In this application note these criteria will be demonstrated using a TRACE 1310 GC coupled to the

ISQ 7000 MS in the VPI (Vacuum Probe Interlock) configuration and the Atomx XYZ P&T system.

Experimental

Instrument and method setup

The TRACE 1310 GC was coupled to the Atomx XYZ P&T system and the ISQ 7000 single quadrupole MS system, fitted with the Thermo Scientific™ ExtractaBrite™ ion source. Chromatographic separation was achieved using a Thermo Scientific™ TraceGOLD™ TG-VMS 20 m x 0.18 mm x 1 µm capillary column (P/N 26080-4950) using helium as carrier gas and nitrogen as purge gas. Full instrument conditions are shown in Tables 1 and 2.

In environmental testing laboratories, it is important to maximize sample throughput to ensure samples results are delivered on time. The modularity of the TRACE 1310 GC and the VPI with ExtractaBrite ion source of the ISQ 7000 MS allows users to easily service the injection ports as well

Table 1. Atomx XYZ method conditions

Standby	Variable	Desorb	Variable
Valve oven temp.	140 °C	Water needle rinse volume	7.00 mL
Transfer line temp.	140 °C	Sweep needle time	0.25 min
Sample mount temp.	60 °C	Desorb preheat temp.	245 °C
Water heater temp.	90 °C	Desorb time	2.00 min
Sample vial temp.	20 °C	Drain flow	300 mL/min
Soil valve temp.	50 °C	Desorb temp.	250 °C
Standby flow	10 mL/min	Methanol needle rinse	Off
Purge ready temp.	40 °C	GC start signal	Begin desorb
Purge	Variable	Bake	Variable
Sample equilibrate time	0.00 min	Methanol glass rinse	Off
Pre-sweep time	0.25 min	Water bake rinses	1
Prime sample fill volume	3.00 mL	Water bake rinse volume	22.00 mL
Sample volume	20.00 mL	Bake rinse sweep time	0.25 min
Sweep sample time	0.25 min	Bake rinse sweep flow	100 mL/min
Sweep sample flow	100 mL/min	Bake rinse drain time	0.40 min
Spurge vessel heater	On	Bake time	20.00 min
Spurge vessel temp.	60 °C	Bake flow	200 mL/min
Pre-purge time	0.00 min	Bake temp	260 °C
Pre-purge flow	0 mL/min	Condensate bake temp.	180 °C
Purge time	11.00 min	Trap	K (Vocarb 3000)
Purge flow	40 mL/min	Purge gas	Nitrogen
Purge temp.	20 °C		
Condensate purge temp.	20 °C		
Dry purge time	2.00 min		
Dry purge flow	100 mL/min		
Dry purge temp.	20 °C		

as to exchange ionization sources and analytical columns without venting the mass spectrometer. This significantly reduces instrument downtime and minimizes sample analysis interruptions. Another consideration is to minimize laboratory costs and maximize the use of consumables such as GC columns. The Atomx XYZ concentrator's efficient trap cooling design reduces sample cycle time and allows for increased sample throughput. The moisture control system improves water vapor removal, thereby reducing peak interference and increasing the GC column life span.

Standards and samples preparation

A 100 µg/mL solution of geosmin and 2-MIB in methanol was purchased from Restek and diluted in methanol to prepare a 50 µg/L and a 10 µg/L working standard. This solution was spiked into 50 mL of deionized water to create a calibration curve in the range 2 ng/L to 100 ng/L. 2-Isobutyl-3-methoxypyrazine and 2,4,6-trichloroanisole standards were purchased from Restek and diluted in methanol to 30 µg/L for use as internal standard. Internal standard (20 µL) was spiked into each sample giving a concentration in sample of 30 ng/L.

Data acquisition, processing, and reporting

The data were acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2. Chromeleon software provides comprehensive system control for both the Atomx XYZ and the GC-MS, eliminating the need for multiple software programs. Consequently, the operator only needs to use one software program for data acquisition, real time data processing, and customized reporting, with all calculations performed within the software. The method can be easily implemented into any lab using a simplified Chromeleon eWorkflow containing all the parameters needed to acquire, process, and report the analytical data, which is available for download via the Thermo Scientific™ AppsLab library.

Results and discussion

Chromatography

Consistent retention times, repeatable peak areas and reliable confirmation ion ratios are essential to provide reliable identification and quantitation. Examples of the extracted ion chromatograms of a 50 ng/L standard are shown in Figure 1.

Table 2. GCMS method conditions

Thermo Scientific TRACE 1310 GC conditions	
Column	TraceGOLD TG VMS, 20 m x 0.18 mm, 1 µm film
Carrier gas and flow	Helium, 0.8 mL/min
Oven profile	35 °C, 2 min, 10 °C/min to 225 °C, 3 min hold
Inlet type and temperature	SSL, 200 °C
Inlet mode	Split
Inlet liner	1.2 mm i.d., 78.5 mm P/N 453A1335
Split ratio	20:1
Purge flow	0.5 mL/min
Run time	24 min
Overall method cycle time	42 min
Thermo Scientific ISQ 7000 MS conditions	
Transfer line temperature	230 °C
Ion source temperature	280 °C
SIM ions (<i>m/z</i>)	2-Isobutyl-3-methoxypyrazine: 124, 151 2-Methylisoborneol: 107, 108, 135 2,4,6-Trichloroanisole: 195, 197, 210 Geosmin: 97, 125, 126
Scan window	2 min
Total scan time	0.3 s
Shortest dwell time	0.04593 s
Emission current	50 µA
Gain	4.00E+006

Linearity

To obtain accurate quantification of results, a calibration curve is essential. Linearity was assessed by injecting eight standards, in singular, covering the range 2–100 ng/L for both analytes. Examples of the calibration curves produced are shown in Figure 2. Excellent linearity was achieved with R^2 values ≥ 0.996 and average calibration factor (AvCF) %RSD values of <7 .

Sensitivity

The low-level analysis that this method requires must be assessed for sensitivity to confirm that the lowest calibration standard is significant compared to the method blank. This was assessed by determining the MDLs for each analyte. To empirically determine the compound's MDL, ten standards at 2 ng/L (corresponding to 2 ng/L in the sample) were prepared and injected.

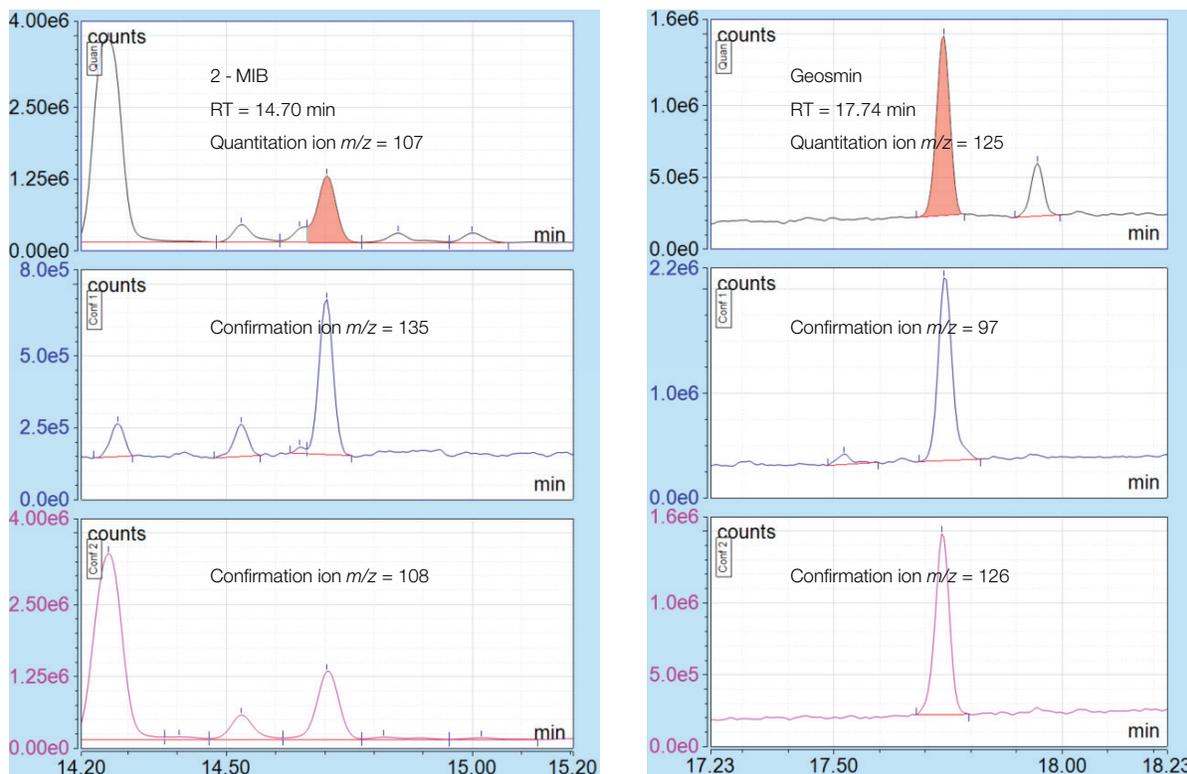


Figure 1. Example of extracted ion chromatograms of a 50 ng/L standard for 2-MIB (left) and geosmin (right), showing quantitation ions (top) and confirmation ions (bottom), annotated with retention time (RT) and m/z of the ions used

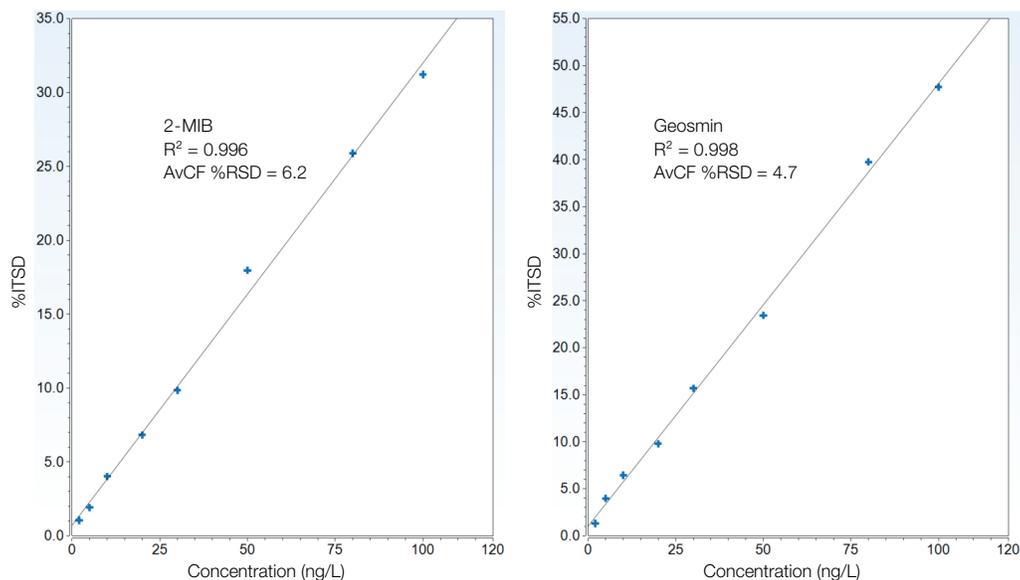


Figure 2. Calibration curves from 2 to 100 ng/L for 2-MIB (left) and geosmin (right), annotated with R^2 and AvCF %RSD with one injection per calibration level

The standard deviation and the students t-test value at the 99% confidence level were then considered to determine the MDL for each compound. Values of 0.37 ng/L and 0.33 ng/L were obtained for 2-MIB and geosmin, respectively, meeting the sensitivity requirements of the method.

Precision and accuracy

Precision and accuracy were assessed using ten replicate analyses of a 50 ng/L standard. The %RSD of the calculated amount and the accuracy compared to theoretical value were assessed and the results are shown in Table 3. The %RSD for both compounds was <20 and the mean accuracy measurement was within the 70–130% limit as required by Standard Method 6040C. In addition, to ensure reliable identification, repeatability of the primary confirmation ion ratio was assessed. The ion ratios were within 20% of the ion ratio obtained from the 50 ng/L calibration standard. This can be easily visualized using interactive charts within Chromeleon software (Figure 3), enabling laboratories to quickly and easily spot any results falling outside the required range.

Table 3. Table showing the precision and accuracy for the two analytes, n=10 at 50 ng/L

	Accuracy (% recovery)	Precision (%RSD calculated amount)
2-Methylisoborneol	94.5	6.4
Geosmin	104.3	7.0

Robustness

It is vital that a method in an analytical testing laboratory produces stable and reproducible results continuously. To demonstrate this, robustness was assessed by performing n=22 injections of a 20 ng/L standard at regular intervals across a 132-injection sequence that lasted over 90 hours. The results were acquired with no user intervention at all on the P&T, GC, or MS system. The mean calculated concentrations were within the allowed range for the continuing calibration check standard of 70–130% with values of 120% and 110% achieved for 2-MIB and geosmin, respectively. The %RSDs of the calculated amount were also less than the allowed 20% at 14.3 and 11.0, respectively. The confirmation ion ratio remained robust throughout the sequence with %RSDs of 10.7 and 2.7, respectively. These results are summarized in Figure 4 and Table 4.

Table 4. %RSD of calculated concentration, mean concentration, and mean accuracy of n=22 20 ng/L standard injections over a 132-injection sequence

Compounds	Average concentration (ng/L)	Accuracy (% recovery)	Precision (%RSD calculated amount)
2-Methylisoborneol	24.0	120	14.3
Geosmin	22.0	120	11.0



Figure 3. Interactive charts showing the primary confirmation ion ratio for 2-MIB (A) and geosmin (B) within a ±20% window of the ion ratio obtained from the 50 ng/L calibration standard

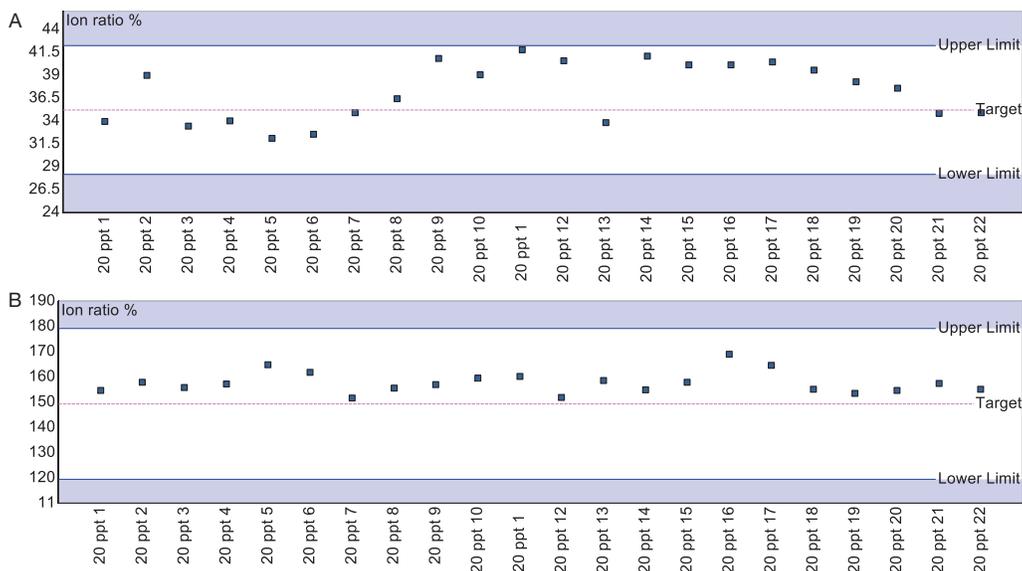


Figure 4. Chromeleon screenshots of the primary confirmation ion ratio of a 20 ng/L standard analyzed over n=132 consecutive injections (over 90 hours of analysis) for 2-MIB (A) and geosmin (B) with ±20% limits indicated. No system maintenance or tuning were performed.

Conclusions

The experiments performed clearly demonstrate the suitability of the TRACE 1310 GC coupled to the ISQ 7000 MS in the VPI configuration and the Atomx XYZ P&T system for the analysis of geosmin and 2-MIB in drinking water in accordance with Standard Method 6040C. This is evidenced by:

- Linearity was assessed over the range 2–100 ng/L with R^2 values ≥ 0.996 and AvCF %RSDs < 7 .
- MDLs calculated from n=10 repeat injections of a 2 ng/L standard showed no evidence of interference and resulted in values < 0.9 ng/L for both compounds.
- Precision and accuracy for n=10 50 ng/L standard injections showed accuracy within $\pm 6\%$ and precision $< 8\%$ RSD, well within the required limits of $\pm 30\%$ and $< 20\%$ RSD.
- System robustness was demonstrated over 132 consecutive injections with the mean recovery calculated from the 20 ng/L standard within the allowed 70–130%

tolerance for the entire analytical sequence, that corresponds to over 90 hours of continuous acquisition. Recovery values averaged 120% and 110% for 2-MIB and geosmin, respectively, with %RSD of calculated concentration 14.3 for 2-MIB and 11 for geosmin.

- The confirmation ion ratio remained robust and within a $\pm 20\%$ range across 132 consecutive injections.

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