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Analysis of volatile organic compounds in environmental samples

A collection of methods in accordance with U.S. EPA regulations

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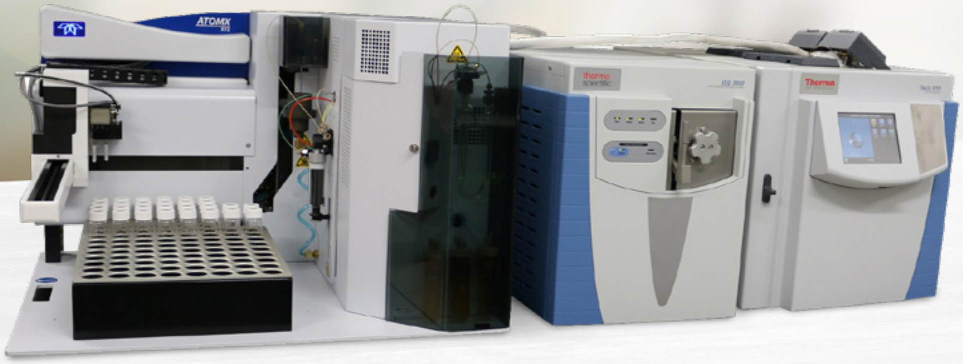
Introduction

Volatile organic compounds, or VOCs, contaminate our environment and cause negative health effects to humans when they are exposed to elevated levels. The testing of environmental samples for the presence of VOCs, including wastewater, drinking water and soil, is essential to ensure the public is safe and our environment is protected and preserved. Analytical environmental testing laboratories face a number of challenges when analyzing VOCs. Paramount is meeting all regulation criteria mandated by the United States Environmental Protection Agency (EPA). Failure to meet one requirement of regulatory methods can lead to entire sample batches failing. Laboratories are also challenged to maintain sample throughput to ensure holding times are not exceeded and important results are not delayed by instrument downtime, reanalysis of samples or inaccurate results. Additionally, pressure to reduce costs force laboratories to consider systems that provide automated operation, require minimum maintenance and are easily managed by technician-level staff.

Regulatory methods for analysis of VOCs in environmental samples are largely the same as they were twenty years ago. Only recently have updates been introduced that allow environmental labs to improve current approaches to VOC analysis. Mirroring the pace of regulatory updates, many environmental testing laboratories rely on outdated instruments because of their ability to meet regulatory method requirements with minimal interruption. Although this strategy has provided adequate productivity in the past, many of the workhorse instruments used today are approaching, or in, obsolescence now. The unavailability of spare parts, absence of support and degradation in performance after years of use creates risk for environmental testing labs whose accreditation and reputation depends on accuracy of sample analysis and availability of instrumentation for timely results reporting. Replacement of aging systems with updated technology provides labs with the ability to increase efficiency and possibly exceed current sample analysis volumes. Additionally, improved technology allows laboratories to take advantage of the flexibility provided by regulatory method updates, perhaps unlocking paths to quicker sample turnaround.

This eBook covers the most common EPA regulations and methods laboratories may employ to meet the challenges of VOC analysis for environmental samples. The technique used for each of these methods utilizes the Teledyne Tekmar Atomx XYZ Purge & Trap (P&T) coupled with the Thermo Scientific™ ISQ™ 7000 GC-MS system and the Thermo Scientific™ TRACE™ 1310 Gas Chromatograph. The Atomx XYZ has several features, including an efficient trap-cooling design for increased sample capacity and moisture control which reduces peak interference and increases consumable life span. The ISQ 7000 VPI removes the daily challenges of environmental laboratories by demonstrating sensitivity that not only meets regulatory requirements, but exceeds them. The ISQ 7000 can also be operated continuously with little user intervention due to automated system readiness with SmartTune as well as inherent robustness. Moreover, when maintenance is required, downtime is eliminated thanks to VPI which allows for the vent-free source removal and analytical column exchange. This means that the system can be up and running again in minutes, not hours. The entire system is controlled by the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, which is easy to set up using eWorkflows which contain a complete template for the methods including data acquisition, process and reporting.



Teledyne Tekmar Atomx XYZ P&T coupled with the ISQ 7000 single quadrupole MS system and the TRACE 1310 Gas Chromatograph

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Purge and trap theory

Broadly speaking, purge and trap is a technique that extracts VOCs from a matrix. After extraction, the VOCs are then concentrated and injected into the Gas Chromatograph (GC) for separation and detection. Consider the case of Figure 1, a sample sealed in a closed vial. Above the sample is a vapor space, which is usually referred to as the headspace. If you allow the sample sufficient time, VOCs in the sample will migrate into the vapor space. After a certain period at a constant temperature, the concentration of the volatile compounds in each phase will be stabilized and the chemical system will have reached equilibrium. At this point, a portion of the headspace can be removed and injected into the GC for analysis. This technique is known as static headspace theory. The amount of material in the vapor phase will be proportional to the partial pressure of the component.

The theory of purging and sweeping the sample with an inert gas, shown in Figure 2, called dynamic headspace theory, sounds simple, but it is a very complex process. Purging a sample to extract analytes is a gas extraction. When purging a sample, the system is no longer at equilibrium. This is because the VOCs that move into the gaseous phase are constantly being removed by the purge gas. Continuously replacing the headspace causes a disequilibrium, due to the higher concentration of VOCs in the liquid phase than in the gaseous phase which creates a net movement of VOCs from liquid to gas, thus, extracting the VOCs from the sample more efficiently and improving sensitivity. Subsequently, the gas is swept away onto the trap where it is then concentrated and released to the GC.

There are many factors that affect the efficiency of this extraction. These factors include vapor pressure, temperature, solubility, type of purge method, and purge volume. Compounds that have a higher vapor pressure will have a higher purge efficiency. An increase in temperature always increases purge efficiency of the VOCs, but the amount of water placed onto the trap doubles for each 10 °C rise in temperature. The more soluble the VOC is in the sample matrix (e.g., water), the harder it will be to remove it from the matrix, thereby reducing purge efficiency. How the inert purge gas is introduced to the sample will influence the purge efficiency as well. The dispersion of many small bubbles will be more efficient than larger bubbles because there will be more surface area interaction between the gas and liquid which facilitates a transfer of VOCs to the gaseous phase. Lastly, an increase in the amount of inert gas purging the sample will improve the purge efficiency, but too much volume will result in breakthrough in the trap, which could result in decreased compound response.

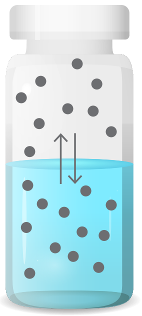


Figure 1. Static headspace theory

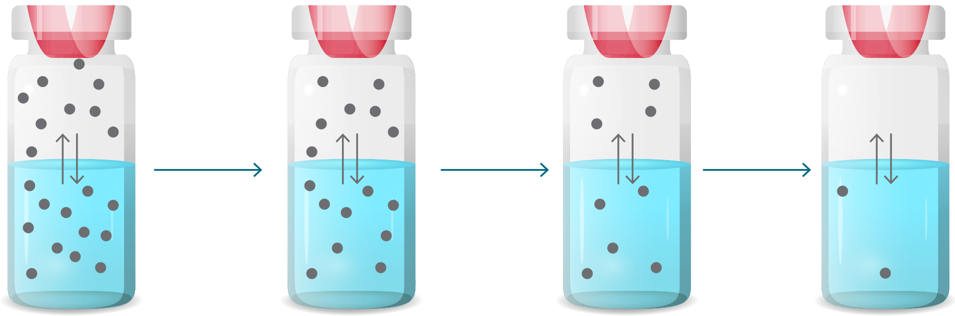


Figure 2. Dynamic headspace theory

Purge and trap technique

A basic purge and trap consists of five main parts: sparger, flow control, 6-port valve, analytical trap and heated transfer line. The sparger is the glassware on the front of the instrument that receives the liquid sample to be purged. Purging the sample extracts the VOCs by dispersing inert gas through the sample matrix for a preset time and flow. This flow is controlled by a mass flow controller or a pressure regulator that monitors and precisely controls the gas flow rate throughout the entire purge and trap process. From there, the 6-port valve directs the gas containing the analytes to the analytical trap for concentration. The 6-port valve is a two-position valve that routes the purge and trap concentrator flows according to each mode of operation. By back flushing carrier gas through the analytical trap, the 6-port valve directs the VOCs to the GC for separation and detection.

The analytical trap is used to enrich and quickly release VOCs swept out of the sample by the purge gas. Trapping the VOCs helps create a narrower injection band of analytes to the GC column, producing sharper peaks with greater signal/noise ratios and lower area/height ratios for better sensitivity and resolution. Once VOCs are captured, the trap is rapidly heated causing the VOCs to desorb. Carrier gas is used to sweep the desorbed VOCs off the analytical trap and carry them through the heated transfer line to the GC. The heated transfer line is the inert piece of tubing that runs down the center of the transfer line heater to ensure the VOCs are transferred to the GC column and stay in their gaseous state.

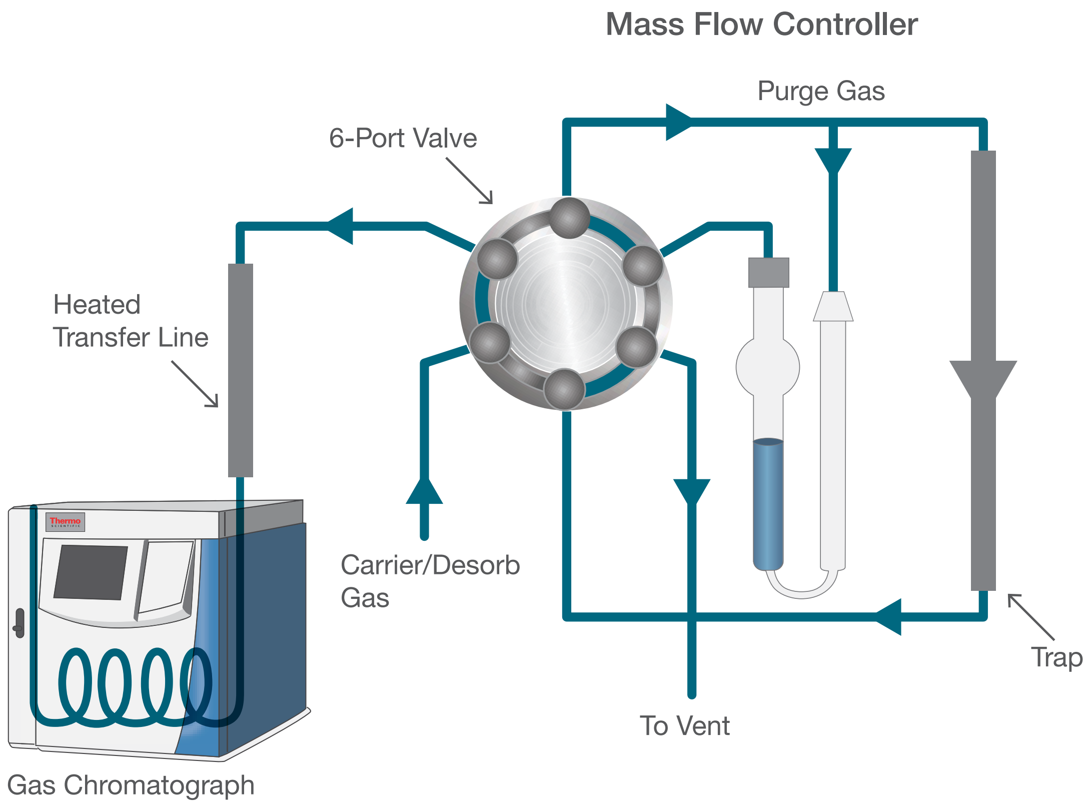
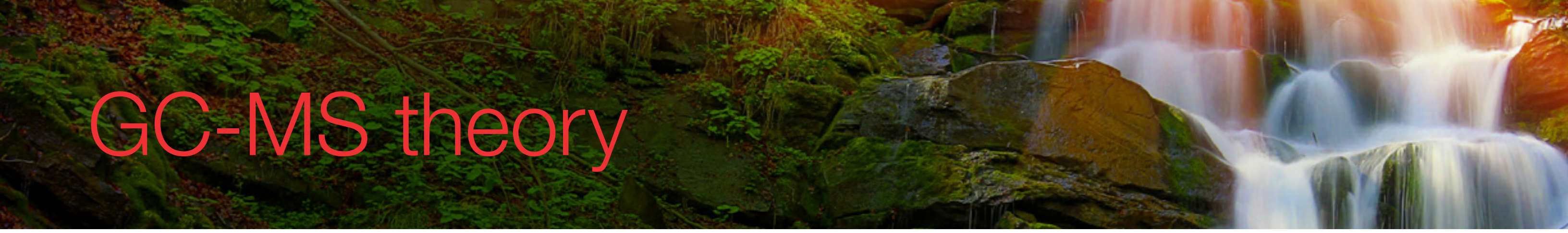


Figure 3: A general purge and trap schematic



GC-MS theory

The ISQ 7000 is a single quadrupole GC-MS system. After the samples are introduced via the purge and trap, the compounds are separated in the GC column via different interactions with the stationary phase under a temperature gradient. The compounds are propelled by the carrier gas and as they become separated, they elute from the column at different times, which is generally referred to as their retention times. These separated compounds then enter the mass spectrometer.

The most common ionization technique used in all of the methods in this eBook is electron impact ionization (EI). This process involves gas phase molecules being bombarded with an electron beam generated by a filament (at 70 eV) and these collisions cause the neutral molecules to produce positively charged ions or fragments. The positive ions are transferred under an electrical field to the mass analyzer which separates them based on their mass-to-charge ratio (*m/z*). A detector at the exit of the mass analyzer generates the mass spectra. The advantage of EI is the production of reproducible spectra which can be searched against MS libraries (e.g., NIST) for elucidation, which enables confirmation of the presence of a compound software feature for elucidation, which enables confirmation of the presence of a compound.

The single quadrupole GC-MS system is operated in full-scan modes for the methods in this eBook. A mass range of interest, for example, 30 to 350 *m/z* is analyzed. In order to produce the full-scan spectrum, the quadrupole scans by alternating the DC voltage across the rod pairs. The detector records all the masses selected at their relative abundances and a full-scan chromatogram and mass spectra are produced. Using the software, an ion of interest, which is normally one of high abundance in a compound, can be selected and used for quantitation.

➜ Additional information on GC-MS theory and applications can be found in the Thermo Fisher Scientific Learning Center.

1. Optional Vacuum Probe Interlock (VPI) enables NeverVent technology
2. Unique Dual Filament design for extended operation and lifetime
3. Solid, homogeneous non-coated, non-heated maintenance-free quadrupoles
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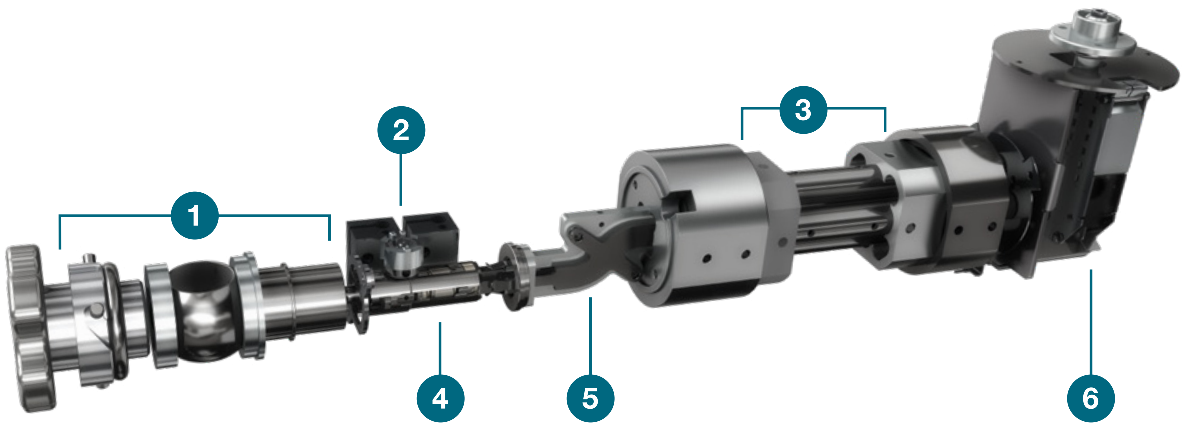
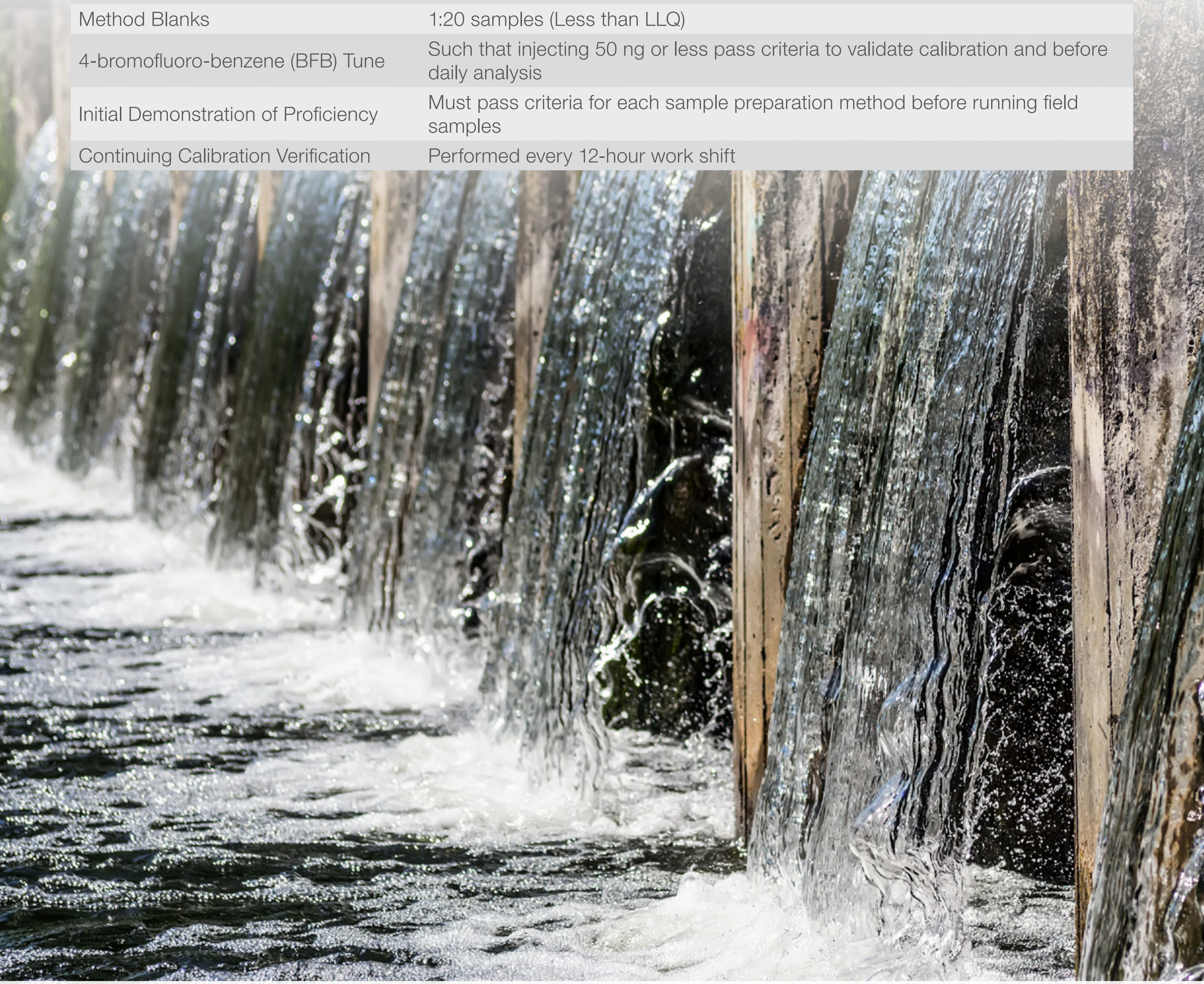


EPA Method 8260C

EPA	8260C
Matrix	Water, soil and solid waste matrices
Compounds	Volatile Organic Compounds
Number of Compounds	111
Calibration	Calculated response factors ±20% RSD, only <10% of analytes can use a linear calibration with R^2 ≥0.99
Initial Calibration Verification (ICV)	±30% mean value
Min. Response Factor (RF) %	49 total compounds; varies from 0.1 to 0.6 depending on the target compound
Method Detection limits (MDLs)	LLOQ ≥lowest calibration curve point. Verification 0.5–2x>LLOQ
Method Blanks	1:20 samples (Less than LLQ)
4-bromofluoro-benzene (BFB) Tune	Such that injecting 50 ng or less pass criteria to validate calibration and before daily analysis
Initial Demonstration of Proficiency	Must pass criteria for each sample preparation method before running field samples
Continuing Calibration Verification	Performed every 12-hour work shift



Analysis of VOCs according to EPA Method 8260

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Goal

Demonstration of an analytical method that meets the requirements outlined in U.S. EPA Method 8260D utilizing U.S. EPA Methods 5030 and 5035 preparation methods for the quantitation of purgeable organic compounds (POCs) in wastewater and soil, using the Teledyne Tekmar Atomx XYZ purge and trap (P&T) system along with a Thermo Scientific™ ISQ™ 7000 Mass Spectrometry (MS) system coupled with a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC) and Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS). Method linearity, method detection limit (MDL), and Initial Demonstration of Capability (IDC) were assessed to evaluate method performance.

Introduction

Volatile organic compounds or VOCs are common in modern life and come from both human-made and natural sources, but the human-made sources of VOCs in populated and industrialized areas are the main contributors to environmental pollution. These VOCs are produced in the processing of, or as, paints, adhesives, petroleum products, pharmaceuticals, and refrigerants. Many of these compounds contaminate our environment today and cause negative health effects to humans when they are exposed to elevated levels. Analytical testing laboratories must monitor the environment to ensure the public is not exposed to elevated levels of VOCs. The latest version of EPA Method 8260—EPA Method 8260D—is used to monitor a variety of solid waste matrices for the presence of VOCs.

To perform EPA Method 8260, all method acceptance criteria must be achieved. These criteria include linearity <20% relative standard deviation (RSD), a minimum response factor (RF), and MDLs for a wide range of target compounds. The analytical method must produce consistent results and be reproducible from day to day, with a continuing calibration verification (CCV) analyzed every 12 hours while samples are being performed. As the method covers varying matrices, it is important that the performance criteria are met in all samples of interest.

The following evaluation describes the use of the ISQ 7000 mass spectrometer coupled to the Atomx XYZ P&T for EPA Method 8260.

Experimental

Sample preparation

A working 50 parts per million (ppm) (mg/L) calibration standard was prepared in methanol from Restek™ standards: 8260B MegaMix™, 8260B Acetate, California Oxygenates, VOA (Ketones), 502.2 Calibration Mix, Hexachloroethane, and 2-Chloroethyl Vinyl Ether. In total, the standard contained 96 compounds.

The water calibration curve was prepared from 0.2 to 200 parts per billion (ppb) (µg/L) for most compounds, while the soil calibration curve was prepared from 1 ppb to 200 ppb. The relative response factor (RF) was calculated for each compound using one of the four internal standards: pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Surrogate standards consisted of dibromofluoromethane, 1,2-dichloroethane-d_4, toluene-d_8, and 4-bromofluorobenzene. Internal and surrogate standards were prepared together in methanol from Restek standards at a concentration of 25 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 25 ppb.

Seven 0.5 ppb water standards and seven 1 ppb soil standards were prepared to calculate the MDL and precision of each compound. Seven 20 ppb water and soil standards were prepared for the assessment of the IDC, precision, and accuracy. A further forty 20 ppb standards were prepared for the assessment of method robustness. All calibration, MDL, precision, robustness, and IDC standards were analyzed with the Atomx XYZ conditions in Tables 1 and 2. GC-MS conditions are shown in Table 3.

Table 1 (part 1). Teledyne Tekmar Atomx XYZ water method parameters

Standby	**Variable**
Valve oven temp.	140 °C
Transfer line temp.	140 °C
Sample mount temp.	90 °C
Water heater temp.	90 °C
Sample vial temp.	20 °C
Soil valve temp.	100 °C
Standby flow	10 mL/min
Condensate ready temp.	45 °C
Purge ready temp.	40 °C
Purge	**Variable**
Sample equilibrate time	0.00 min
Pre-sweep time	0.25 min
Prime sample fill volume	3.00 mL
Sample volume	5.00 mL
Sweep sample time	0.25 min
Sweep sample flow	100 mL/min
Sparge vessel heater	Off
Sparge vessel temp.	20 °C
Pre-purge time	0.00 min
Pre-purge flow	0 mL/min
Purge time	11.00 min
Purge flow	40 mL/min
Purge temp.	20 °C
Condensate purge temp.	20 °C
Dry purge time	1.00 min
Dry purge flow	100 mL/min
Desorb	**Variable**
Methanol needle rinse	Off
Methanol needle rinse volume	0.00 mL
Water needle rinse volume	7.00 mL
Sweep needle time	0.25 min
Dry purge temp.	20 °C
Desorb preheat temp.	245 °C
GC start signal	Begin Desorb
Desorb time	2.00 min
Drain flow	300 mL/min
Desorb temp.	250 °C

Table 1 (part 2). Teledyne Tekmar Atomx XYZ water method parameters

Bake	Variable
Methanol glass rinse	Off
Number of methanol glass rinses	0
Methanol glass rinse volume	0.00 mL
Water bake rinses	1
Water bake rinse volume	7.00 mL
Bake rinse sweep time	0.25 min
Bake rinse sweep flow	100 mL/min
Bake rinse drain time	0.40 min
Bake time	2.00 min
Bake flow	200 mL/min
Bake temp.	260 °C
Condensate bake temp.	200 °C
Trap	#9
Purge gas	Nitrogen

Table 2 (part 1). Teledyne Tekmar Atomx XYZ Soil method parameters

Standby	Variable
Valve oven temp.	140 °C
Transfer line temp.	140 °C
Sample mount temp.	90 °C
Water heater temp.	90 °C
Sample vial temp.	40 °C
Soil valve temp.	100 °C
Standby flow	10 mL/min
Condensate ready temp.	45 °C
Purge ready temp.	40 °C

Table 2 (part 2). Teledyne Tekmar Atomx XYZ soil method parameters

Purge	Variable
Pre-purge time	0.00 min
Pre-purge flow	0 mL/min
Pre-heat mix speed	Slow
Sample pre-heat time	0.00 min
Pre-sweep time	0.25 min
Water volume	10.00 mL
Sweep water time	0.25 min
Sweep water flow	100 mL/min
Sparge vessel heater	Off
Purge mix speed	Medium
Purge time	11.00 min
Purge flow	40 mL/min
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
Desorb	**Variable**
Methanol needle rinse	Off
Methanol needle rinse volume	0.00 mL
Water needle rinse volume	7.00 mL
Sweep needle time	0.25 min
Desorb preheat temp.	245 °C
GC start signal	Begin Desorb
Desorb time	2.00 min
Drain flow	300 mL/min
Desorb temp.	250 °C
Bake	Variable
Bake time	2.00 min
Bake flow	400 mL/min
Bake temp.	280 °C
Condensate bake temp.	200 °C
Trap	#9
Purge gas	Nitrogen

Instrument control and data processing

Data were acquired, processed, and reported using Chromeleon CDS software, version 7.2. This software can control both the GC-MS system and the Tekmar Atomx XYZ P&T. This allows a single software to be utilized for the full workflow simplifying the instrument operation. Figure 1 shows the Chromeleon control of the Atomx XYZ P&T. The fully optimized method used within this application note is available for download as a Chromeleon eWorkflow™ via Thermo Scientific™ AppsLab. AppsLab contains all the parameters needed to acquire, process, and report the analytical data for EPA Method 8260.[2]

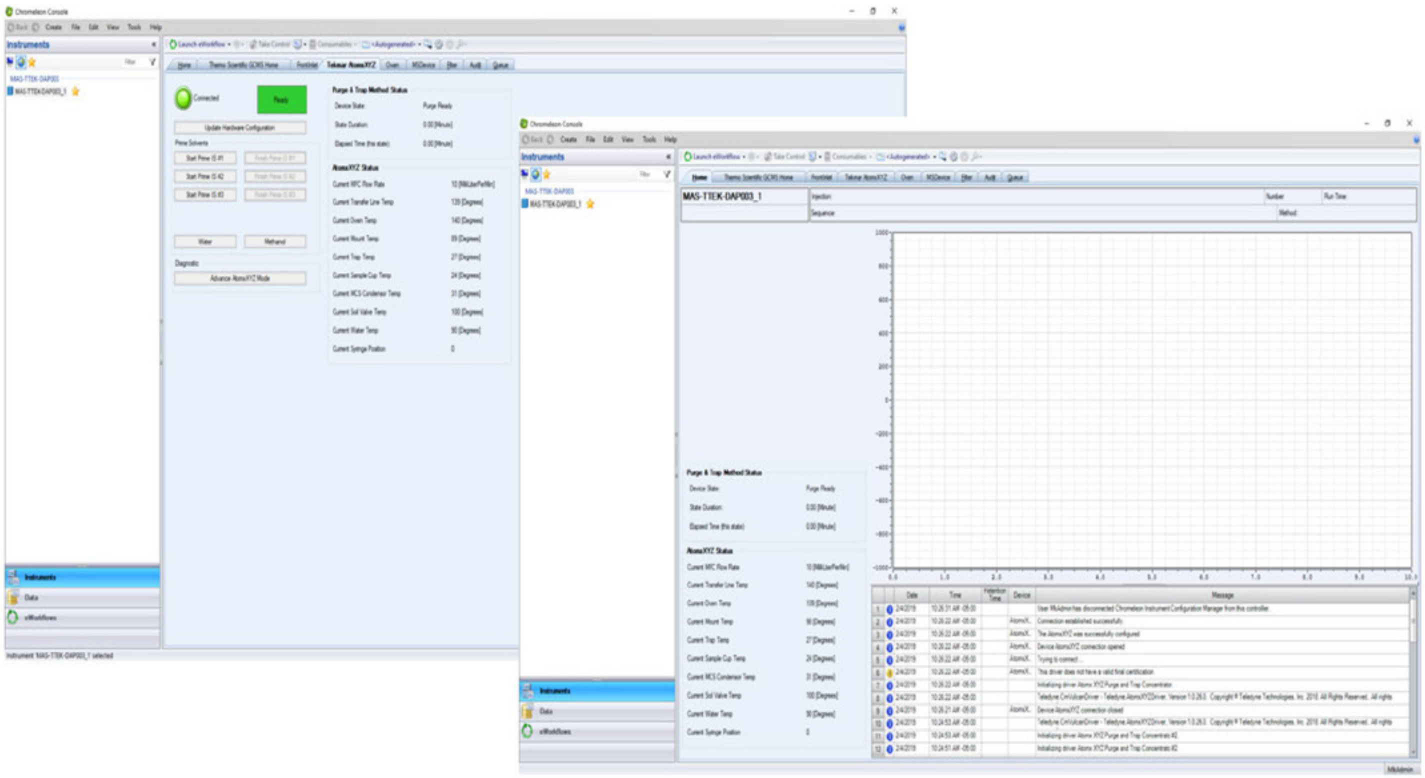

Figure 1. Chromeleon control of the Atomx XYZ P&T

GC-MS parameters

A TRACE 1310 GC was coupled to the ISQ 7000 system equipped with the Thermo Scientific™ NeverVent™ vacuum probe interlock (VPI) and a Thermo Scientific™ ExtractaBrite™ ion source. Expanded method parameters for the GC-MS system are displayed in Table 3.

Table 3. GC-MS conditions

TRACE 1310 GC	
Column	Thermo Scientific™ TraceGOLD™ TG-VMS GC, 20 m × 0.18 mm, 1 µm Film Helium: 1 mL/min
Oven profile	35 °C, 3 min, 12 °C/min to 85 °C, 25 °C/min to 225 °C, 2 min hold Run time: 14.767 min
Inlet	200 °C, 50:1 Split
ISQ 7000 MS	
Temp.	Transfer line: 230 °C Ion source: 280 °C
Scan	Range: 35–260 amu Solvent delay: 0.50 min Dwell/scan time: 0.15 s
Current	Emission current: 25 µA Gain: 3.00E+005

Results and discussion

Chromatography

Excellent chromatographic separation was achieved using the conditions described in Table 3. The chromatography was consistent and unaffected by matrix type showing consistent peak shape and separation. Figure 2 and Figure 3 display examples of chromatography for a 5 ppb VOC standard in water and soil samples, respectively.

Linearity and sensitivity

The water calibration curve was prepared from 0.2 to 200 ppb (µg/L) for all compounds, while the soil calibration curve was prepared from 1 to 200 ppb (µg/kg). The average response factor RSD for the calibration solutions was <20% for all compounds across the specified concentration range for water and soil calibration curves. The MDL and precision were assessed using n=7 replicates of a 0.5 ppb water standard and n=7 replicates of a 1 ppb soil standard. Calculated MDLs were <0.25 ppb and RSDs of calculated results were <10% for most compounds in both the soil and water matrices. Appendixes I and II display the information for the calibration curves and the calculated MDLs for water and soil, respectively.

Peaks:
59. Tetrachloroethylene
60. 4-Methyl-2-oentanone
61. *trans*-1,3-Dichloropropene
62. 1,1,2-Trichloroethane
63. Ethyl methacrylate
64. Dibromochloromethane
65. 1,3-Dichloropropane
66. 1,2-Dibromoethane
67. Butyl acetate
68. 2-Hexanone

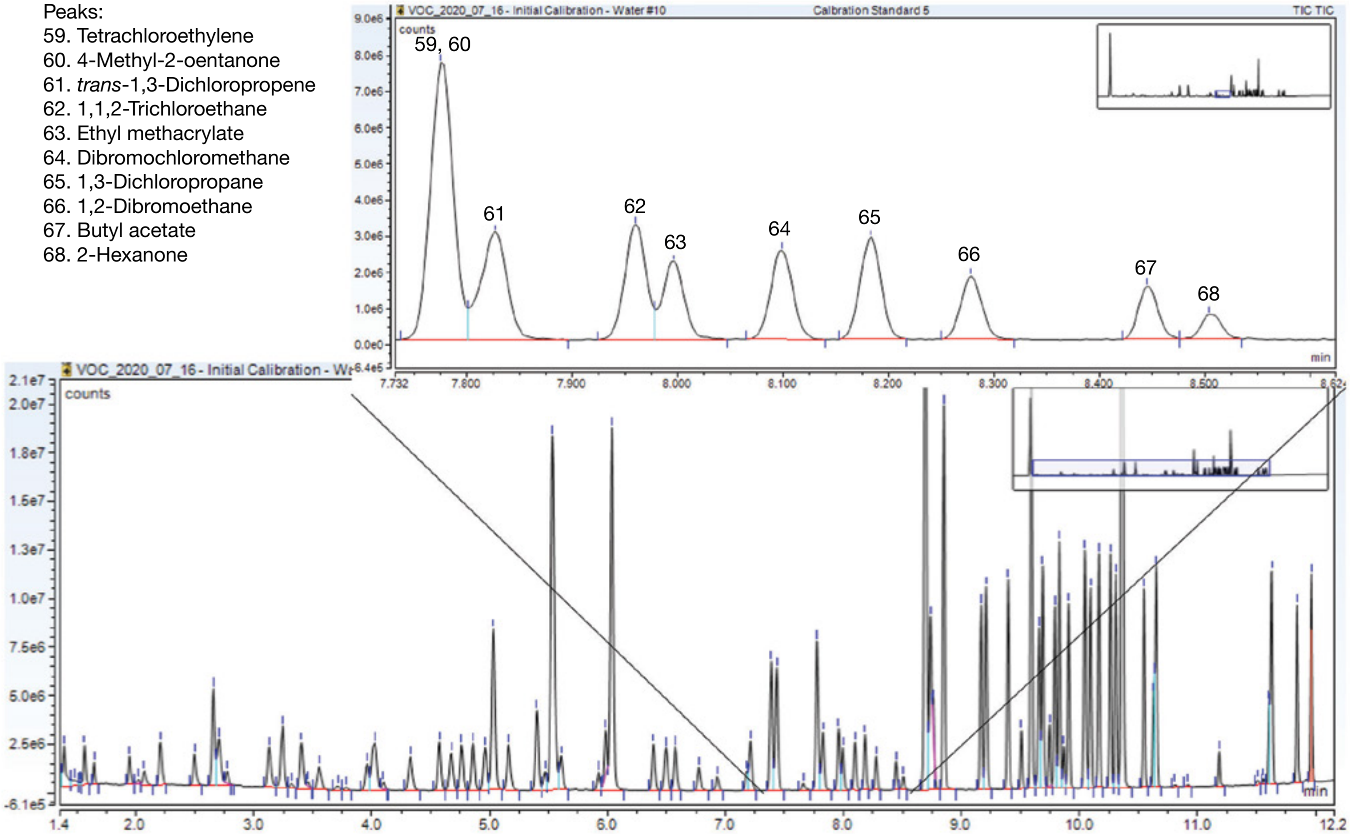

Figure 2. Total ion chromatogram (TIC) of a water method 5 ppb (µg/L) VOC standard with an inset indicating peak shapes and separation

Peaks:
77. Isopropylbenzene
78. Amyl acetate
80. 4-Bromofluorobenzene (Surr)
81. Bromobenzene
82. 1,3,5-Trimethylbenzene
83. *n*-Propylbenzene
84. 1,1,2,2-Tetrachloroethane
85. 2-Chlorotoluene
86. 1,2,3-Trichloropropane
87. *trans*-1,4-Dichloro-2-butene
88. *cis*-1,4-Dichloro-2-butene
89. 4-Chlorotoluene

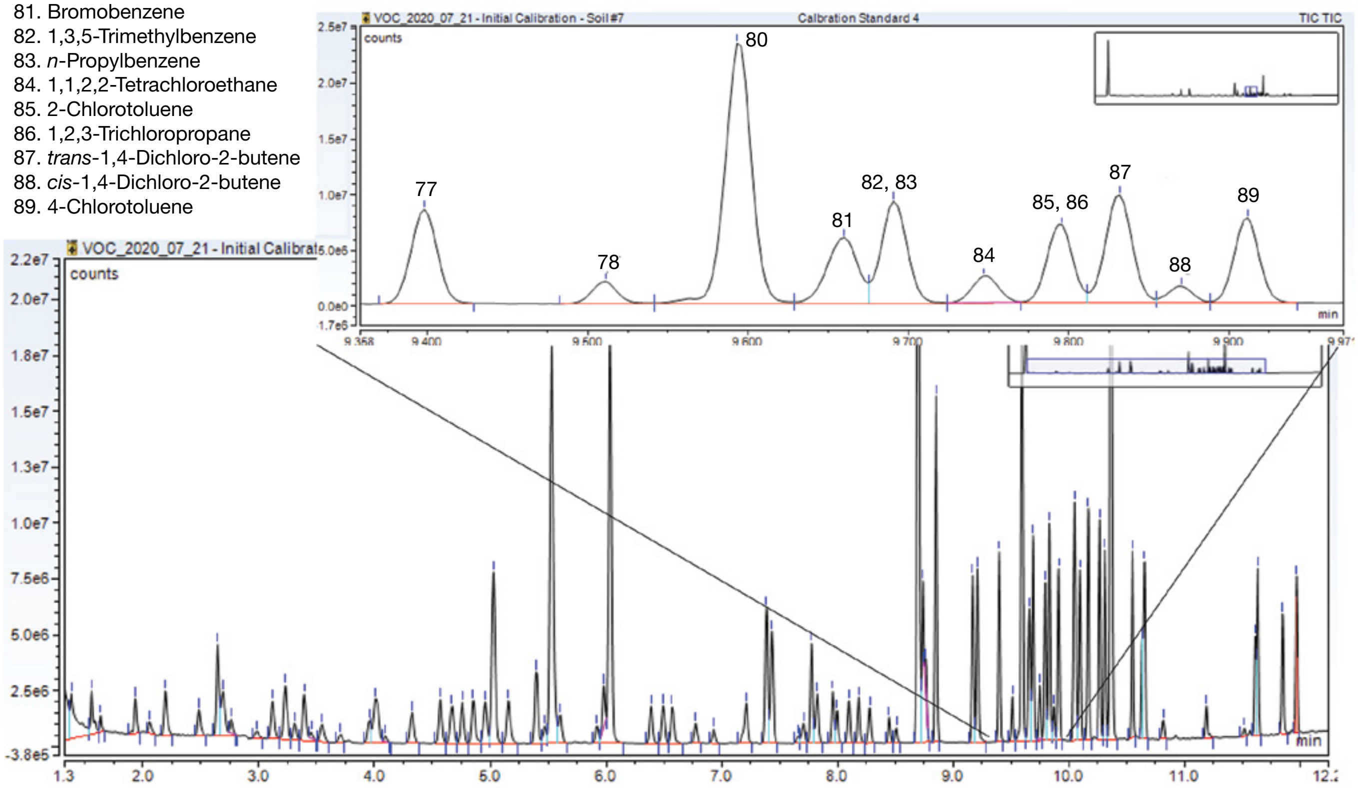

Figure 3. Total ion chromatogram (TIC) of a soil method 5 ppb (µg/kg) VOC standard with an inset indicating peak shapes and separation

Examples of the linearity for the water calibration curve for chloromethane and 1,2-dichlorobenzeneare are shown in Figures 4 and 5. These figures show the lowest point of the water calibration curve at 0.2 ppb, producing an excellent response, and the linearity of the curve giving R^2 value above 0.99 and average response factor RSD <20%. Figures 5 and 6 show similar data for the soil calibration for dibromomethane and styrene. The lowest point of the curve was 1 ppb, and even in soil, the peak response meets the regulatory requirements.

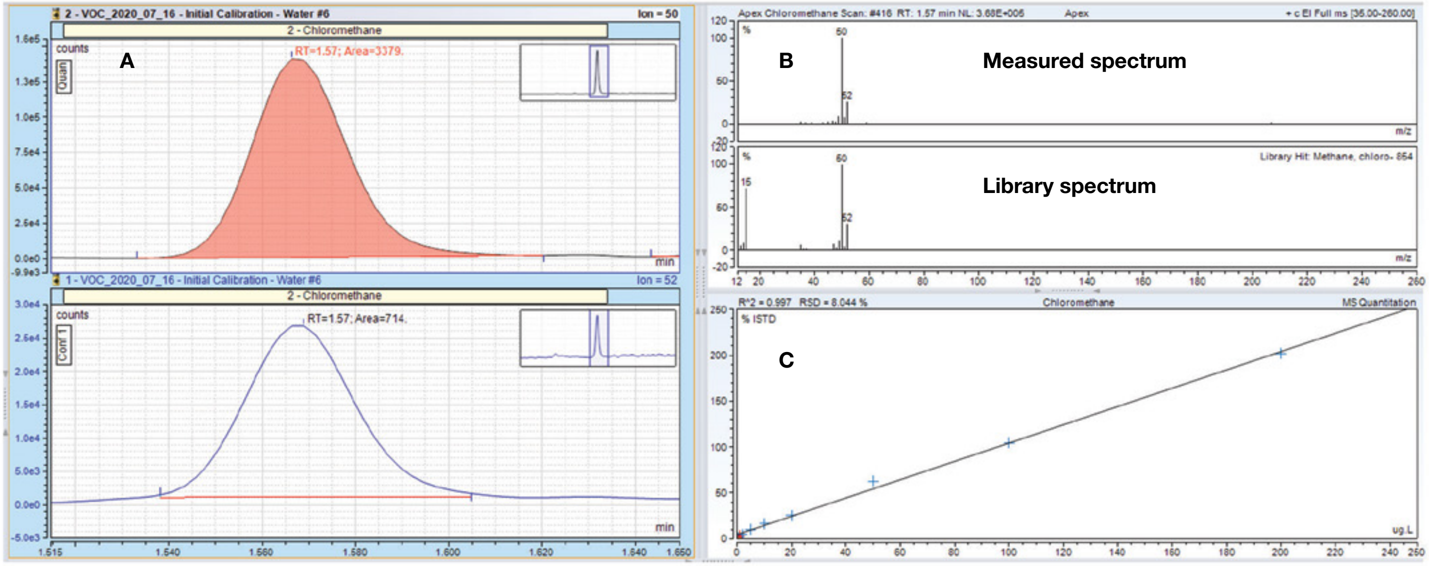

Figure 4. Chromeleon results browser showing extracted ion chromatograms for chloromethane in the 0.2 ppb water standard, quantitation ion and two confirming ions (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 0.2 ppb to 200 ppb (μg/L) (C)

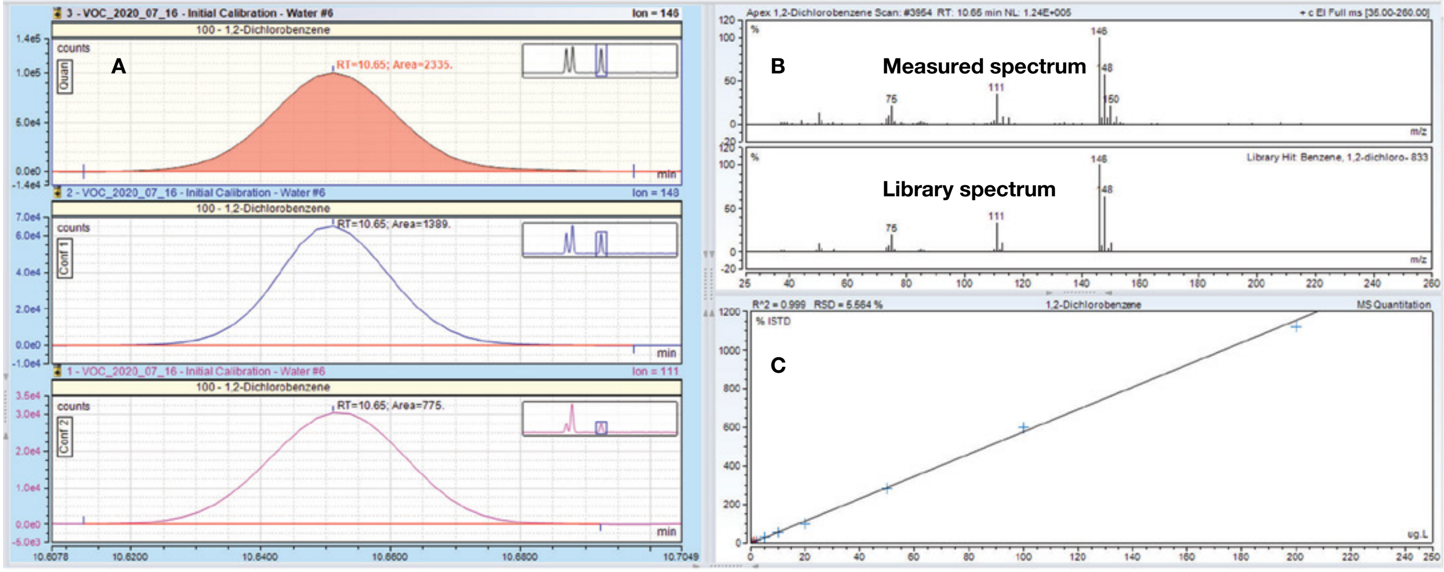

Figure 5. Chromeleon results browser showing extracted ion chromatograms for 1,2-dichlorobenzene in the 0.2 ppb water standard, quantitation ion and two confirming ions (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 0.2 ppb to 200 ppb (C)

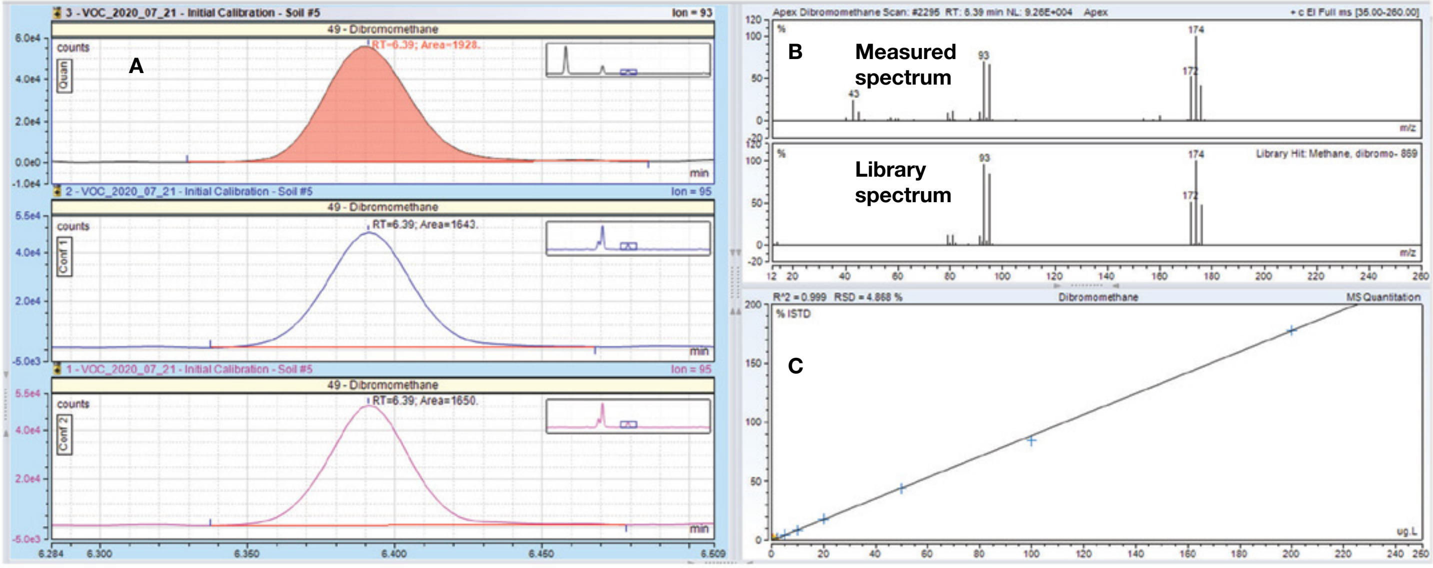

Figure 6. Chromeleon results browser showing extracted ion chromatograms for dibromomethane in the 1 ppb soil standard, quantitation ion and two confirming ions (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 1 ppb to 200 ppb (C)

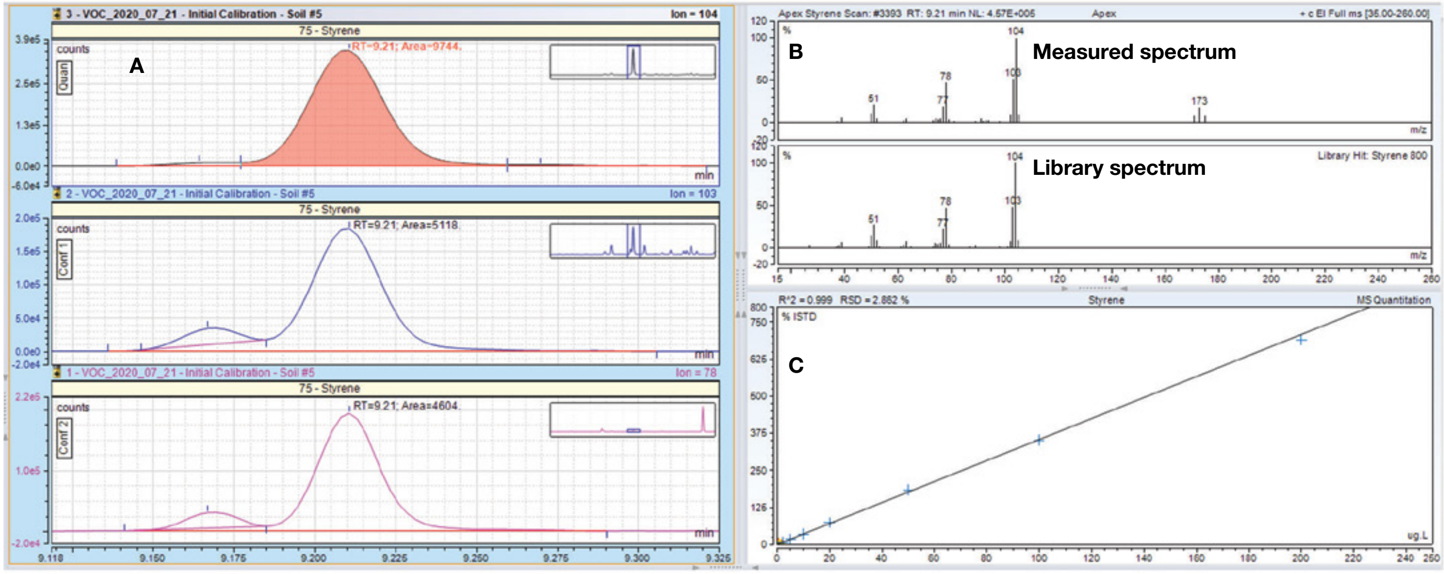

Figure 7. Chromeleon results browser showing extracted ion chromatograms for styrene in the 1 ppb soil standard, quantitation ion (*m/z* 104) and two confirming ions (*m/z* 103 and *m/z* 74) (A), a matching measured spectrum to the NIST library (B), and a linear response over a concentration range of 1 to 200 ppb (corresponding to µg/L) (C)

Precision and accuracy

Precision and accuracy were assessed by injection of n=7 replicates of a 20 ppb of matrix-matched standards. The results are displayed in Appendix I and Appendix II. For all compounds assessed, the %RSD of the calculated concentration is <20 and the mean recovery is within ±30% of the true value, meeting the requirements of EPA Method 8260 for IDC. In order to validate the quality control of the calibration curves, this IDC procedure must be completed and continuing calibration checks must be performed with samples to ensure data quality. Figure 8 shows a cross section of compounds of a representative soil standard at 20 ppb. The standard was prepared by spiking 5 mL of deionized water with standards with an in-vial purge representing a 5 g soil sample. This standard was used to demonstrate the accuracy and precision of the method.

Method robustness

For the analytical method to be used as a standard testing method, it is extremely important that it be stable and reproducible. To demonstrate this, 20 ppb standards (n=40) in water were injected at intervals over a 240-sample injection sequence over three days. The water standards were acquired with no user intervention at all on the P&T, GC, or MS system and the absolute peak areas were plotted to demonstrate the stability of the results. Figure 9 shows the reproducibility of seven of the compounds over 240 injections with excellent percentage RSDs. The accuracy and precision for all the compounds in the 240-injection series are shown in Appendix III.

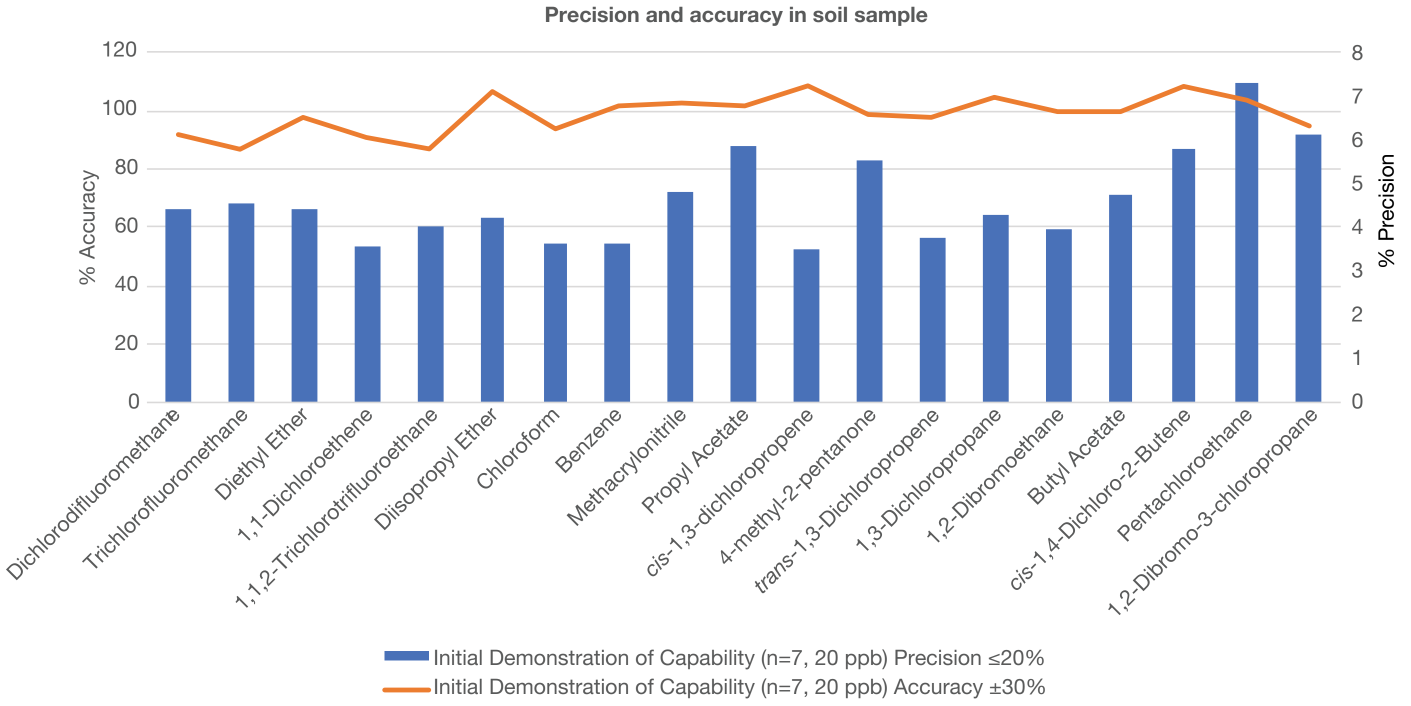

Figure 8. Demonstration of accuracy (% recovery) and precision (calculated concentration) by analyzing n=7 replicates of a 20 ppb soil standard

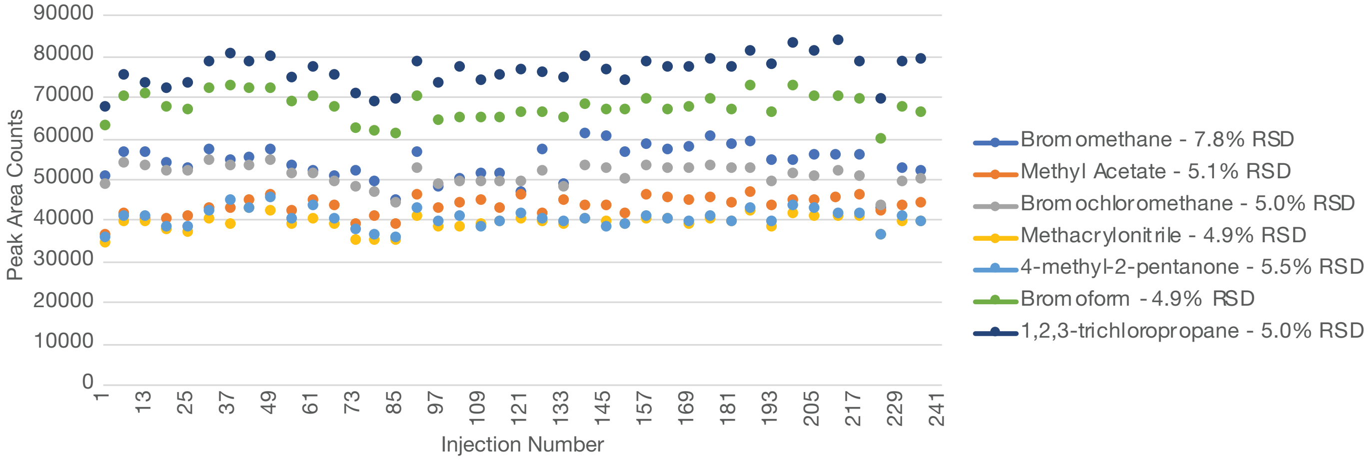

Figure 9. Repeatability (absolute peak area) of a 20 ppb water standard assessed over n=240 consecutive injections over three days of analysis

Conclusion

The combined analytical solution of the TRACE 1310 GC coupled with the ISQ 7000 system and the Atomx XYZ P&T system provides clear advantages for analytical testing laboratories that analyze environmental samples following the EPA Method 8260 requirements.

The experiments performed clearly demonstrate the suitability of this analytical configuration for the analysis of VOCs in various environmental samples in accordance with EPA Method 8260 with the following performance parameters as evidence:

- The modularity of the TRACE 1310 GC and the ISQ 7000 VPI and ExtractaBrite ion source allows users to easily service the injection ports and to exchange ionization sources and analytical columns without venting the mass spectrometer. This significantly reduces instrument downtime and minimizes sample analysis interruptions. 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.

- The ISQ 7000 VPI coupled with the Tekmar Atomx XYZ P&T exceeds all the requirements outlined in EPA Method 8260 for analysis of VOCs in wastewater and solid waste.

- MDLs calculated from n=7 repeat injections of 0.5 ppb water standards and n=7 analyzed of 1 ppb soil standards showed no interference from unwanted water entering the system and resulted in values <0.25 ppb for most compounds.

- Precision and accuracy for n=7 20 ppb water standards showed excellent results with %RSD <20% with 100 of 103 compounds having <10% RSD and a mean recovery of 88% for the compounds.

- Precision and accuracy (assessed from n=7 repeat injections of a 20 ppb soil standard) showed excellent values with all compounds having %RSD <11% for the calculated concentration and recovery values between 76% and 117%, with an average recovery of 98%.

- System robustness was tested by continuously acquiring 240 injections of environmental samples over three days with no user intervention at all. The average %RSD of the calculated concentration was 8.30% with an average compound recovery of 90%.

- Combined, these technologies effectively address the challenges of routine VOC analysis in environmental samples and provide a robust, sensitive solution needed for ensuring maximized instrument output and regulatory method compliance.

- Further information on VOC analysis using the ISQ 7000 system and the Atomx XYZ P&T can be found in the Thermo Scientific AppsLab library.[2]

References

1. United States Environmental Protection Agency, Method 8260D Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry. https://www.epa.gov/sites/production/files/2017-04/documents/method_8260d_update_vi_final_03-13-2017.pdf
2. Thermo Scientific AppsLab Library. https://appslab.thermofisher.com/
3. Thermo Scientific Application Note 65632: Routine analysis of volatile organic compounds in drinking water with ISQ 7000 GC-MS, https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-65632-gc-ms-volatile-organic-compounds-drinking-water-an65632-en.pdf

Appendix

Appendix I (part 1). Calibration, MDL, and IDC results for wastewater

Compounds	Calibration (0.5–200 ppb)			Method detection limit (n=7, 0.5 ppb)		Initial Demonstration of Capability (n=7, 20 ppb)	
	Ret. Time (min)	Linarity (%RSD)	Avg. RF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Dichlorodifluoromethane[1,9]	1.39	0.998	0.266	0.10	8.9	7.8	66
Chloromethane[1,5,7]	1.57	0.994	0.628	0.20	9.2	6.3	84
Vinyl chloride	1.65	8.76	0.218	0.13	9.9	6.1	79
Bromomethane[4,7]	1.95	19.0	0.268	0.18	7.7	4.9	78
Chloroethane	2.08	4.62	0.182	0.07	5.0	5.1	75
Trichlorofluoromethane	2.21	16.7	0.478	0.10	7.1	6.4	82
Diethyl ether	2.50	8.11	0.203	0.08	5.6	5.7	83
1,1-Dichloroethene	2.66	5.71	0.304	0.09	6.2	6.8	80
1,1,2-Trichlorotrifluoroethane	2.71	18.1	0.305	0.11	8.3	7.0	82
Iodomethane[1,6,8]	2.78	0.999	0.267	6.73	11.6	11.6	92
Allyl chloride	3.14	12.9	0.188	0.08	5.8	4.9	80
Carbon disulfide	3.14	12.2	0.187	0.08	5.6	4.8	81
Methylene chloride	3.24	19.0	0.506	0.10	6.3	3.4	79
trans-1,2-Dichloroethene	3.41	5.30	0.365	0.13	8.4	6.5	86
Methyl acetate	3.46	8.65	0.144	0.25	18.0	5.5	81
Methyl *tert* butyl ether	3.56	14.0	0.395	0.11	9.7	6.3	85
tert-Butyl alcohol	3.72	7.07	0.013	0.47	7.2	5.9	73
Acetonitrile[1,4,7]	3.78	0.999	0.047	0.74	4.3	7.9	94
Diisopropyl ether	3.96	8.89	0.388	0.09	7.5	5.0	83
Acrylonitrile	4.01	15.0	0.296	0.12	10.2	6.3	90
Chloroprene	4.01	15.2	0.296	0.12	9.9	6.3	90
Propionitrile	4.01	18.7	0.380	0.12	10.0	7.2	97
1,1-Dichloroethane	4.03	10.0	0.483	0.09	6.1	5.4	86
tert-Butyl ethyl ether	4.32	17.2	0.425	0.10	8.0	5.3	102
Vinyl acetate	4.33	15.4	0.283	0.07	10.3	8.9	90
cis-1,2-Dichloroethene	4.57	6.15	0.464	0.08	5.2	5.6	92
2,2-Dichloropropane	4.67	11.3	0.415	0.10	7.2	6.0	84
Bromochloromethane	4.76	3.47	0.213	0.08	6.4	4.8	75
Chloroform	4.86	2.42	0.606	0.07	5.1	5.3	74
Carbon tetrachloride	4.96	15.5	0.469	0.10	7.8	5.9	87
Methyl acrylate	5.02	16.8	0.143	0.08	7.1	5.9	83
Ethyl acetate	5.03	19.1	0.174	0.06	5.7	7.9	80
Dibromofluoromethane (surr)	5.03	6.38	0.260		2.1	9.2	96
1,1,1-Trichloroethane	5.04	11.8	0.509	0.09	6.9	15.1	90
Tetrahydrofuran	5.04	15.5	0.100	0.08	7.1	6.8	77
1,1-Dichloropropene	5.16	14.6	0.324	0.09	7.5	5.7	90
2-Butanone[3]	5.19	9.14	0.034	0.17	4.0	4.6	76
Benzene	5.40	4.39	1.14	0.08	6.4	6.1	85

Appendix I (part 2). Calibration, MDL, and IDC results for wastewater

Compounds	**Calibration (0.5–200 ppb)**			**Method detection limit (n=7, 0.5 ppb)**		**Initial Demonstration of Capability (n=7, 20 ppb)**	
	Ret. Time (min)	**Linarity (%RSD)**	**Avg. RF**	**MDL (ppb)**	**Precision (≤20%)**	**Precision (≤20%)**	**Accuracy (±30%)**
Methacrylonitrile	5.48	6.31	0.139	0.10	8.9	5.4	66
Pentafluorobenzene (ISTD)	5.53						84
1,2-Dichloroethane-d_4 (surr)	5.54	10.4	0.088		3.0	1.8	79
tert-Amyl methyl ether	5.56	9.82	0.396	0.08	6.2	4.6	78
1,2-Dichloroethane	5.61	7.29	0.482	0.12	8.2	5.3	75
Isobutanol[4,7]	5.68	13.3	0.008	2.1	14.3	7.2	82
Isopropyl acetate	5.93	17.9	0.354	0.06	4.1	5.8	83
Trichloroethene	5.99	10.6	0.438	0.11	8.8	7.4	80
1,4-Difluorobenzene (ISTD)	6.04						82
Dibromomethane	6.39	5.00	0.289	0.09	6.4	5.5	92
1,2-Dichloropropane	6.49	8.26	0.312	0.07	5.2	5.9	80
Bromodichloromethane	6.58	4.05	0.557	0.11	7.9	5.6	81
Methyl methacrylate	6.78	17.6	0.217	0.14	11.1	6.5	79
Propyl acetate	6.94	15.9	0.284	0.15	13.1	6.1	86
2-Chloroethyl vinyl ether	7.18	18.2	0.112	0.08	5.3	5.7	81
cis-1,3-Dichloropropene	7.21	9.53	0.434	0.04	3.8	4.8	85
Toluene-d_8 (surr)	7.39	2.69	0.345		1.9	1.1	73
Toluene	7.43	5.30	1.77	0.07	4.9	6.9	94
2-Nitropropane	7.66	11.6	0.085	0.10	6.1	5.7	83
Tetrachloroethylene	7.78	19.5	0.822	0.15	11.1	15.5	90
4-Methyl-2-pentanone	7.82	13.6	0.082	0.30	9.2	5.4	90
trans-1,3-Dichloropropene	7.83	17.0	0.494	0.09	7.2	6.0	97
1,1,2-Trichloroethane	7.96	11.7	0.277	0.08	6.4	6.1	86
Ethyl methacrylate	8.00	12.2	0.355	0.07	6.3	5.9	102
Dibromochloromethane	8.10	13.0	0.449	0.09	7.6	5.6	90
1,3-Dichloropropane	8.18	10.9	0.553	0.04	3.3	5.1	92
1,2-Dibromoethane	8.28	11.7	0.386	0.05	4.0	6.0	84
Butyl acetate	8.45	12.8	0.324	0.09	6.9	6.5	75
2-Hexanone	8.51	12.0	0.052	0.35	10.7	5.6	74
Chlorobenzene-d_5 (ISTD)	8.69						87
Chlorobenzene	8.70	4.14	1.25	0.09	6.0	6.2	83
Ethylbenzene	8.74	5.39	1.83	0.07	4.8	6.5	80
1,1,1,2-Tetrachloroethane	8.76	5.23	0.312	0.09	7.0	5.1	96
m,p-Xylene	8.85	7.21	0.634	0.18	6.9	7.4	90
o-Xylene	9.17	6.84	0.613	0.06	4.4	7.0	77
Styrene	9.21	6.48	0.996	0.09	7.7	6.3	87
Bromoform	9.22	9.40	0.290	0.08	7.3	7.1	81
Isopropylbenzene	9.40	9.90	1.48	0.07	5.8	7.4	86
Amyl acetate	9.51	7.03	0.329	0.06	5.4	7.8	80
4-Bromofluorobenzene (surr)	9.59	4.64	0.525		2.0	1.9	100

Appendix I (part 3). Calibration, MDL, and IDC results for wastewater

Compounds	Calibration (0.5–200 ppb)			Method detection limit (n=7, 0.5 ppb)		Initial Demonstration of Capability (n=7, 20 ppb)	
	Ret. Time (min)	Linarity (%RSD)	Avg. RF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Bromobenzene	9.66	6.00	0.942	0.10	7.4	6.8	87
1,3,5-Trimethylbenzene	9.69	13.7	0.092	0.19	16.0	7.5	92
n-Propylbenzene	9.69	12.0	2.30	0.08	6.8	6.6	90
1,1,2,2-Tetrachloroethane	9.75	7.56	0.444	0.12	9.4	5.6	83
2-Chlorotoluene	9.79	6.88	1.60	0.09	7.1	6.3	85
1,2,3-Trichloropropane	9.83	7.57	0.372	0.12	9.3	6.5	86
cis-1,4-Dichloro-2-butene	9.87	9.99	0.164	0.09	7.7	4.5	90
trans-1,4-Dichloro-2-butene	9.87	11.2	0.124	0.13	10.1	8.5	85
4-Chlorotoluene	9.91	8.64	1.56	0.09	7.6	6.7	89
Pentachloroethane	10.04	17.0	0.160	0.11	9.2	7.5	95
tert-Butylbenzene	10.05	12.9	1.69	0.14	11.5	6.1	92
1,2,4-Trimethylbenzene	10.09	18.8	1.61	0.10	7.6	6.6	113
sec-Butylbenzene	10.17	16.0	2.12	0.09	8.0	6.8	94
p-Isopropyltoluene[2]	10.26	17.3	1.76	0.09	7.5	6.6	115
1,3-Dichlorobenzene	10.31	5.59	1.47	0.08	5.9	6.6	84
1,4-Dichlorobenzene-d_4 (ISTD)	10.36						
1,4-Dichlorobenzene	10.37	6.68	1.57	0.09	6.9	6.2	82
n-Butylbenzene	10.55	17.7	1.48	0.11	7.9	6.8	113
Hexachloroethane	10.63	11.9	0.549	0.07	11.6	7.0	81
1,2-Dichlorobenzene	10.65	5.56	1.47	0.07	5.3	5.5	82
1,2-Dibromo-3-chloropropane	11.18	8.11	0.172	0.14	10.1	7.6	81
Nitrobenzene	11.56	12.0	0.022	0.14	9.0	7.2	71
Hexachlorobutadiene	11.61	8.19	0.064	0.14	10.8	7.6	84
1,2,4-Trichlorobenzene	11.63	8.94	0.972	0.12	8.1	6.5	85
Naphthalene	11.85	6.32	1.95	0.07	5.6	8.4	89
1,2,3-Trichlorobenzene	11.97	9.86	0.961	0.10	7.2	7.4	86

[1] Linear calibration
[2] Calibration range 0.5–200 ppb
[3] Calibration range 1.25–500 ppb
[4] Calibration range 2–200 ppb
[5] Calibration range 5–200 ppb
[6] Calibration range 10–200 ppb
[7] 5 ppb MDL
[8] 20 ppb MDL
[9] Compound displayed interference with the CO_2 peak during desorb

Appendix II (part 1). Calibration, MDL, and IDC results for solid waste

	Calibration (1–200 ppb)			Method detection limit (n=7, 1 ppb)		Initial Demonstration of Capability (n=7, 20 ppb)	
Compounds	**Ret. Time (min)**	**Linarity (%RSD)**	**Avg. RF**	**MDL (ppb)**	**Precision (≤20%)**	**Precision (≤20%)**	**Accuracy (±30%)**
Dichlorodifluoromethane[1]	1.39	0.999	0.192	0.19	5.9	4.4	92
Chloromethane[1,3]	1.56	0.993	0.471	0.59	3.2	5.1	117
Vinyl chloride	1.64	8.84	0.180	0.17	5.4	4.3	91
Bromomethane[1,3]	1.94	0.996	0.266	0.48	2.8	5.6	110
Chloroethane	2.06	7.97	0.142	0.23	6.6	4.9	97
Trichlorofluoromethane	2.20	6.73	0.444	0.17	5.9	4.6	87
Diethyl ether	2.49	4.17	0.156	0.22	6.7	4.4	97
1,1-Dichloroethene	2.64	6.85	0.270	0.11	3.8	3.6	91
1,1,2-Trichlorotrifluoroethane	2.69	4.88	0.292	0.14	5.2	4.0	87
Iodomethane[1,4,5]	2.77	0.996	0.467	3.39	4.6	4.6	116
Allyl chloride	3.12	5.09	0.156	0.11	3.3	4.1	96
Carbon disulfide	3.12	5.53	0.156	0.13	3.8	4.0	97
Methylene chloride	3.23	18.4	0.398	0.25	5.5	2.8	85
trans-1,2-Dichloroethene	3.39	3.73	0.344	0.09	2.9	4.0	95
Methyl acetate	3.46	7.91	0.135	0.51	13.3	3.0	92
Methyl *tert* butyl ether	3.55	2.27	0.333	0.17	5.8	4.0	101
tert-Butyl alcohol	3.78	7.40	0.028	1.95	9.0	5.6	95
Acetonitrile[1,2]	3.83	0.999	0.024	1.16	6.6	5.0	105
Diisopropyl Ether	3.96	2.94	0.319	0.15	5.0	4.2	106
Acrylonitrile	4.00	11.5	0.296	0.14	5.7	4.4	100
Chloroprene	4.00	12.0	0.297	0.13	5.4	4.5	100
Propionitrile	4.00	17.0	0.399	0.12	5.4	4.0	98
1,1-Dichloroethane	4.03	5.72	0.407	0.14	4.0	3.9	100
tert-Butyl ethyl ether	4.33	16.7	0.368	0.20	8.2	4.3	96
Vinyl acetate	4.33	1.92	0.285	0.10	3.6	9.5	103
cis-1,2-Dichloroethene	4.57	4.53	0.413	0.11	3.3	3.8	103
2,2-Dichloropropane	4.67	6.35	0.388	0.15	4.8	4.2	101
Bromochloromethane	4.76	5.22	0.163	0.09	2.9	3.3	87
Chloroform	4.86	5.48	0.493	0.19	5.7	3.6	94
Carbon tetrachloride	4.96	5.87	0.437	0.12	4.2	3.9	99
Methyl acrylate	5.02	7.60	0.144	0.31	9.2	5.6	111
1,1,1-Trichloroethane	5.03	4.64	0.463	0.12	3.9	3.7	102
Dibromofluoromethane (surr)	5.03	4.02	0.283		4.9	3.9	96
Ethyl acetate	5.03	8.35	0.202	0.32	9.7	4.1	101
Tetrahydrofuran	5.04	16.6	0.105	0.14	4.2	3.8	95
1,1-Dichloropropene	5.16	3.69	0.320	0.15	5.6	3.7	107
2-Butanone[1]	5.20	1.00	0.042	0.99	12.7	7.0	108
Benzene	5.40	4.13	0.984	0.12	4.0	3.6	102

Appendix II (part 2). Calibration, MDL, and IDC results for solid waste

	Calibration (0.5–200 ppb)			Method detection limit (n=7, 0.5 ppb)		Initial Demonstration of Capability (n=7, 20 ppb)	
Compounds	**Ret. Time (min)**	**Linarity (%RSD)**	**Avg. RF**	**MDL (ppb)**	**Precision (≤20%)**	**Precision (≤20%)**	**Accuracy (±30%)**
Methacrylonitrile	5.48	3.25	0.119	0.14	4.5	4.8	102
Pentafluorobenzene (ISTD)	5.53						
1,2-Dichloroethane-d$_4$ (surr)	5.54	10.4	0.076		1.5	2.3	108
tert-Amyl methyl ether	5.57	3.89	0.307	0.13	4.6	4.1	96
1,2-Dichloroethane	5.61	5.19	0.370	0.15	4.5	2.9	97
Isobutanol[2]	5.75	9.98	0.012	1.26	6.8	7.9	97
Isopropyl acetate	5.93	13.2	0.368	0.14	5.1	5.0	101
Trichloroethene	5.98	8.32	0.413	0.13	4.5	3.4	106
1,4-Difluorobenzene (ISTD)	6.03						
Dibromomethane	6.39	4.87	0.222	0.16	4.8	3.6	99
1,2-Dichloropropane	6.50	6.98	0.272	0.16	4.9	3.3	111
Bromodichloromethane	6.58	5.23	0.459	0.13	4.2	3.5	101
Methyl methacrylate	6.78	16.9	0.199	0.30	9.9	5.6	108
Propyl acetate	6.94	6.94	0.293	0.17	5.7	5.8	102
2-Chloroethyl vinyl ether	7.18	14.6	0.064	0.17	8.9	5.1	76
cis-1,3-Dichloropropene	7.21	3.76	0.358	0.16	5.8	3.5	108
Toluene-d$_8$ (surr)	7.39	3.72	0.346		1.2	1.5	97
Toluene	7.44	3.80	1.59	0.14	4.5	3.3	101
2-Nitropropane	7.66	13.5	0.094	0.24	7.1	5.4	94
Tetrachloroethylene	7.78	9.44	0.614	0.09	3.2	10.8	95
4-Methyl-2-pentanone	7.82	7.08	0.084	0.78	10.6	5.5	99
trans-1,3-Dichloropropene	7.83	15.0	0.424	0.07	2.8	3.7	98
1,1,2-Trichloroethane	7.96	3.07	0.226	0.16	5.2	4.2	105
Ethyl methacrylate	8.00	16.1	0.287	0.21	8.9	5.3	94
Dibromochloromethane	8.10	3.39	0.371	0.12	4.0	3.7	99
1,3-Dichloropropane	8.19	2.20	0.446	0.12	4.1	4.3	104
1,2-Dibromoethane	8.28	2.15	0.317	0.11	3.8	4.0	99
Butyl acetate	8.45	7.13	0.294	0.17	6.4	4.8	99
2-Hexanone	8.51	10.5	0.060	0.53	7.2	5.5	98
Chlorobenzene-d$_5$ (ISTD)	8.69						
Chlorobenzene	8.71	3.53	1.08	0.10	3.4	3.3	96
Ethylbenzene	8.74	5.06	1.64	0.08	2.8	2.8	98
1,1,1,2-Tetrachloroethane	8.76	5.11	0.250	0.15	5.4	3.3	95
m,p-Xylene	8.85	6.01	0.584	0.19	3.5	3.4	102
o-Xylene	9.17	4.85	0.549	0.12	4.5	4.1	95
Styrene	9.21	2.86	0.884	0.10	3.9	3.6	97
Bromoform	9.22	2.67	0.239	0.15	5.4	3.8	98
Isopropylbenzene	9.40	7.12	1.41	0.11	4.5	4.3	97
Amyl acetate	9.51	3.44	0.263	0.20	7.8	5.3	105
4-Bromofluorobenzene (surr)	9.60	3.38	0.543		1.8	2.2	99

Appendix II (part 3). Calibration, MDL, and IDC results for solid waste

Compounds	Calibration (0.5–200 ppb)			Method detection limit (n=7, 0.5 ppb)		Initial Demonstration of Capability (n=7, 20 ppb)	
	Ret. Time (min)	Linarity (%RSD)	Avg. RF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Bromobenzene	9.66	0.99	0.887	0.22	7.0	5.9	98
1,3,5-Trimethylbenzene	9.69	4.69	0.100	0.29	10.8	6.5	98
n-Propylbenzene	9.69	4.08	2.45	0.19	6.9	6.2	106
1,1,2,2-Tetrachloroethane	9.75	2.50	0.409	0.22	6.8	7.3	99
2-Chlorotoluene	9.80	3.58	1.56	0.20	6.5	5.4	102
1,2,3-Trichloropropane	9.84	2.30	0.350	0.25	7.7	6.4	103
cis-1,4-Dichloro-2-butene	9.87	8.91	0.129	0.24	8.9	5.8	108
trans-1,4-Dichloro-2-butene	9.87	4.15	0.116	0.23	8.1	4.6	105
4-Chlorotoluene	9.91	4.34	1.55	0.19	6.6	6.0	101
Pentachloroethane	10.05	8.18	0.169	0.16	6.2	7.3	104
tert-Butylbenzene	10.05	7.37	1.89	0.19	7.1	8.3	106
1,2,4-Trimethylbenzene	10.10	16.5	1.67	0.15	7.0	5.6	93
sec-Butylbenzene	10.17	7.73	2.37	0.17	6.8	6.5	112
p-Isopropyltoluene	10.27	15.2	1.94	0.13	6.5	5.5	97
1,3-Dichlorobenzene	10.31	1.63	1.39	0.22	7.2	5.1	92
1,4-Dichlorobenzene-d_4 (ISTD)	10.36						
1,4-Dichlorobenzene	10.37	4.68	1.44	0.23	7.6	5.8	86
n-Butylbenzene	10.55	14.5	1.63	0.16	6.9	6.1	97
Hexachloroethane	10.63	6.17	0.549	0.08	5.3	5.8	101
1,2-Dichlorobenzene	10.65	1.25	1.29	0.21	7.0	5.5	93
1,2-Dibromo-3-chloropropane	11.19	2.25	0.154	0.27	7.9	6.1	94
Nitrobenzene	11.57	13.9	0.020	0.27	8.6	8.1	66
Hexachlorobutadiene	11.61	4.69	0.077	0.23	8.0	6.1	84
1,2,4-Trichlorobenzene	11.63	8.02	0.824	0.22	7.5	5.8	79
Naphthalene	11.85	10.1	1.57	0.23	7.5	5.8	94
1,2,3-Trichlorobenzene	11.97	8.09	0.783	0.18	5.8	6.2	84

[1] Linear calibration
[2] Calibration range 2–200 ppb
[3] Calibration range 5–200 ppb
[4] Calibration range 10–200 ppb
[5] 20 ppb MDL

Appendix III (part 1). Repeatability of a 20 ppb VOC water standard assessed over n=240 consecutive injections for n=40 injections

Compounds	Analyte recovery n=40	
	Precision (%)	Accuracy (%)
Dichlorodifluoromethane[1]	10.4	55
Chloromethane	12.4	82
Vinyl chloride	11.8	87
Bromomethane	9.4	100
Chloroethane	10.7	93
Trichlorofluoromethane	12.8	85
Diethyl ether	8.2	106
1,1-Dichloroethene	11.6	84
1,1,2-Trichlorotrifluoroethane	13.0	79
Iodomethane	5.5	94
Allyl chloride	7.9	88
Carbon disulfide	7.9	89
Methylene chloride	10.7	111
trans-1,2-Dichloroethene	9.5	99
Methyl acetate	9.7	111
Methyl *tert* butyl ether	4.8	87
tert-Butyl alcohol	7.6	82
Acetonitrile	8.8	119
Diisopropyl ether	5.2	90
Acrylonitrile	11.8	92
Chloroprene	12.0	92
Propionitrile	11.9	95
1,1-Dichloroethane	9.3	106
tert-Butyl ethyl ether	4.4	88
Vinyl acetate	27.1	97
cis-1,2-Dichloroethene	6.9	100
2,2-Dichloropropane	15.7	74
Bromochloromethane	6.4	83
Chloroform	8.0	86
Carbon tetrachloride	11.7	88
Methyl acrylate	6.6	91
Ethyl acetate	7.9	98
Tetrahydrofuran	7.1	91
Dibromofluoromethane (surr)	2.3	100
1,1,1-Trichloroethane	11.0	91
1,1-Dichloropropene	11.5	88
2-Butanone	10.6	107
Benzene	8.8	93

Compounds	Analyte recovery n=40	
	Precision (%)	Accuracy (%)
Methacrylonitrile	8.2	103
Pentafluorobenzene (ISTD)		
1,2-Dichloroethane-d$_4$ (surr)	4.9	127
tert-Amyl methyl ether	4.5	81
1,2-Dichloroethane	8.1	113
Isobutanol	16.2	115
Isopropyl acetate	7.7	105
Trichloroethene	12.6	87
1,4-Difluorobenzene (ISTD)		
Dibromomethane	6.9	101
1,2-Dichloropropane	8.0	110
Bromodichloromethane	7.5	102
Methyl methacrylate	4.6	92
Propyl acetate	5.9	96
2-Chloroethyl vinyl ether	4.1	81
cis-1,3-Dichloropropene	4.5	91
Toluene-d$_8$ (surr)	1.4	103
Toluene	8.2	87
2-Nitropropane	6.0	101
Tetrachloroethylene	26.2	81
4-Methyl-2-pentanone	7.2	97
trans-1,3-Dichloropropene	4.5	96
1,1,2-Trichloroethane	8.3	106
Ethyl methacrylate	4.1	86
Dibromochloromethane	6.8	93
1,3-Dichloropropane	7.1	102
1,2-Dibromoethane	6.8	96
Butyl acetate	5.3	93
2-Hexanone	7.4	100
Chlorobenzene-d$_5$ (ISTD)		
Chlorobenzene	6.7	90
Ethylbenzene	8.6	89
1,1,1,2-Tetrachloroethane	7.9	87
m,p-Xylene	8.5	82
o-Xylene	7.4	71
Styrene	6.4	81
Bromoform	6.1	81
Isopropylbenzene	10.1	75

Appendix III (part 2). Repeatability of a 20 ppb VOC water standard assessed over n=240 consecutive injections for n=40 injections

Compounds	Analyte recovery n=40	
	Precision (%)	Accuracy (%)
Amyl acetate	7.6	89
4-Bromofluorobenzene (surr)	2.7	99
Bromobenzene	6.5	88
1,3,5-Trimethylbenzene	10.1	80
n-Propylbenzene	9.7	82
1,1,2,2-Tetrachloroethane	5.2	90
2-Chlorotoluene	7.4	78
1,2,3-Trichloropropane	6.1	97
cis-1,4-Dichloro-2-butene	4.1	90
trans-1,4-Dichloro-2-butene	4.3	90
4-Chlorotoluene	6.8	82
Pentachloroethane	11.5	83
tert-Butylbenzene	12.1	77
1,2,4-Trimethylbenzene	9.1	83

Compounds	Analyte recovery n=40	
	Precision (%)	Accuracy (%)
sec-Butylbenzene	10.8	80
p-Isopropyltoluene[2]	10.5	71
1,3-Dichlorobenzene	5.9	78
1,4-Dichlorobenzene-d_4 (ISTD)		
1,4-Dichlorobenzene	5.4	77
n-Butylbenzene	10.9	79
Hexachloroethane	8.4	76
1,2-Dichlorobenzene	5.2	76
1,2-Dibromo-3-chloropropane	4.3	73
Nitrobenzene	5.5	67
Hexachlorobutadiene	10.3	71
1,2,4-Trichlorobenzene	5.6	71
Naphthalene	5.8	71
1,2,3-Trichlorobenzene	4.2	78

[1] Compound displayed interference with the CO_2 peak during desorb

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Analysis of VOCs in soil using automated methanol extraction

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Keywords: EPA, VOCs, purge and trap, trace analysis, gas chromatography, single quadrupole mass spectrometry, selected ion monitoring, sensitivity, GRO, THM, environmental laboratories, automated extraction, analytical testing laboratories

Goal

Demonstration of the analysis of volatile organic compounds in soil according to U.S. EPA Method 5035 used in accordance with U.S. EPA Method 8260C. This method employs an automated methanol extraction with the Teledyne Tekmar Atomx XYZ purge and trap (P&T) system along with a Thermo Scientific™ ISQ™ 7000 Mass Spectrometry (MS) system coupled with a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC). Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software was used to fully control the analytical instruments as well as to acquire, process, and report the data. Method linearity, carryover, and Initial Demonstration of Capability (IDC) were assessed to evaluate method performance.

Introduction

It is essential to test for volatile organic compounds (VOCs) in soil due to their potential detrimental health effects on humans. Contaminated soil in which crops are grown and consumed by the populations can cause humans to be exposed to these harmful VOCs. Analytical testing laboratories must monitor soil contaminants to protect the public. U.S. EPA Method 5035 allows for two sample collection options that can be used in accordance with U.S. EPA Method 8260C.[1,2] The first option is to collect 5 grams (g) of soil into a pre-weighed vial containing a prescribed amount of a water miscible solvent (methanol). An aliquot of this sample is taken and purged using U.S. EPA Method 5030.[3]

The second option is to collect a bulk soil sample on site. Once back in the lab, the bulk soil is separated into individual sub-samples containing a water miscible solvent (methanol). Then an aliquot of the sample is taken and purged using U.S. EPA Method 5030.[3]

In this study, spiked baked sand samples were placed in a vial, methanol was added, and the sample agitated to release the VOCs for analysis. The Teledyne Tekmar Atomx XYZ P&T system along with a Thermo Scientific ISQ 7000 MS system coupled with a Thermo Scientific TRACE 1310 GC and Thermo Scientific CDS software were used for the analysis. Method linearity, carryover, and Initial Demonstration of Capability (IDC) were assessed to evaluate method performance.

Experimental

Sample preparation

A 1000 parts per million (ppm) or milligram per liter (mg/L) working calibration standard was prepared in methanol from a 9-compound Restek™ PVOC/GRO Mix (Wisconsin) standard. A 5-point methanol extraction calibration curve was prepared from 200 ppb to 1000 ppb (µg/L). The relative response factor (RF) was calculated for each compound using one of the four internal standards: pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Surrogate standards consisted of: dibromofluoromethane, 1,2-dichloroethane-d_4, toluene-d_8, and 4-bromofluorobenzene. Internal and surrogate standards were prepared together in methanol from Restek standards at a concentration of 25 ppm, after which 5 microliters (µL) were then mixed with each 5 mL sample for a resulting concentration of 25 ppb.

Seven, 5 g spiked baked sand samples were prepared for the IDC accuracy and precision calculations. Five grams of baked sand were weighed out and put in a 40 mL VOA vial with a stir bar. These replicates of baked sand were then spiked with the 1000 ppm PVOC/GRO Mix (Wisconsin) standard. The methanol extracted samples were then diluted 1:50 in 5 mL of DI water by the Atomx XYZ for a final concentration of 600 ppb. Atomx XYZ conditions for all calibration and IDC samples are found in Table 1. A Trace 1310 GC was coupled to the ISQ 7000 mass spectrometer equipped with the Thermo Scientific™ NeverVent™ vacuum probe interlock (VPI) and a Thermo Scientific™ ExtractaBrite™ ion source. Expanded method parameters for the GC-MS system are displayed in Table 2.

Table 1. Teledyne Tekmar Atomx XYZ method parameters

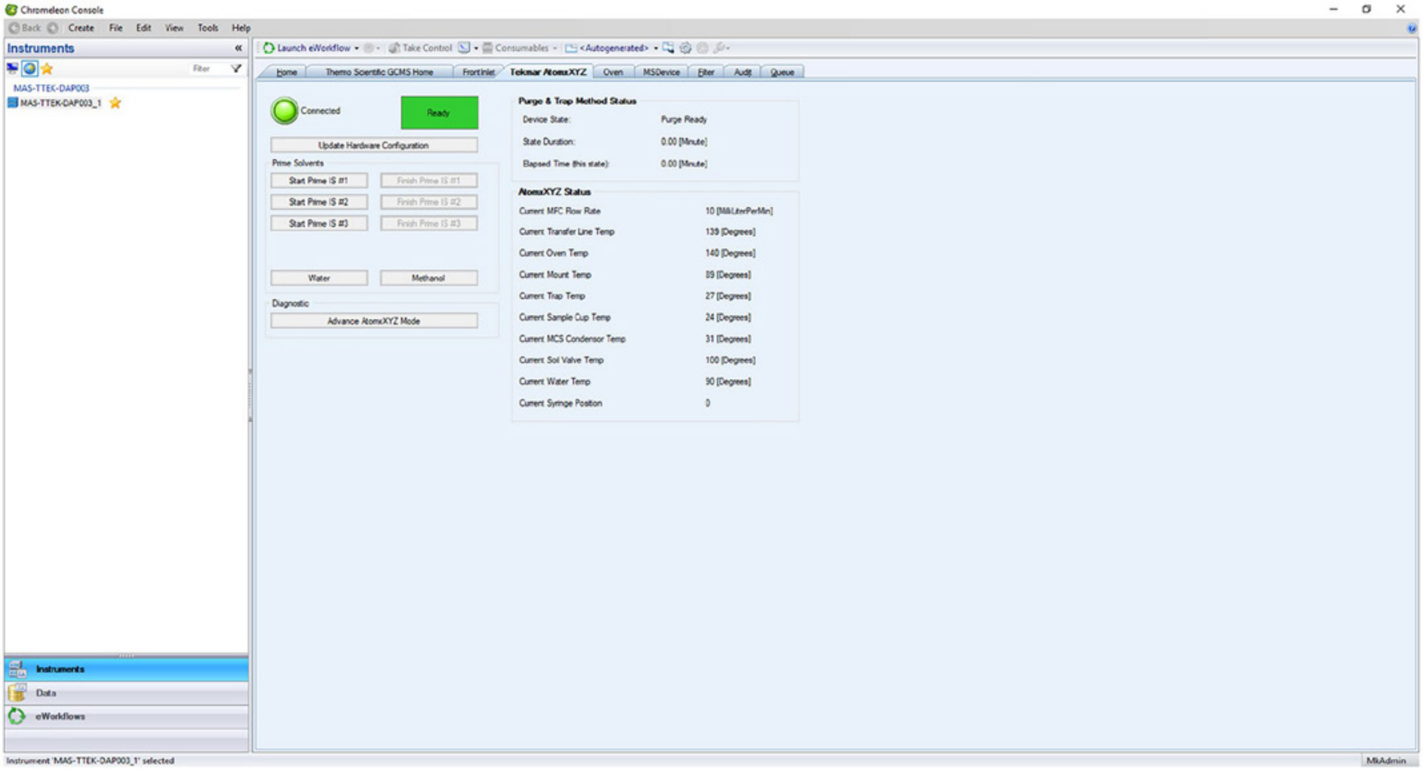
Standby	Variable
Valve oven temperature	140 °C
Transfer line temperature	140 °C
Sample mount temperature	90 °C
Water heater temperature.	90 °C
Soil valve temperature	100 °C
Standby flow	10 mL/min
Purge ready temperature	40 °C
Purge	**Variable**
Presweep time	0.25 min
Methanol volume	10.0 mL
Sparge vessel heater	Off
Sample mix speed	Medium
Sample mix time	2.00 min
Sample mix settle time	2.00 min
Sample sweep time	0.25 min
Sample sweep flow	100 mL/min
Purge time	11.00 min
Purge flow	40 mL/min
Purge temperature	20 °C
MCS purge temperature	20 °C
Dry purge time	1.00 min
Dry purge flow	100 mL/min
Dry purge temperature	20 °C
Desorb	**Variable**
Desorb	Variable
Methanol needle rinse	On
Methanol needle rinse volume	2.0 mL
Water needle rinse volume	7.0 mL
Sweep needle time	0.25 min
Desorb preheat temperature	245 °C
GC start signal	Begin desorb
Desorb time	2.00 min
Drain flow	300 mL/min
Desorb temperature	250 °C
Bake	**Variable**
Methanol glass rinse	On
Methanol glass rinse volume	3.0 mL
Number of methanol glass rinses	1
Number of water bake rinses	1
Water bake rinse volume	7.0 mL
Bake rinse sweep time	0.25 min
Bake rinse sweep flow	100 mL/min
Bake rinse drain time	0.40 min
Bake time	2.00 min
Bake flow	200 mL/min
Bake temperature	280 °C
MCS bake temperature	180 °C
Trap	9
Chiller tray	Off
Purge gas	Helium

Table 2. GC-MS conditions

Thermo Scientific TRACE 1310 GC conditions	
Column	Thermo Scientific™ TraceGOLD™ TG-VMS GC, 20 m × 0.18 mm, 1 µm film, P/N 26080-4950 Helium – 0.8 mL/min
Oven profile	35 °C, 3 min, 12 °C/min to 85 °C, 25 °C/min to 225 °C, 2 min hold Run time: 14.767 min
Inlet	200 °C, 50:1 split ratio Purge flow: 0.5 mL/min
SSL mode	Split
Split liner	1.2 mm ID, P/N 453A1335
O-ring	P/N MI-290AA1-0001
ISQ 7000 MS system conditions	
Temperature	Transfer line: 230 °C Ion source: 280 °C
Scan	Range: 35 amu to 260 amu Solvent delay: 0.50 min Dwell/scan time: 0.15 s
Gain	Emission current: 25 µA Detector gain: 3.00E+005

Instrument control and data processing

Data were acquired, processed, and reported using Chromeleon CDS software, version 7.2. This software can control both the GC-MS system and the Tekmar Atomx XYZ P&T. This allows a single software to be utilized for the full workflow, simplifying the instrument operation. Figure 1 shows the Chromeleon CDS control of the Atomx XYZ P&T. The fully optimized method used within this application note is available for download via Thermo Scientific™ AppsLab. AppsLab contains all the parameters needed to acquire, process, and report the analytical data for EPA Method 8260.[4]



Purge & Trap Method Status

Device State:	Purge Ready
State Duration:	0.00 [Minute]
Elapsed Time (this state):	0.00 [Minute]

AtomxXYZ Status

Current MFC Flow Rate	10 [MilliLiterPerMin]
Current Transfer Line Temp	139 [Degrees]
Current Oven Temp	140 [Degrees]
Current Mount Temp	89 [Degrees]
Current Trap Temp	27 [Degrees]
Current Sample Cup Temp	24 [Degrees]
Current MCS Condensor Temp	31 [Degrees]
Current Sol Valve Temp	100 [Degrees]
Current Water Temp	90 [Degrees]
Current Syringe Position	0

Instrument 'MAS-TTEK-DAP003_1' selected

Figure 1. Chromeleon control of the Atomx XYZ P&T

Results and discussion

Chromatography

Excellent chromatographic separation was achieved using the conditions described in Table 2. The chromatography was consistent and unaffected by the matrix, showing consistent peak shape and separation. Figure 2 displays a 200 ppb PVOC/GRO Mix (Wisconsin) (final concentration) standard spiked baked sand sample, methanol extracted and purged by the Atomx XYZ, indicating excellent peak resolution with minimal water interference of all VOCs.

Linearity and sensitivity

The 5-point methanol extraction calibration curve was prepared from 200 ppb to 1000 ppb (µg/L) for all compounds. The average response factor RSD for the calibration solutions was <20% for all compounds. Table 3 shows the calibration and IDC results. The IDC with precision and accuracy were assessed using seven individually extracted standard replicates of a 600 ppb (µg/L) soil standard.

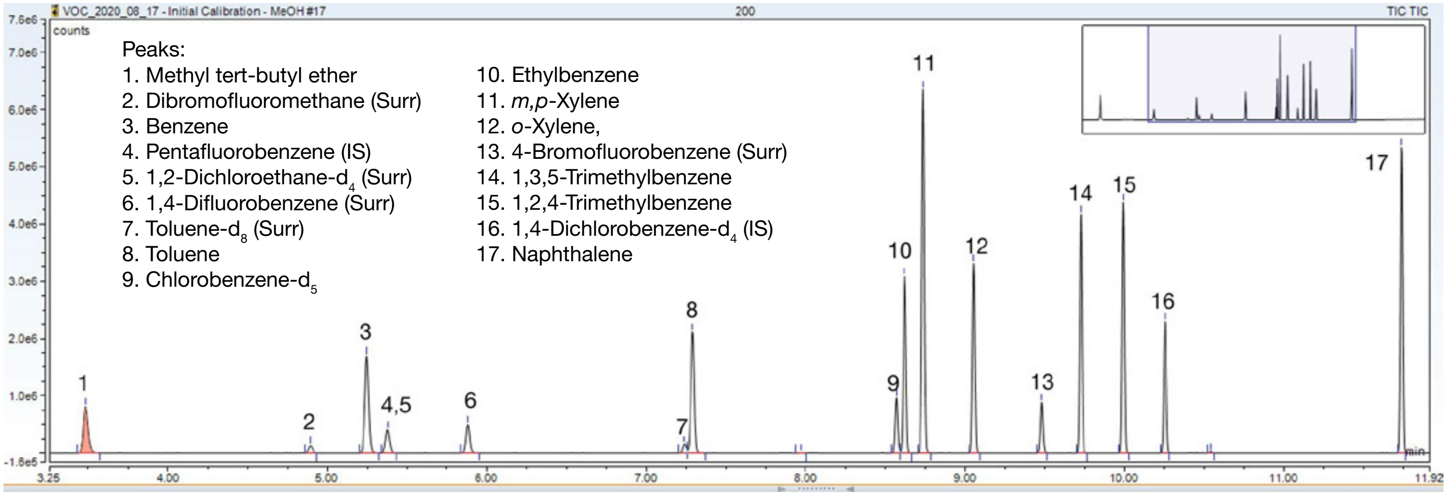


Figure 2. Total ion chromatogram of a methanol extracted 5 g spiked baked sand sample containing a final concentration of 200 ppb (µg/L) PVOC/GRO Mix (Wisconsin)

Table 3. Calibration and IDC results for soil samples

Peak name	Ret. time (min)	Quant ion (*m/z*)	Linearity (AvRF %RSD)	Avg RF	Precision ≤20%	Accuracy ±30%
Methyl tert-butyl ether	3.47	73	6.19	0.254	6.0	114
Dibromofluoromethane (Surr)	4.89	111	16.4	0.130	6.6	85
Benzene	5.25	78	10.3	0.346	4.4	91
Pentafluorobenzene (IS)	5.37	168	–	–	–	–
1,2-Dichloroethane-d$_4$ (Surr)	5.40	65	12.9	0.061	4.9	82
1,4-Difluorobenzene (IS)	5.88	114	–	–	–	–
Toluene-d$_8$ (Surr)	7.24	98	8.44	0.431	3.7	103
Toluene	7.29	91	8.84	0.628	6.1	104
Chlorobenzene-d$_5$ (IS)	8.57	117	–	–	–	–
Ethylbenzene	8.62	91	13.3	0.724	6.4	106
m,p-Xylene	8.74	106	13.8	0.304	8.0	103
o-Xylene	9.06	106	10.8	0.162	8.2	109
1-Bromo-4-fluorobenzene (Surr)	9.48	95	3.13	0.422	2.4	103
1,3,5-Trimethylbenzene	9.73	105	9.69	0.383	4.4	117
1,2,4-Trimethylbenzene	9.99	105	8.81	0.409	5.2	114
1,4-Dichlorobenzene-d4 (IS)	10.26	152	–	–	–	–
Naphthalene	11.74	128	13.6	0.537	6.8	105

Figure 3 shows a total ion chromatogram of (n=7 replicates) 1,2,4-trimethylbenzene in methanol extract of 5 g spiked baked sand sample at a final concentration of 600 ppb (µg/L) PVOC/GRO Mix (Wisconsin), displaying very good reproducibility with a 5.3% RSD and a 114% recovery.

Examples of the linearity for the soil calibration curve are shown in Figures 4 and 5. These figures show the lowest point of the water calibration curve at 200 ppb (equivalent to 200 µg/kg in matrix), producing an excellent response and an average response factor RSD <20%.

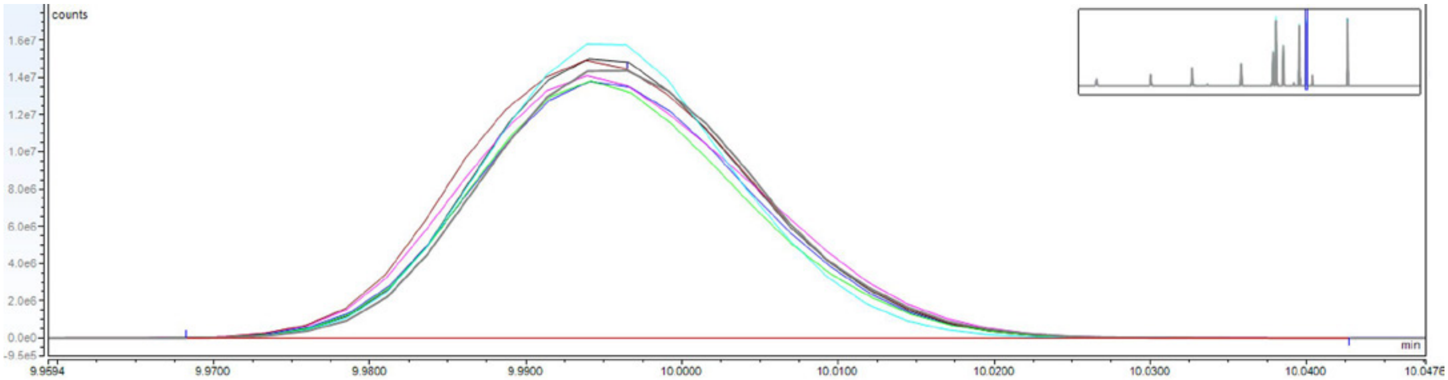


Figure 3. Total ion chromatogram of (n=7 replicates) of 1,2,4-trimethylbenzene in methanol extract of 5 g spiked baked sand sample, containing a final concentration of 600 ppb PVOC/GRO Mix (Wisconsin), displaying good reproducibility with a 5.3% RSD and a 114% recovery

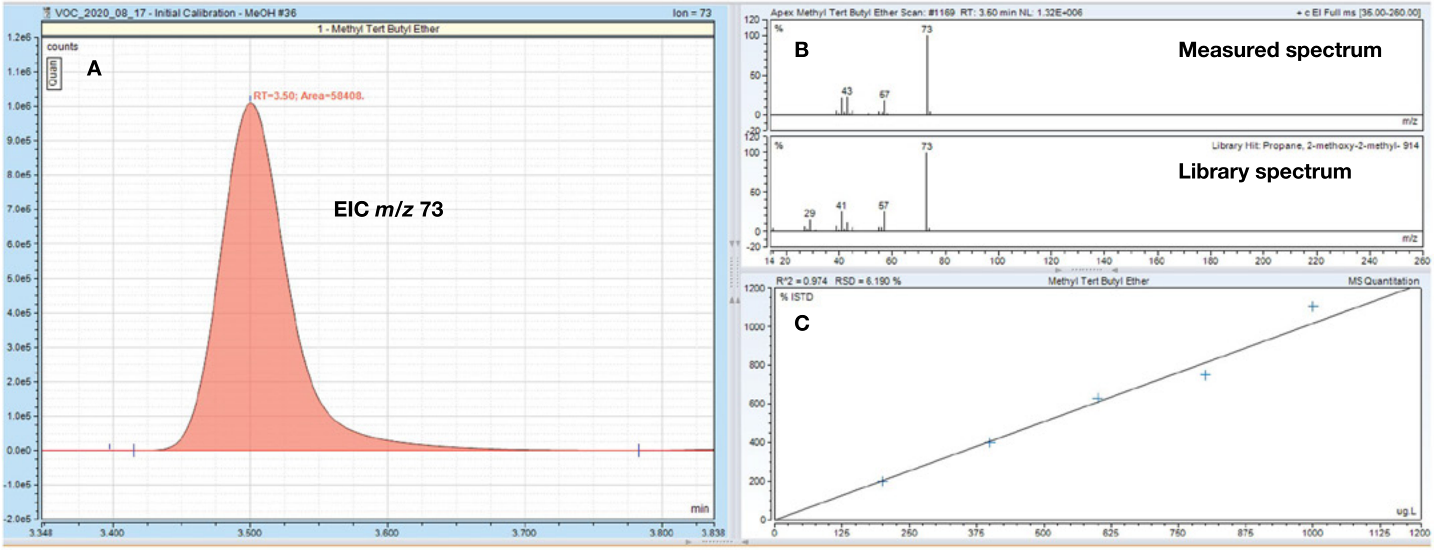


Figure 4. Chromeleon CDS results browser showing extracted ion chromatogram for methyl tert-butyl ether (MTBE) (*m/z* 73) in the methanol extract of 5 g baked sand sample containing a final concentration of 200 ppb PVOC/GRO Mix (Wisconsin) standard, quantitation ion (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 200 ppb to 1000 ppb(C)

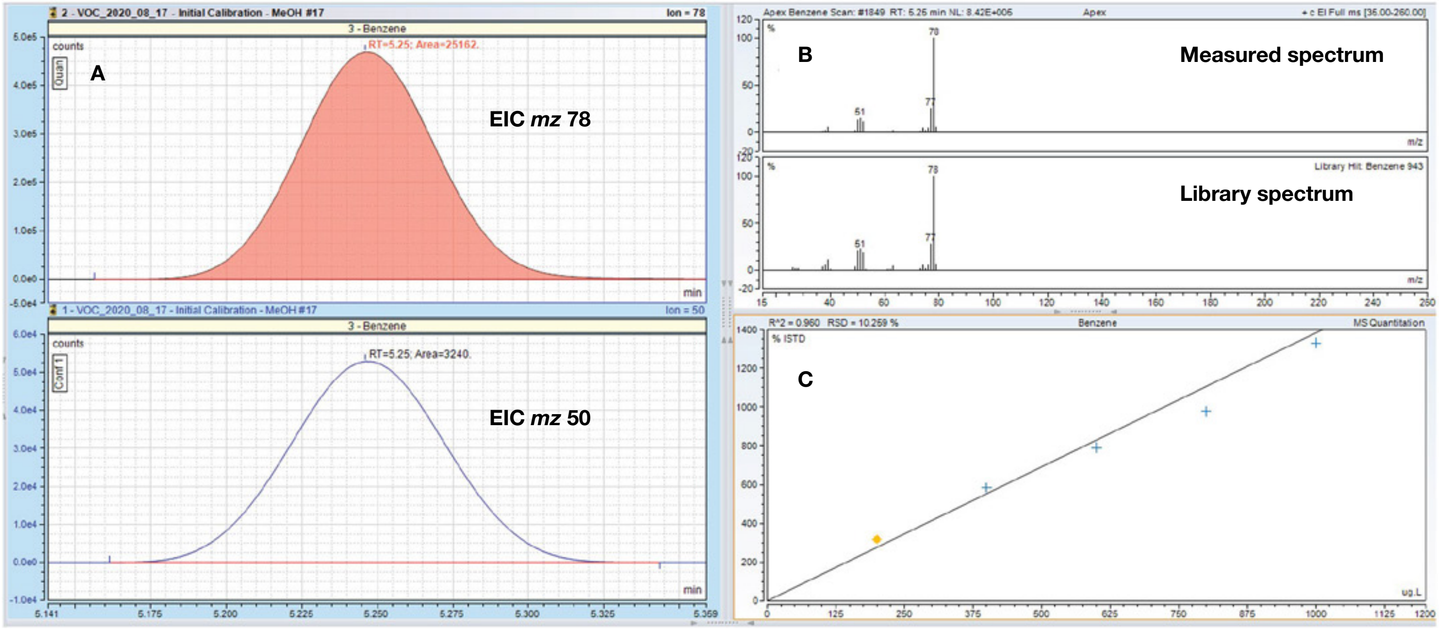


Figure 5. Chromeleon CDS results browser showing extracted ion chromatograms (quan ion *m/z* 78, confirmatory ion *m/z* 50) for benzene in the methanol extract of 5 g baked sand sample containing a final concentration of 200 ppb PVOC/GRO Mix (Wisconsin) standard, quantitation ion and one confirming ion (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 200 ppb to 1000 ppb (C)

Assessment of carryover

When analyzing high-level soil samples, system carryover can be a concern. Within the EPA regulation an exact number is not assigned to carryover. The method does, however, state repeat blanks with organic-free reagent water until you are confident there will be no carryover into the next sample. Carryover below 2% is an acceptable level. Carryover from the Atomx XYZ's automated methanol extraction method (Table I) was evaluated with two replicates of blanks analyzed directly after a 5 g spiked baked sand sample with a final concentration of 1000 ppb. Table 4 shows carryover even with high-level samples is minimal.

Table 4. Assessment of carryover for PVOC/GRO Mix (Wisconsin) methanol extraction

Compounds	First blank carryover (%)	Second blank carryover (%)	Average carryover (%)
Methyl tert-butyl ether	0.008	0.001	0.005
Benzene	0.05	0.005	0.03
Toluene	0.06	0.03	0.05
Ethylbenzene	0.12	0.04	0.08
m,p-Xylene	0.13	0.06	0.10
o-Xylene	0.07	0.02	0.04
1,3,5-Trimethylbenzene	0.15	0.05	0.10
1,2,4-Trimethylbenzene	0.20	0.07	0.13
Naphthalene	0.66	0.15	0.40

Conclusion

The combined analytical solution with the TRACE 1310 GC coupled with the ISQ 7000 single quadrupole MS and the Atomx XYZ P&T system provides clear advantages for analytical testing laboratories that analyze soil samples following the U.S. EPA Method 5035 in accordance with U.S. EPA Method 8260C. 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 GC column life span. The modularity of the TRACE 1310 GC and the ISQ 7000 VPI system with the ExtractaBrite ion source allows users to easily service the injection ports and to exchange ionization sources and analytical columns without venting the mass spectrometer, significantly reducing instrument downtime and minimizing sample analysis interruptions.

The experiments performed clearly demonstrate the suitability of this analytical configuration for the analysis of VOCs in soil samples with automated methanol extraction.

- The average linearity (AvRF %RSD) for all the compounds was 10.5% over a 5-point calibration curve from 200 to 1000 ppb.
- Precision and accuracy (assessed from n=7 repeated injections of a 600 ppb soil standard) showed excellent values with all compounds having RSD <9% for the calculated concentration.
- The automated methanol extraction allowed for compounds recovery values between 82% and 117% with an average value of 91%.
- The Atomx XYZ allowed for <0.4% average (n=2 blank replicates) system carryover as determined from high level soil samples spiked with 1000 ppm PVOC/GRO Mix (Wisconsin) standard to a final concentration of 1000 ppb.
- Combined, these technologies effectively address the challenges of VOC analysis in environmental samples and provide a robust, sensitive solution needed for ensuring maximized instrument output and regulatory method compliance.

Further information on VOC analysis using the ISQ 7000 system and the Atomx XYZ P&T can be found in the Thermo Fisher Scientific AppsLab library[4]. Further information on the analysis of VOCs in accordance to EPA Method 8260 can be found here.

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EPA Method 524.2

EPA	**524.2**
Matrix	Surface, ground, and drinking water
Compounds	Volatile Organic Compounds
Number of Compounds	84
Calibration	Average RF ≤20%RSD
IDP Accurancy	±20% Initial Demonstration Proficiency (IDP). Recommend 2–5 ppb, n=2–5 ppb LFB.
Response Factor Criteria	±30% mean value measured in initial calibration
Method Detection limits (MDLs)	0.02–1.5 ppb, min. of 7 Lab Fortified Blanks (LFB) prepared at low concentration
BFB Tune Check	Must pass to validate calibration and pass before daily analysis
Initial Demonstration of Capability	Must pass criteria for each analyst before they run field samples—accuracy of ±20% for each analyte
Continuing Calibration Check (CCC)	Must be performed at beginning of each 12-hour work shift

APPLICATION NOTE 65632

Routine analysis of volatile organic compounds in drinking water with ISQ 7000 GC-MS

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Keywords: EPA 524.2, VOCs, drinking water, trace analysis, gas chromatography, single quadrupole mass spectrometry, purge and trap, sensitivity, THM, environmental laboratory, environmental sample analysis, contract laboratories

Goal

Demonstration of a routine analytical method that meets the requirements outlined in U.S. EPA Method 524.2 for the quantitation of volatile organic compounds (VOCs) in drinking water, using a purge and trap (P&T) system coupled to a single quadrupole GC-MS. Method detection limit (MDL), linearity, precision, and accuracy were assessed to evaluate method performance.

Introduction

U.S. EPA Method 524.2 is widely used in routine environmental analysis laboratories to test water samples for VOCs.[1] The method tests for a wide range of VOCs, including the four trihalomethane disinfection by-products that have sufficiently high volatility and low water solubility, to be removed from water samples with P&T procedures. Routine drinking water monitoring regulatory standards require contract testing labs to analyze for the presence of VOCs due to the potentially negative health effects associated with public water source contamination. It is extremely important that routine laboratories ensure both accurate and rapid detection and quantitation of VOCs to ensure public safety.

There are several challenges that routine analysis laboratories face when performing U.S. EPA Method 524.2. Initially, laboratories must demonstrate achievement of method acceptance criteria including detection limit requirements for an assortment of compounds over a wide range of concentrations. The analytical method must be robust and reproducible to ensure consistent results are reported. Another significant challenge is the management of the moisture when analyzing water samples. Analysis of water samples can introduce moisture into the GC analytical column and cause damage if not properly managed. The resulting unplanned downtime of an analytical instrument can disrupt or delay sample reporting, which could in turn jeopardize the safety of a public water system.

The following evaluation describes the use of the Thermo Scientific™ ISQ™ 7000 MS system coupled to the Teledyne Tekmar Atomx XYZ purge and trap (P&T) system for U.S. EPA Method 524.2.

Experimental

Sample preparation

A 25 µg/mL (parts per million or ppm) calibration working standard was prepared in methanol from the following Restek® standards: Drinking Water VOA MegaMix®, Ketone Mix, and 502.2 Calibration Mix. In total, the standards contained 80 compounds.

The calibration curve was prepared from 0.05 µg/L to 50 µg/L (parts per billion or ppb) for all compounds. The relative response factor (RRF) was calculated for each compound using one internal standard: fluorobenzene. Surrogate standards consisted of 4-bromofluorobenzene and 1,2-dichlorobenzene-D_4. Internal and surrogate standards were prepared in methanol from Restek standards at a concentration of 25 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 25 ppb.

A quantity of seven 0.5 ppb standards were prepared in deionized water to calculate the MDL and precision for all compounds. Also, seven 5 ppb standards were prepared to determine the accuracy and precision of recovery of each compound. All calibration, MDL, and recovery standards were analyzed with the Atomx XYZ conditions in Table 1.

Table 1. Teledyne Tekmar Atomx XYZ water method conditions

Standby	Variable	Desorb	Variable
Valve Oven Temp	140 °C	Methanol Needle Rinse	Off
Transfer Line Temp	140 °C	Methanol Needle Rinse Volume	0.00 mL
Sample Mount Temp	90 °C	Water Needle Rinse Volume	7.00 mL
Transfer Line Temp	140 °C	Methanol Needle Rinse Volume	0.00 mL
Sample Vial Temp	20 °C	Desorb Preheat Temp	245 °C
Soil Valve Temp	100 °C	GC Start Signal	Begin Desorb
Standby Flow	10 mL/min	Desorb Time	4.00 min
Condensate Ready Temp	45 °C	Drain Flow	300 mL/min
Purge Ready Temp	40 °C	Desorb Temp	250 °C
Purge	Variable	Bake	Variable
Sample Equilibrate Time	0.00 min	Methanol Glass Rinse	Off
Pre-sweep Time	0.25 min	Number of Methanol Glass Rinses	0
Prime Sample Fill Volume	3.00 mL	Methanol Glass Rinse Volume	0.00 mL
Sample Volume	5.00 mL	Water Bake Rinses	1
Sweep Sample Time	0.25 min	Water Bake Rinse Volume	7.00 mL
Sweep Sample Flow	100 mL/min	Bake Rinse Sweep Time	0.25 min
Sparge Vessel Heater	Off	Bake Rinse Sweep Flow	100 mL/min
Sparge Vessel Temp	20 °C	Bake Rinse Drain Time	0.40 min
Pre-purge Time	0.00 min	Bake Time	2.00 min
Pre-purge Flow	0 mL/min	Bake Flow	200 mL/min
Purge Time	11.00 min	Bake Temp	280 °C
Purge Flow	40 mL/min	Condensate Bake Temp	180 °C
Purge Temp	20 °C		
Condensate Purge Temp	20 °C		
Dry Purge Time	1.00 min	Trap	K
Dry Purge Flow	100 mL/min	Chiller Tray	Off
Dry Purge Temp	20 °C	Purge Gas	Nitrogen

GC-MS conditions

A Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC) was coupled to the ISQ 7000 system equipped with the Thermo Scientific™ NeverVent™ Vacuum probe interlock (VPI) and a Thermo Scientific™ ExtractaBrite™ ion source. An Rtx® VMS column (20 m, 0.18 mm, 1 µm film) from Restek, which is equivalent to the Thermo Scientific™ TraceGOLD TG-VMS 20 m, 0.18 mm, 1 µm film (P/N 26080-4950), was used for compounds separation, with a run time under 15 minutes. The TRACE 1310 GC was equipped with an iConnect SSL injector operating in split mode. The ISQ 7000 MS system was operated in full scan mode, offering sufficient sensitivity to achieve the required limits of detection. Note: The instrument can also be operated in Selected Ion Monitoring (SIM) mode to increase selectivity. This is particularly useful in samples such as sludge that have matrix interferences. Expanded method parameters for the ISQ 7000 MS system are displayed in Table 2. The data were acquired, processed, and reported using Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software.

Results and discussion

Chromatography

Using the GC conditions described in Table 2, all compounds of interest were well resolved chromatographically.

Table 2. GC-MS conditions

Thermo Scientific TRACE 1310 GC conditions	
Column	Rtx® VMS, 20 m × 0.18 mm 1 µm film
Carrier gas	Helium – 0.8 mL/min constant flow
Oven temperature	35 °C, 3 min 12 °C/min to 85 °C 25 °C/min to 225 °C 2 min Hold Run time 14.767 min
Inlet temperature and injection mode	SSL, 200 °C, 50:1 split
Thermo Scientific ISQ 7000 MS conditions	
Transfer line temperature	230 °C
Ion source temperature	280 °C
Acquisition mode	Full scan 35 *m/z* to 260 *m/z* Solvent delay 0.50 min Dwell time 0.15 s
Emission current	25 µA Gain 1.00E+005

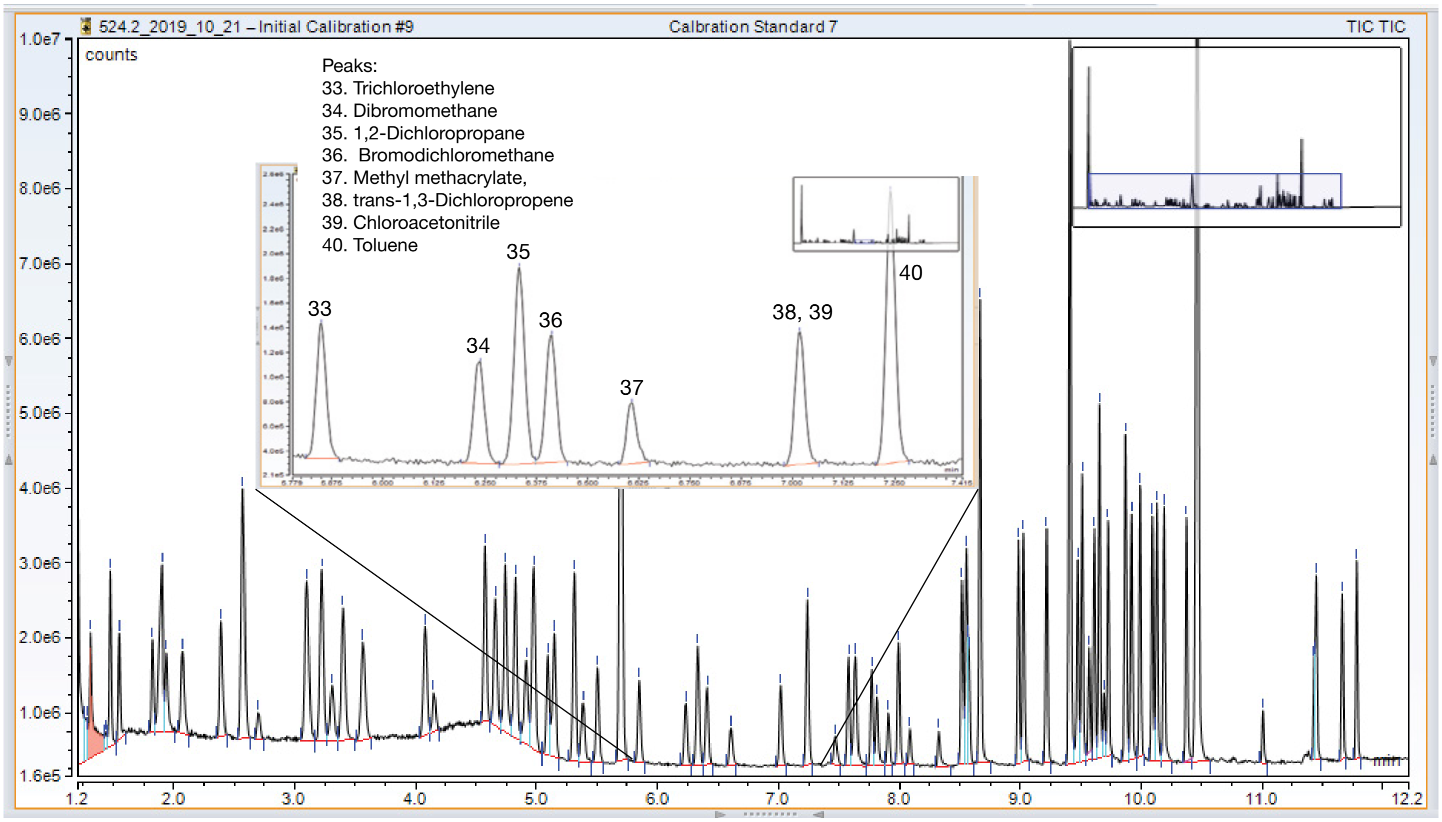

Figure 1. Total ion chromatogram (TIC) of a 5 ppb VOC standard (analyzed using the water method) with an inset indicating consistent peak shapes and separation with minimal water interference

It is evident that there is minimal water transfer compared with traditional purge and trap analysis as there were no detrimental effects to peak shape due to moisture entering the analytical column. This resulted in optimized chromatography that was maintained in lower concentration samples. Figure 1 displays consistent peak shape and separation of a 5 ppb VOC standard with minimal water interference.

Linearity and sensitivity

The calibration range of 0.05 ppb to 50 ppb was assessed for all compounds. Figure 2 shows a summary of the data for the calculated concentration for a 0.5 ppb standard for seven injections and the calculated MDLs for seven compounds over the chromatographic range.

Table 3 displays the relative standard deviation (%RSD) of the response factors (RFs), which were <20% for all compounds, except for iodomethane, which used a linear calibration and achieved R^2=0.997. The table also shows the MDL for each analyte is <0.25 ppb along with the accuracy and precision data. Figure 3 demonstrates the quantitation of 1,4-dichlorobenzene at 5 ppb in a VOC standard with excellent library spectral matching and calibration curve. Figure 4 displays several 0.05 ppb (the lowest calibration standard) VOC standards exhibiting excellent peak shape. In U.S. EPA Method 524.2 the lowest calibration point is typically 0.2 ppb. This method demonstrates that all compounds can be detected below the normal lowest calibration point.

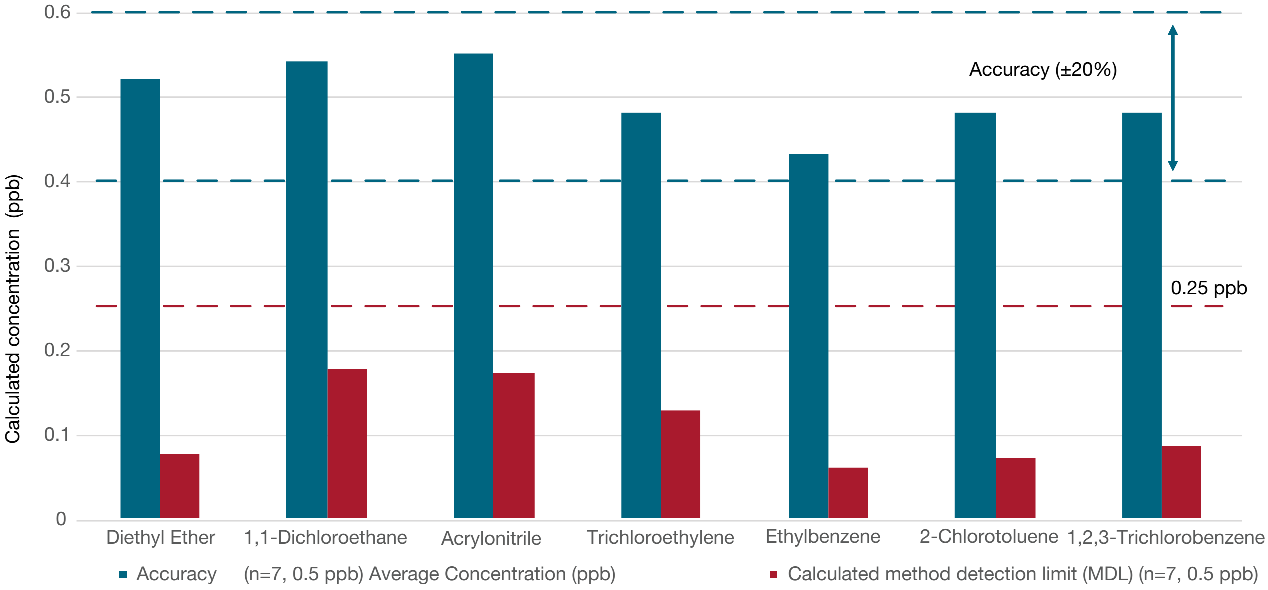

Figure 2. Calculated concentration for standard at 0.5 ppb for seven injections with calculated MDL of less than 0.25 ppb for all compounds

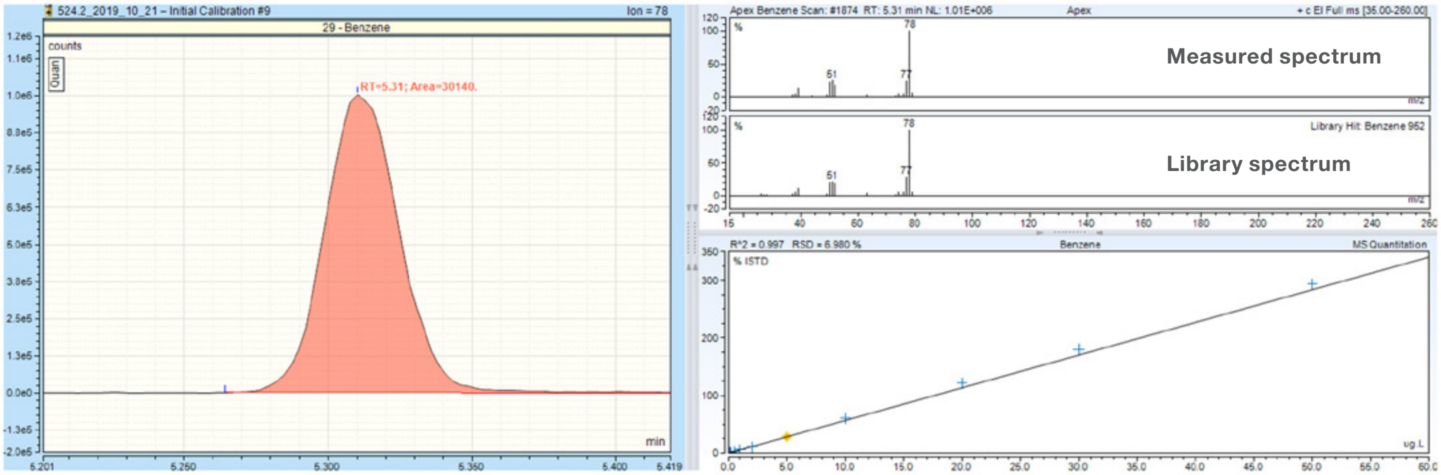

Figure 3. Chromeleon results browser showing extracted ion chromatogram for benzene (*m/z* 78), as well as NIST library results and a linear calibration range of 0.05 ppb to 50 ppb

Table 3 (part 1). U.S. EPA Method 524.2 calibration, accuracy, and precision data

	Calibration			Accuracy and precision (n=7, 0.5 ppb)			Analyte recovery (n=7, 5 ppb)	
Compound	**Retention time**	**Linearity (RF %RSD)**	**Average RF**	**Average conc. (ppb)**	**MDL (ppb)**	**Precision (≤20%)**	**Accuracy (±20%)**	**Precision (≤20%)**
Dichlorodifluoromethane	1.31	14.7	0.46	0.52	0.15	8.9	111	7.6
Chloromethane[4]	1.48	19.1	1.28	0.56	0.17	9.5	102	4.2
Vinyl Chloride	1.55	15.2	0.64	0.52	0.21	13.0	109	5.7
Bromomethane	1.83	19.2	0.52	0.68	0.21	9.7	107	9.1
Chloroethane	1.94	10.0	0.56	0.52	0.13	7.8	106	4.5
Trichlorofluoromethane	2.07	18.6	0.57	0.54	0.19	11.2	114	6.4
Diethyl Ether	2.4	8.2	0.58	0.52	0.08	4.6	110	2.6
1,1-Dichloroethene	2.57	9.6	0.47	0.51	0.16	9.9	103	6.8
Carbon Disulfide[2]	2.58	9.1	1.99	0.56	0.17	9.4	104	6.1
Iodomethane[1,3,5]	2.71	n.a.	0.37	0.28	0.05	5.9	71	19.7
Allyl Chloride	3.09	9.7	0.33	0.55	0.15	8.8	109	5.6
Methylene Chloride	3.22	12.3	1.47	0.57	0.17	9.3	107	4.7
trans-1,2-Dichloroethene	3.4	8.9	0.93	0.56	0.15	8.7	110	4.0
Methyl-t-Butyl Ether	3.57	14.3	0.91	0.49	0.08	4.9	113	1.6
1,1-Dichloroethane	4.08	11.7	1.29	0.54	0.18	10.3	110	5.1
Acrylonitrile	4.15	15.0	0.34	0.55	0.17	10.0	106	3.6
Propionitrile	4.16	14.2	0.34	0.57	0.17	9.3	107	3.6
cis-1,2-Dichloroethene	4.57	9.6	0.98	0.57	0.18	10.2	114	3.8
2,2-Dichloropropane	5.66	8.6	0.62	0.51	0.14	8.8	98	6.7
Bromochloromethane[3]	4.74	18.5	1.09	0.58	0.12	6.4	108	3.7
Chloroform	4.82	10.1	1.04	0.57	0.16	9.1	111	5.3
Carbon Tetrachloride	4.91	11.5	0.37	0.49	0.13	8.4	116	7.3
Methyl Acrylate	4.97	5.7	0.37	0.5	0.14	9.1	107	3.7
1,1,1-Trichloroethane	4.98	7.8	0.56	0.53	0.15	9.1	116	5.7
Tetrahydrofuran[4]	4.99	11.3	0.37	0.62	0.10	4.9	111	4.3
1,1-Dichloropropene	5.09	14.0	0.43	0.44	0.11	7.6	98	4.1
2-Butanone	5.14	11.7	0.06	0.96	0.26	8.7	108	5.6
1-Chlorobutane[3]	5.14	14.0	0.67	0.46	0.12	8.2	103	6.1
Benzene	5.31	7.0	1.42	0.46	0.09	6.3	102	4.2
Methacrylonitrile	5.39	9.8	0.16	0.49	0.15	9.5	94	3.5
1,2-Dichloroethane	5.5	7.4	0.64	0.54	0.11	6.6	112	1.5
Fluorobenzene (IS)	5.7							
Trichloroethylene	5.85	10.6	0.28	0.48	0.13	8.4	106	4.9
Dibromomethane	6.23	8.0	0.29	0.54	0.09	5.4	108	3.4
1,2-Dichloropropane	6.33	6.8	0.43	0.47	0.06	3.8	104	1.3
Bromodichloromethane	6.41	5.8	0.49	0.48	0.07	4.6	110	1.6
Methyl Methacrylate	6.62	9.1	0.13	0.48	0.15	10.2	92	2.5
trans-1,3-Dichloropropene	7.01	16.3	0.41	0.44	0.04	3.2	100	1.7
Chloroacetonitrile	7.03	6.6	0.02	0.48	0.09	10.1	103	8.9
Toluene	7.24	8.8	1.10	0.44	0.15	6.4	98	4.7
2-Nitropropane[2]	7.47	8.5	0.31	0.47	0.10	7.0	97	2.8
Tetrachloroethene	7.58	12.5	0.20	0.52	0.20	11.8	111	9.8
4-Methyl-2-pentanone	7.62	14.1	0.38	0.53	0.05	3.1	110	3.7
cis-1,3-Dichloropropene	7.65	12.8	0.36	0.42	0.06	4.5	95	3.7
1,1,2-Trichloroethane	7.78	12.5	0.24	0.49	0.08	5.4	112	2.6
Ethyl Methacrylate	7.82	10.7	0.28	0.43	0.04	3.0	94	3.8

1. Compounds were linear regressed.
2. Calibration curve 0.1 ppb–50 ppb.
3. Calibration curve 0.2 ppb–50 ppb.
4. Calibration curve 0.5 ppb–50 ppb
5. Compound is a poor purger. Analyte recovery is out of method range.

Table 3 (part 2). U.S. EPA Method 524.2 calibration, accuracy, and precision data

	Calibration			Accuracy and precision (n=7, 0.5 ppb)			Analyte recovery (n=7, 5 ppb)	
Compound	**Retention time**	**Linearity (RF %RSD)**	**Average RF**	**Average conc. (ppb)**	**MDL (ppb)**	**Precision (≤20%)**	**Accuracy (±20%)**	**Precision (≤20%)**
Dibromochloromethane	7.91	7.5	0.21	0.47	0.09	6.2	105	2.5
1,3-Dichloropropane	7.99	15.2	0.46	0.49	0.09	5.8	108	1.7
1,2-Dibromoethane	8.09	8.3	0.22	0.46	0.07	5.0	104	2.8
2-Hexanone	8.32	12.4	0.29	0.5	0.12	7.9	97	3.3
Chlorobenzene	8.52	13.7	0.63	0.49	0.11	7.3	102	3.0
Ethylbenzene	8.55	13.4	1.08	0.43	0.06	4.4	92	4.4
1,1,1,2-Tetrachloroethane	8.57	10.0	0.16	0.48	0.12	8.1	108	2.8
m-,p-Xylene	8.67	18.1	0.42	0.83	0.21	8.2	94	2.9
o-Xylene	8.99	9.7	0.39	0.44	0.14	10.3	92	3.6
Styrene	9.03	16.0	0.66	0.4	0.11	8.7	91	4.4
Bromoform	9.04	12.7	0.12	0.43	0.09	6.9	99	1.6
Isopropylbenzene	9.22	15.8	0.87	0.41	0.11	8.4	95	5.4
4-Bromofluorobenzene (SURR)	9.41	7.1	0.42	25		5.7	97	4.5
Bromobenzene	9.48	8.1	0.70	0.58	0.15	8.2	111	4.1
n-Propylbenzene	9.51	17.4	1.39	0.46	0.15	10.1	102	5.2
1,1,2,2-Tetrachloroethane	9.57	7.8	0.45	0.48	0.06	3.8	102	3.5
2-Chlorotoluene	9.61	6.0	0.93	0.48	0.07	4.9	101	3.4
1,2,3-Trichloropropane	9.65	9.3	0.36	0.48	0.08	5.4	109	4.3
1,2,4-Trimethylbenzene[3]	9.66	19.3	0.92	0.39	0.13	10.5	95	3.4
trans-1,4-Dichloro-2-butene[2]	9.69	8.3	0.11	0.47	0.12	8.4	99	4.9
4-Chlorotoluene	9.73	11.7	0.99	0.42	0.10	8.0	100	3.6
tert-Butylbenzene[4]	9.87	10.1	0.79	0.39	0.11	9.2	81	5.1
1,3,5-Trimethylbenzene[3]	9.92	20.0	0.92	0.37	0.10	8.5	95	3.4
sec-Butylbenzene[4]	9.99	19.6	1.13	0.35	0.10	8.6	95	5.8
p-Isopropyltoluene[3]	10.09	19.8	0.73	0.36	0.11	9.4	92	4.2
1,3-Dichlorobenzene	10.13	12.1	0.61	0.47	0.09	6.2	111	3.6
1,4-Dichlorobenzene	10.19	11.4	0.58	0.47	0.10	6.7	108	3.5
n-Butylbenzene	10.37	16.7	0.93	0.43	0.11	8.3	97	5.2
Hexachloroethane	10.45	15.0	0.09	0.5	0.24	15.2	104	8.5
1,2-Dichlorobenzene-d$_4$ (SURR)	10.46	5.7	0.37	24.1		5.4	103	3.6
1,2-Dichlorobenzene	10.47	8.9	0.65	0.49	0.11	6.9	106	3.1
1,2-Dibromo-3-Chloropropane	11.01	12.4	0.10	0.57	0.15	8.2	114	5.9
Nitrobenzene[4]	11.38	13.7	0.03	0.45	0.16	11.0	110	6.4
Hexachlorobutadiene[3]	11.43	12.4	0.03	0.62	0.20	10.0	120	4.9
1,2,4-Trichlorobenzene	11.45	11.4	0.28	0.57	0.17	9.4	100	2.0
Naphthalene	11.67	6.2	0.79	0.48	0.09	5.8	94	4.3
1,2,3-Trichlorobenzene	11.79	9.2	0.33	0.48	0.09	5.7	93	4.4

1. Compounds were linear regressed.
2. Calibration curve 0.1 ppb–50 ppb.
3. Calibration curve 0.2 ppb–50 ppb.
4. Calibration curve 0.5 ppb–50 ppb
5. Compound is a poor purger. Analyte recovery is out of method range.

Table 3 (part 2). U.S. EPA Method 524.2 calibration, accuracy, and precision data

	Calibration			Accuracy and precision (n=7, 0.5 ppb)			Analyte recovery (n=7, 5 ppb)	
Compound	Retention time	Linearity (RF %RSD)	Average RF	Average conc. (ppb)	MDL (ppb)	Precision (≤20%)	Accuracy (±20%)	Precision (≤20%)
Dibromochloromethane	7.91	7.5	0.21	0.47	0.09	6.2	105	2.5
1,3-Dichloropropane	7.99	15.2	0.46	0.49	0.09	5.8	108	1.7
1,2-Dibromoethane	8.09	8.3	0.22	0.46	0.07	5.0	104	2.8
2-Hexanone	8.32	12.4	0.29	0.5	0.12	7.9	97	3.3
Chlorobenzene	8.52	13.7	0.63	0.49	0.11	7.3	102	3.0
Ethylbenzene	8.55	13.4	1.08	0.43	0.06	4.4	92	4.4
1,1,1,2-Tetrachloroethane	8.57	10.0	0.16	0.48	0.12	8.1	108	2.8
m-,p-Xylene	8.67	18.1	0.42	0.83	0.21	8.2	94	2.9
o-Xylene	8.99	9.7	0.39	0.44	0.14	10.3	92	3.6
Styrene	9.03	16.0	0.66	0.4	0.11	8.7	91	4.4
Bromoform	9.04	12.7	0.12	0.43	0.09	6.9	99	1.6
Isopropylbenzene	9.22	15.8	0.87	0.41	0.11	8.4	95	5.4
4-Bromofluorobenzene (SURR)	9.41	7.1	0.42	25		5.7	97	4.5
Bromobenzene	9.48	8.1	0.70	0.58	0.15	8.2	111	4.1
n-Propylbenzene	9.51	17.4	1.39	0.46	0.15	10.1	102	5.2
1,1,2,2-Tetrachloroethane	9.57	7.8	0.45	0.48	0.06	3.8	102	3.5
2-Chlorotoluene	9.61	6.0	0.93	0.48	0.07	4.9	101	3.4
1,2,3-Trichloropropane	9.65	9.3	0.36	0.48	0.08	5.4	109	4.3
1,2,4-Trimethylbenzene[3]	9.66	19.3	0.92	0.39	0.13	10.5	95	3.4
trans-1,4-Dichloro-2-butene[2]	9.69	8.3	0.11	0.47	0.12	8.4	99	4.9
4-Chlorotoluene	9.73	11.7	0.99	0.42	0.10	8.0	100	3.6
tert-Butylbenzene[4]	9.87	10.1	0.79	0.39	0.11	9.2	81	5.1
1,3,5-Trimethylbenzene[3]	9.92	20.0	0.92	0.37	0.10	8.5	95	3.4
sec-Butylbenzene[4]	9.99	19.6	1.13	0.35	0.10	8.6	95	5.8
p-Isopropyltoluene[3]	10.09	19.8	0.73	0.36	0.11	9.4	92	4.2
1,3-Dichlorobenzene	10.13	12.1	0.61	0.47	0.09	6.2	111	3.6
1,4-Dichlorobenzene	10.19	11.4	0.58	0.47	0.10	6.7	108	3.5
n-Butylbenzene	10.37	16.7	0.93	0.43	0.11	8.3	97	5.2
Hexachloroethane	10.45	15.0	0.09	0.5	0.24	15.2	104	8.5
1,2-Dichlorobenzene-d_4 (SURR)	10.46	5.7	0.37	24.1		5.4	103	3.6
1,2-Dichlorobenzene	10.47	8.9	0.65	0.49	0.11	6.9	106	3.1
1,2-Dibromo-3-Chloropropane	11.01	12.4	0.10	0.57	0.15	8.2	114	5.9
Nitrobenzene[4]	11.38	13.7	0.03	0.45	0.16	11.0	110	6.4
Hexachlorobutadiene[3]	11.43	12.4	0.03	0.62	0.20	10.0	120	4.9
1,2,4-Trichlorobenzene	11.45	11.4	0.28	0.57	0.17	9.4	100	2.0
Naphthalene	11.67	6.2	0.79	0.48	0.09	5.8	94	4.3
1,2,3-Trichlorobenzene	11.79	9.2	0.33	0.48	0.09	5.7	93	4.4

1. Compounds were linear regressed.
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5. Compound is a poor purger. Analyte recovery is out of method range.

Table 3 (part 2). U.S. EPA Method 524.2 calibration, accuracy, and precision data

	Calibration			Accuracy and precision (n=7, 0.5 ppb)			Analyte recovery (n=7, 5 ppb)	
Compound	**Retention time**	**Linearity (RF %RSD)**	**Average RF**	**Average conc. (ppb)**	**MDL (ppb)**	**Precision (≤20%)**	**Accuracy (±20%)**	**Precision (≤20%)**
Dibromochloromethane	7.91	7.5	0.21	0.47	0.09	6.2	105	2.5
1,3-Dichloropropane	7.99	15.2	0.46	0.49	0.09	5.8	108	1.7
1,2-Dibromoethane	8.09	8.3	0.22	0.46	0.07	5.0	104	2.8
2-Hexanone	8.32	12.4	0.29	0.5	0.12	7.9	97	3.3
Chlorobenzene	8.52	13.7	0.63	0.49	0.11	7.3	102	3.0
Ethylbenzene	8.55	13.4	1.08	0.43	0.06	4.4	92	4.4
1,1,1,2-Tetrachloroethane	8.57	10.0	0.16	0.48	0.12	8.1	108	2.8
m-,p-Xylene	8.67	18.1	0.42	0.83	0.21	8.2	94	2.9
o-Xylene	8.99	9.7	0.39	0.44	0.14	10.3	92	3.6
Styrene	9.03	16.0	0.66	0.4	0.11	8.7	91	4.4
Bromoform	9.04	12.7	0.12	0.43	0.09	6.9	99	1.6
Isopropylbenzene	9.22	15.8	0.87	0.41	0.11	8.4	95	5.4
4-Bromofluorobenzene (SURR)	9.41	7.1	0.42	25		5.7	97	4.5
Bromobenzene	9.48	8.1	0.70	0.58	0.15	8.2	111	4.1
n-Propylbenzene	9.51	17.4	1.39	0.46	0.15	10.1	102	5.2
1,1,2,2-Tetrachloroethane	9.57	7.8	0.45	0.48	0.06	3.8	102	3.5
2-Chlorotoluene	9.61	6.0	0.93	0.48	0.07	4.9	101	3.4
1,2,3-Trichloropropane	9.65	9.3	0.36	0.48	0.08	5.4	109	4.3
1,2,4-Trimethylbenzene[3]	9.66	19.3	0.92	0.39	0.13	10.5	95	3.4
trans-1,4-Dichloro-2-butene[2]	9.69	8.3	0.11	0.47	0.12	8.4	99	4.9
4-Chlorotoluene	9.73	11.7	0.99	0.42	0.10	8.0	100	3.6
tert-Butylbenzene[4]	9.87	10.1	0.79	0.39	0.11	9.2	81	5.1
1,3,5-Trimethylbenzene[3]	9.92	20.0	0.92	0.37	0.10	8.5	95	3.4
sec-Butylbenzene[4]	9.99	19.6	1.13	0.35	0.10	8.6	95	5.8
p-Isopropyltoluene[3]	10.09	19.8	0.73	0.36	0.11	9.4	92	4.2
1,3-Dichlorobenzene	10.13	12.1	0.61	0.47	0.09	6.2	111	3.6
1,4-Dichlorobenzene	10.19	11.4	0.58	0.47	0.10	6.7	108	3.5
n-Butylbenzene	10.37	16.7	0.93	0.43	0.11	8.3	97	5.2
Hexachloroethane	10.45	15.0	0.09	0.5	0.24	15.2	104	8.5
1,2-Dichlorobenzene-d_4 (SURR)	10.46	5.7	0.37	24.1		5.4	103	3.6
1,2-Dichlorobenzene	10.47	8.9	0.65	0.49	0.11	6.9	106	3.1
1,2-Dibromo-3-Chloropropane	11.01	12.4	0.10	0.57	0.15	8.2	114	5.9
Nitrobenzene[4]	11.38	13.7	0.03	0.45	0.16	11.0	110	6.4
Hexachlorobutadiene[3]	11.43	12.4	0.03	0.62	0.20	10.0	120	4.9
1,2,4-Trichlorobenzene	11.45	11.4	0.28	0.57	0.17	9.4	100	2.0
Naphthalene	11.67	6.2	0.79	0.48	0.09	5.8	94	4.3
1,2,3-Trichlorobenzene	11.79	9.2	0.33	0.48	0.09	5.7	93	4.4

1. Compounds were linear regressed.
2. Calibration curve 0.1 ppb–50 ppb.
3. Calibration curve 0.2 ppb–50 ppb.
4. Calibration curve 0.5 ppb–50 ppb
5. Compound is a poor purger. Analyte recovery is out of method range.

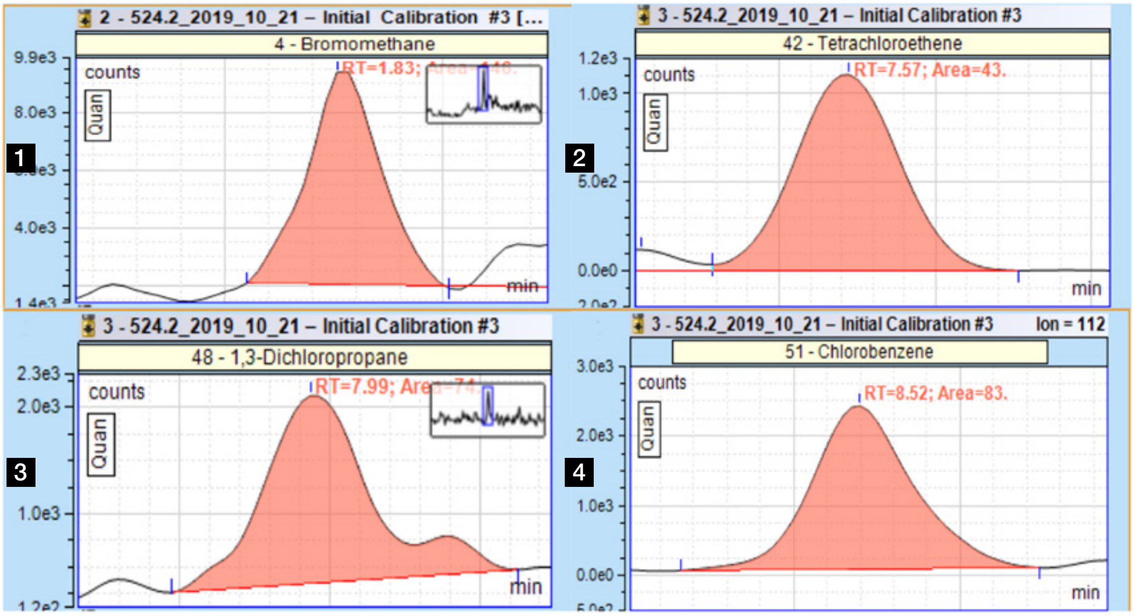

Figure 4. Example of chromatography (full scan, EI) from the lowest calibration level at 0.05 ppb: 1, bromomethane; 2, tetrachloroethene; 3, 1,3-dichloropropane; 4, chlorobenzene

Method robustness

To assess the stability of the method, 5 ppb calibration check standards were injected at intervals over a 75-sample injection sequence. No maintenance was performed on any part of the system during this extended test. Figure 5 shows the repeatability of five of the compounds over 75 injections with excellent percentage RSDs. Table 4 displays the accuracy and precision of ten 5 ppb calibration check standards for all compounds. Figure 6 shows the accuracy and precision for ten injections of a 5 ppb standard for a selection of compounds over the chromatographic range.

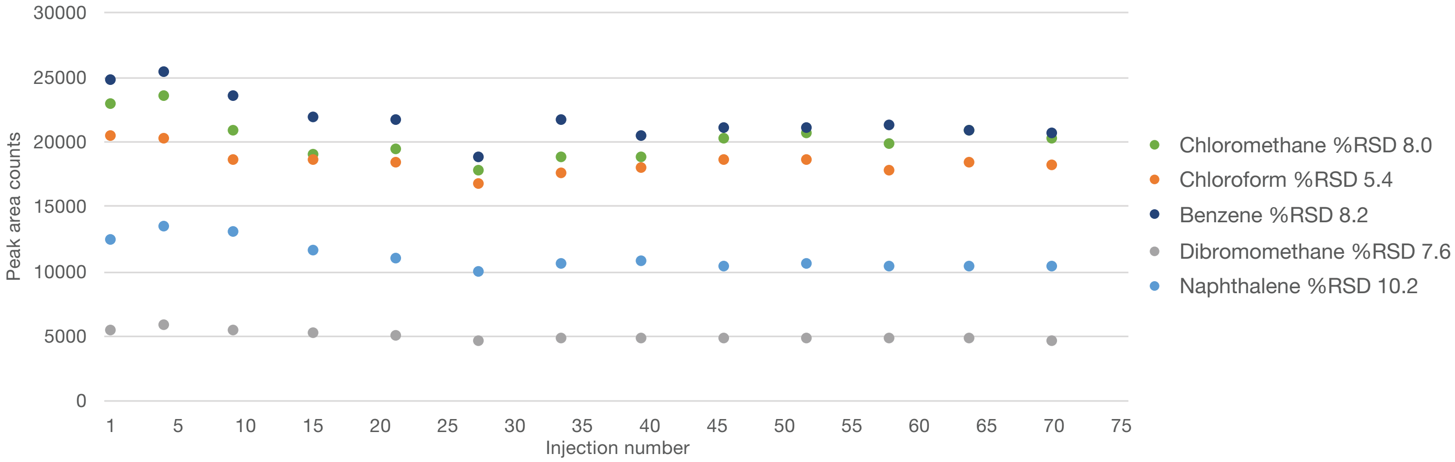

Figure 5. Repeatability of a 5 ppb VOC standard (as absolute peak area counts) assessed over n=75 consecutive injections

Table 4. U.S. EPA Method 524.2 accuracy and precision data for 5 ppb calibration check standards

Compound	Analyte recovery (n=10, 5 ppb)			
	Quantitation ion	Average conc. (ppb)	Accuracy (±20%)	Precision (≤20%)
Dichlorodifluoromethane	85	5.6	111	12.9
Chloromethane	50	5.2	103	9.7
Vinyl Chloride	62	5.3	105	10.0
Bromomethane	94	5.1	102	5.6
Chloroethane	64	5.3	105	8.5
Trichlorofluoromethane	101	5.6	112	10.8
Diethyl Ether	45	5.6	112	3.4
1,1-Dichloroethene	96	5.0	100	10.5
Carbon Disulfide	76	5.0	101	9.8
Iodomethane	142	3.9	77	18.1
Allyl Chloride	76	5.2	104	7.9
Methylene Chloride	49	5.5	110	5.7
trans-1,2-Dichloroethene	61	5.6	112	8.4
Methyl-t-Butyl Ether	73	5.5	109	2.4
1,1-Dichloroethane	63	5.7	113	7.2
Acrylonitrile	53	5.4	109	4.3
Propionitrile	53	5.5	110	4.3
cis-1,2-Dichloroethene	61	5.9	118	7.0
2,2-Dichloropropane	77	3.7	73	6.4
Bromochloromethane	49	5.8	115	5.1
Chloroform	83	5.8	116	7.2
Carbon Tetrachloride	117	5.8	116	9.4
Methyl Acrylate	55	5.2	105	3.2
1,1,1-Trichloroethane	97	5.8	116	9.0
Tetrahydrofuran	42	5.8	115	5.4
1,1-Dichloropropene	75	4.6	92	8.5
2-Butanone	72	5.4	108	7.1
1-Chlorobutane	56	4.8	97	8.9
Benzene	78	5.0	99	5.3
Methacrylonitrile	67	4.5	89	2.1
1,2-Dichloroethane	62	5.9	118	3.6
Fluorobenzene (IS)	96			
Trichloroethylene	95	5.1	102	8.0
Dibromomethane	93	5.6	111	3.6
1,2-Dichloropropane	63	5.2	104	3.9
Bromodichloromethane	83	5.6	111	3.9
Methyl Methacrylate	69	4.5	90	3.7
trans-1,3-Dichloropropene	75	4.6	91	2.0
Chloroacetonitrile	48	4.8	95	7.8
Toluene	91	4.7	94	7.1
2-Nitropropane	43	4.6	92	7.4
Tetrachloroethene	164	5.9	118	15.8
4-Methyl-2-pentanone	43	5.5	111	3.7
cis-1,3-Dichloropropene	75	4.3	86	2.9
1,1,2-Trichloroethane	83	5.6	112	3.3
Ethyl Methacrylate	69	4.6	92	4.2
Dibromochloromethane	129	5.2	104	2.8
1,3-Dichloropropane	76	5.5	109	2.3
1,2-Dibromoethane	107	5.2	104	3.4
2-Hexanone	43	4.8	97	6.5
Chlorobenzene	112	5.0	100	5.4
Ethylbenzene	91	4.4	87	7.2
1,1,1,2-Tetrachloroethane	131	5.4	109	4.3
m-,p-Xylene	106	8.7	87	7.4
o-Xylene	106	4.4	89	5.5
Styrene	104	4.2	83	7.3
Bromoform	173	4.7	94	4.5
Isopropylbenzene	105	4.4	88	7.3
4-Bromofluorobenzene (SURR)	95	25.0	100	5.6
Bromobenzene	77	5.4	109	4.7
n-Propylbenzene	91	4.8	96	7.6
1,1,2,2-Tetrachloroethane	83	4.9	98	4.8
2-Chlorotoluene	91	4.8	95	7.0
1,2,3-Trichloropropane	75	5.6	111	2.9
1,2,4-Trimethylbenzene	105	4.3	87	7.3
trans-1,4-Dichloro-2-butene	53	4.7	93	8.2
4-Chlorotoluene	91	4.6	92	5.6
tert-Butylbenzene	119	4.2	84	5.5
1,3,5-Trimethylbenzene	105	4.3	86	7.7
sec-Butylbenzene	105	4.3	86	8.2
p-Isopropyltoluene	119	4.1	83	8.5
1,3-Dichlorobenzene	146	5.3	106	6.0
1,4-Dichlorobenzene	146	5.1	102	4.4
n-Butylbenzene	91	4.5	90	8.8
Hexachloroethane	201	5.1	101	8.8
1,2-Dichlorobenzene-d_4 (SURR)	152	27.0	108	5.2
1,2-Dichlorobenzene	146	5.2	104	5.4
1,2-Dibromo-3-Chloropropane	75	5.9	118	5.0
Nitrobenzene	51	5.5	109	7.0
Hexachlorobutadiene	225	6.0	119	10.7
1,2,4-Trichlorobenzene	180	4.7	95	7.5
Naphthalene	128	4.5	90	4.0
1,2,3-Trichlorobenzene	180	4.5	90	4.8

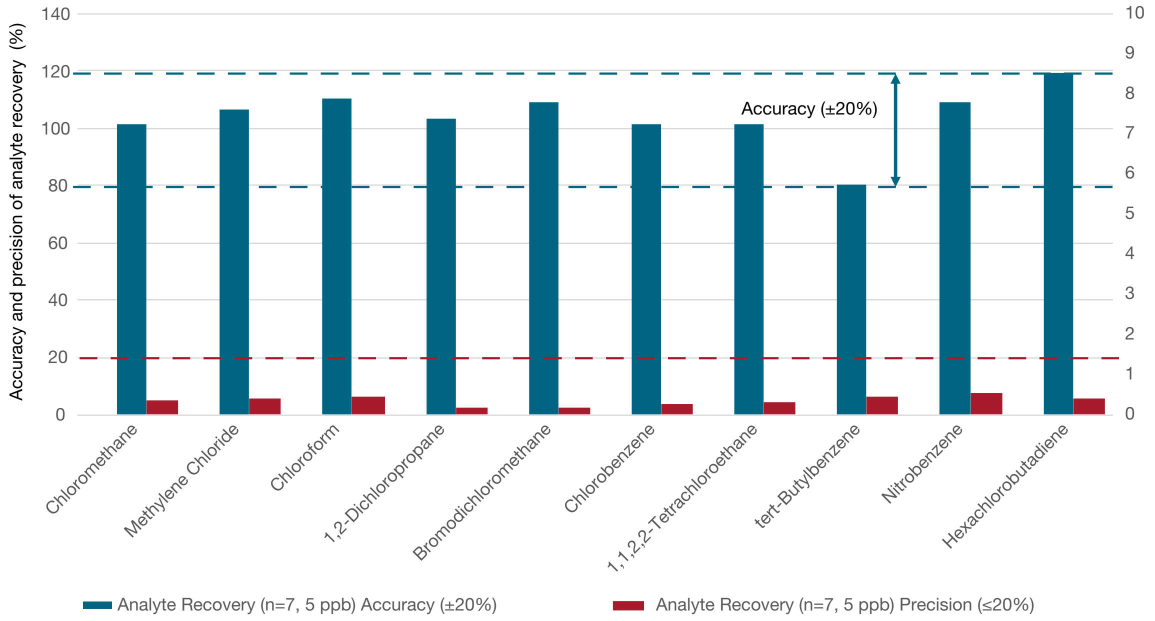

Figure 6. Accuracy and precision for ten injections of a 5 ppb standard for a selection of compounds

Conclusion

The combined analytical solution with the TRACE 1310 GC coupled to the ISQ 7000 MS system and the Atomx XYZ P&T system provides clear advantages for U.S. EPA Method 524.2.

- The Thermo Scientific ISQ 7000 VPI coupled with the Teledyne Tekmar Atomx XYZ P&T meets and exceeds all the requirements outlined in EPA method 524.2 for analysis of VOCs in water.
- Excellent linearity for all compounds was demonstrated with the %RSD of the calibration response factors passing all method requirements.
- MDL, precision, and accuracy for seven 0.5 ppb (μg/L) standards showed no interference from excessive water and delivered very reproducible results.

The Atomx XYZ concentrator's efficient trap cooling design reduces sample cycle time, allowing for more soil or water samples to be processed in a 12-hour period. The system also utilizes a moisture control system that improves water vapor removal, thereby, reducing peak interference and increasing GC column life span.

The robust performance and design of the ISQ 7000 VPI and ExtractaBrite ion source allows users to exchange ionization sources and analytical columns without venting the instrument significantly reducing instrument downtime and minimizing sample analysis interruptions.

Combined, these complementary technologies effectively address the challenges of routine VOC analysis and provide a robust, sensitive solution needed for ensuring maximized instrument output and routine regulatory method compliance.

Reference

1. U.S. Environmental Protection Agency. Method 524.2. Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry (https://www.epa.gov/sites/production/files/2015-06/documents/epa-524.2.pdf)

Find out more at **thermofisher.com**

EPA Method 524.4

EPA	524.4
Matrix	Drinking water using Nitrogen as purge gas
Compounds	Volatile Organic Compounds
Number of Compounds	82
Calibration	Linear or Quadratic regression $R^2 \geq 0.995$
Initial Calibration (IC) of at Least 7 Points	The lowest concentration in the curve must be ±50% of their true value, all other points must be within ±30%
BFB Tune Check	Must pass criteria before calibration curve performed or after a major change to MS parameters
IDP Accurancy	±20%
Response Factor Criteria	≥70% initial RF
Minimum Reporting Level (MRL)	Initial lowest calibration standard as well as lowest CCC≤MRL
Upper Predition Interval Results (PIR)%	Upper PIR limit ≤150% recovery using n=7 LFB at ≤MRL concentration
Lower Predition Interval Results (PIR)%	Lower PIR limit ≥50% recovery using n=7 LFB at ≤MRL concentration
Surrogate Recovery	±30%
Laboratory Reagent Blank (LRB)	≤1/2xMRL
Quality Control Sample (QCS)	±30% at mid level
Continuing Calibration Check (CCC)	Performed before, between every 10, and after daily field samples—±30% of true value. Lowest level must be within ±50%
Internal Standard (IS)	±30% in recent CCC. ±50% average area in IC
Laboratory Fortified Sample Matrix (LFSM)	Analytes ≤2xMRL results accuracy must be ±50%. Analytes >2xMRL results accuracy must be ±30%
Initial Demonstration of Capability	Must pass criteria for each analyst before they run field samples—±20% of the true value

APPLICATION NOTE 73415

Routine analysis of purgeable organic compounds in drinking water with ISQ 7000 GC-MS

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Keywords: EPA, VOCs, phthalates, trace analysis, gas chromatography, single quadrupole mass spectrometry, selected ion monitoring, sensitivity, GRO, THM, volatiles, environmental lab, environmental sample analysis, contract labs

Goal

Demonstration of a routine analytical method that meets the requirements outlined in U.S. EPA Method 524.4 for the quantitation of purgeable organic compounds (POCs) in drinking water, using the Teledyne Tekmar Atomx XYZ purge and trap (P&T) system along with a Thermo Scientific™ ISQ™ 7000 Mass Spectrometry (MS) system coupled with a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC) along with a single software control for the entire system, the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS). Method linearity, method detection limit (MDL), precision, accuracy, and minimum reporting level (MRL) confirmation were assessed to evaluate method performance.

Introduction

It is essential that routine environmental laboratories monitor drinking water for the presence of purgeable organic compounds. POCs have the potential to cause negative health effects when consumed. EPA Method 524.4 is used in environmental analysis labs to test water samples for volatile organic compounds (VOCs).[1] It is extremely important that routine laboratories accurately detect and quantitate VOCs to ensure water is safe for the public. This method is a revised version of EPA Method 524.2 on which more details can be found here. Due to technological advances in analytical instrumentation and techniques, this method allows the analyst to modify P&T parameters and GC/MS conditions. This can result in reduced sample run time and increased laboratory throughput in a 12-hour period.

With this method flexibility comes strict quality control (QC) requirements for EPA Method 524.4. Along with MDL and Initial Demonstration of Capability (IDC) calculations, MRL confirmation is required. The MRL is the minimum concentration that can be reported by a lab and can be very difficult to achieve as you have to determine the ±50% limits of the low level standard in the calibration. These limits are used for low level Calibrating Check Standards and determine if the calibration is still valid during routine analysis.

In order to perform EPA Method 524.4, method acceptance criteria must be achieved. These criteria include assessing the linearity and detection limits for a wide range of compounds. The analytical method must produce consistent results and be reproducible from day to day. As the sample matrix is water, it is essential that moisture is not introduced into the analytical column as this could damage the column and affect the results.

The following evaluation describes the use of the ISQ 7000 MS system coupled to the Atomx XYZ P&T for U.S. EPA Method 524.4.

Experimental

Sample preparation

A 25 parts per million (ppm) calibration working standard was prepared in methanol from the following Restek standards: 524.3 VOA MegaMix® and 524.3 Gas Calibration Mix. In total, the standards contained 75 compounds.

A nine-point calibration curve was prepared from 0.2 to 50 parts per billion (ppb) for all compounds. The relative response factor (RF) was calculated for each compound using three internal standards: 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Surrogate standards consisted of methyl-tert-butyl ether-d_3, 4-bromofluorobenzene, and 1,2-dichlorobenzene-d_4. Internal and surrogate standards were prepared in methanol from Restek standards at a concentration of 12.5 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 12.5 ppb.

Seven 0.5 ppb standards were prepared to calculate the MDL and MRL confirmation calculations. Seven 5 ppb standards were prepared for the assessment of precision and accuracy, and a further twenty 5 ppb standards were prepared for the assessment of method robustness. All calibration, MDL, accuracy, precision, robustness, and MRL standards were analyzed with the Atomx XYZ conditions in Table 1. GC-MS conditions are shown in Table 2.

Instrument control and data processing

Data were acquired, processed, and reported using Chromeleon CDS software, version 7.2. This software can control both the GC/MS system and the Tekmar Atomx XYZ P&T. This allows a single software to be utilized for the full workflow simplifying the instrument operation. Figure 1 shows the Chromeleon control of the Atomx XYZ P&T. The fully optimized method used within this application note is available for download via Thermo Scientific™ AppsLab. AppsLab contains all the parameters needed to acquire, process, and report the analytical data for EPA Method 524.4.[2]

GC-MS parameters

A Thermo Scientific™ TRACE™ 1310 GC was coupled to the ISQ 7000 MS system equipped with the Thermo Scientific™ NeverVent™ vacuum probe interlock (VPI) and a Thermo Scientific™ ExtractaBrite ion source. A Thermo Scientific™ TraceGOLD™ TG-VMS 20 m × 0.18 mm, 1 µm film (P/N 26080-4950) was used for compound separation. The GC run time is under 15 minutes and a 50 to 1 split injection was used. The ISQ 7000 MS system was operated in full scan mode, which gave enough sensitivity to meet the regulatory requirements. Expanded method parameters for the GC-MS system are displayed in Table 2.

Table 1. Tekmar Atomx XYZ water method parameters

Standby	Variable	Desorb	Variable
Valve oven temperature	140 °C	Methanol needle rinse	Off
Transfer line temperature	140 °C	Methanol needle rinse volume	0.00 mL
Sample mount temperature	90 °C	Water needle rinse volume	7.00 mL
Water heater temperature	90 °C	Sweep needle time	0.25 min
Sample vial temperature	20 °C	Desorb preheat temperature	245 °C
Soil valve temperature	100 °C	GC start signal	Begin Desorb
Standby flow	10 mL/min	Desorb time	1.00 min
Purge ready temperature	40 °C	Drain flow	300 mL/min
		Desorb temperature	250 °C
Purge	**Variable**	**Bake**	**Variable**
Sample equilibrate time	0.00 min	Methanol glass rinse	Off
Pre-sweep time	0.25 min	Number of methanol glass rinses	0
Prime Sample fill volume	3.00 mL	Methanol glass rinse volume	0.00 mL
Sample volume	5.00 mL	Water bake rinses	1
Sweep sample time	0.25 min	Water bake rinse volume	7.00 mL
Sweep sample flow	100 mL/min	Bake rinse sweep time	0.25 min
Sparge vessel heater	Off	Bake rinse sweep flow	100 mL/min
Sparge vessel temperature	N/A	Bake rinse drain time	0.40 min
Pre-purge time	0.00 min	Bake time	6.00 min
Pre-purge flow	0 mL/min	Bake flow	200 mL/min
Purge time	5.50 min	Bake temperature	280 °C
Purge flow	80 mL/min	Condensate bake temperature	180 °C
Purge temperature	20 °C		
Condensate purge temperature	20 °C		
Dry purge time	0.00 min	Trap	K
Dry purge flow	0 mL/min	Chiller tray	On
Dry purge temperature	20 °C	Purge gas	Nitrogen

Table 2. GC/MS conditions

Parameter	Value
TRACE 1310 GC	
Column	TraceGOLD TG-VMS, 20 m x 0.18 mm, 1 µm film Carrier gas: helium @ 1 mL/min
Oven temperature program	35 °C, 3 min, 12 °C/min to 85 °C, 25 °C/min to 225 °C, 2 min hold Run time 14.8 min
Inlet	200 °C, 50:1 split Purge flow 0.5 mL/min
ISQ 7000 MS	
	Transfer line 230 °C; Ion source 280 °C
Scan mode	Range: 35 amu to 260 amu; Solvent delay: 0.50 min Dwell/scan time: 0.15 s
Filament current	Emission current: 25 µA Detector gain: 3.00E+005

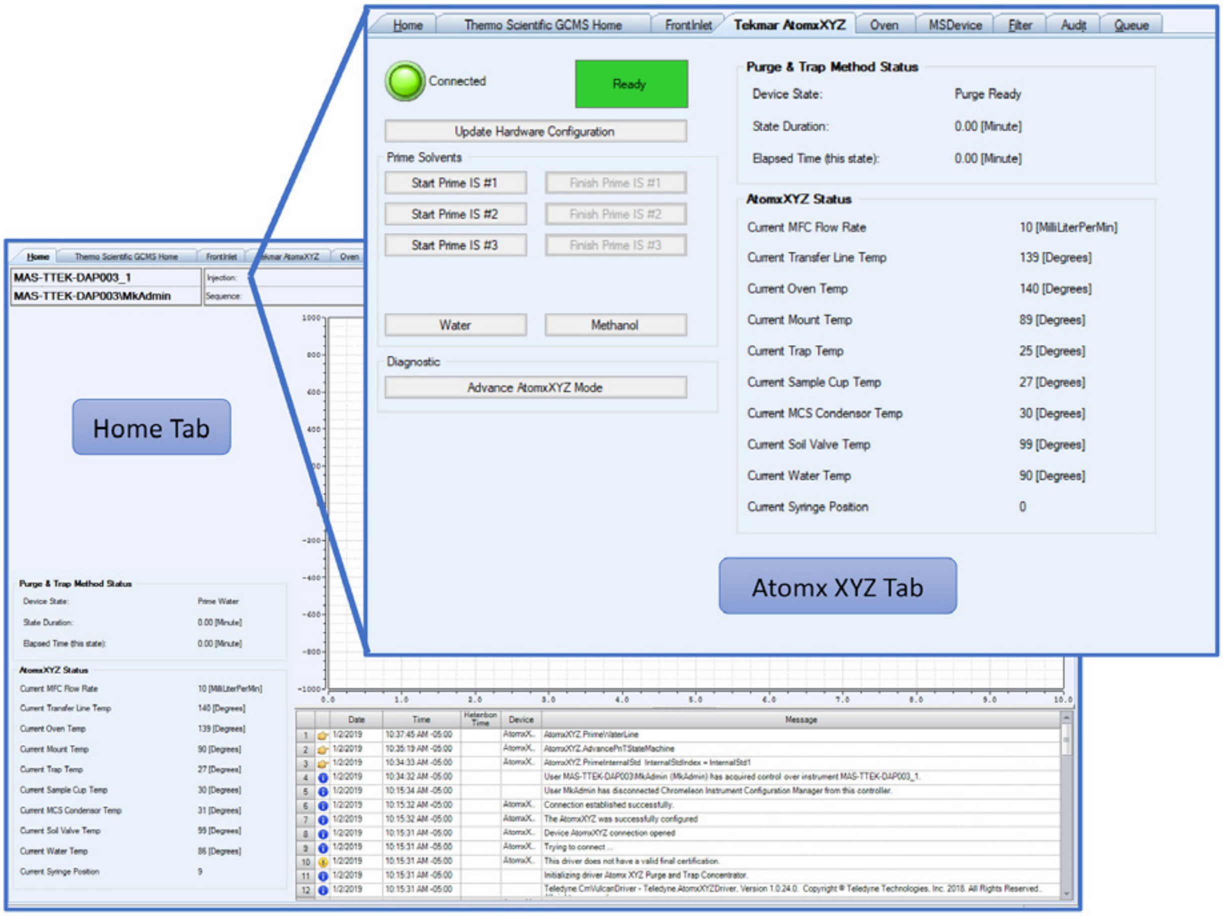
Results and discussion

Chromatography

Excellent chromatography was achieved using the conditions described in Table 2. The moisture transferred onto the analytical column was minimized using the Atomx XYZ P&T, which limits any damage to the analytical column and increases method robustness. Figure 2 displays consistent peak shape and separation of a 5 ppb VOC standard with minimal water interference.

Linearity and sensitivity

A calibration range of 0.2–50 ppb was assessed for all compounds. Table 3 displays the R^2 value, which was ≥0.995 for all compounds across the specified concentration range. The MDL and the MRL were assessed using n=7 replicates of a 0.5 ppb standard. The MDL, which is <0.25 ppb, and the precision data, which is <20 %RSD, are shown in Table 3, alongside the MRL confirmation data, with upper prediction interval of results (PIR) limit ≤150% and lower PIR limit ≥50% for all analytes. Iodomethane was outside these limits because the compound broke down after several injections -- a higher concentration was used. Figure 3 demonstrates the quantitation of bromochloromethane in the 5 ppb standard with very good library spectral matching and calibration curve. Figure 4 shows several compounds at 0.2 ppb that are being detected at a low level with excellent peak shape and minimal water interference.



Purge & Trap Method Status

Device State: Purge Ready
State Duration: 0.00 [Minute]
Elapsed Time (this state): 0.00 [Minute]

AtomxXYZ Status

Current MFC Flow Rate	10 [MilliLiterPerMin]
Current Transfer Line Temp	139 [Degrees]
Current Oven Temp	140 [Degrees]
Current Mount Temp	89 [Degrees]
Current Trap Temp	25 [Degrees]
Current Sample Cup Temp	27 [Degrees]
Current MCS Condensor Temp	30 [Degrees]
Current Soil Valve Temp	99 [Degrees]
Current Water Temp	90 [Degrees]
Current Syringe Position	0

MAS-TTEK-DAP003_1
MAS-TTEK-DAP003\MkAdmin

Purge & Trap Method Status

Device State: Prime Water
State Duration: 0.00 [Minute]
Elapsed Time (this state): 0.00 [Minute]

AtomxXYZ Status

Current MFC Flow Rate	10 [MilliLiterPerMin]
Current Transfer Line Temp	140 [Degrees]
Current Oven Temp	139 [Degrees]
Current Mount Temp	90 [Degrees]
Current Trap Temp	27 [Degrees]
Current Sample Cup Temp	30 [Degrees]
Current MCS Condensor Temp	31 [Degrees]
Current Soil Valve Temp	99 [Degrees]
Current Water Temp	86 [Degrees]
Current Syringe Position	9

```
    Date      Time               Retention Time  Device     Message
1   1/2/2019  10:37:45 AM -05:00                 AtomxX...  AtomxXYZ.PrimeWaterLine
2   1/2/2019  10:35:19 AM -05:00                 AtomxX...  AtomxXYZ.AdvancePnTStateMachine
3   1/2/2019  10:34:33 AM -05:00                 AtomxX...  AtomxXYZ.PrimeInternalStd  InternalStdIndex = InternalStd1
4   1/2/2019  10:34:32 AM -05:00                            User MAS-TTEK-DAP003\MkAdmin (MkAdmin) has acquired control over instrument MAS-TTEK-DAP003_1.
5   1/2/2019  10:15:34 AM -05:00                            User MkAdmin has disconnected Chromeleon Instrument Configuration Manager from this controller.
6   1/2/2019  10:15:32 AM -05:00                 AtomxX...  Connection established successfully.
7   1/2/2019  10:15:32 AM -05:00                 AtomxX...  The AtomxXYZ was successfully configured
8   1/2/2019  10:15:31 AM -05:00                 AtomxX...  Device AtomxXYZ connection opened
9   1/2/2019  10:15:31 AM -05:00                 AtomxX...  Trying to connect ...
10  1/2/2019  10:15:31 AM -05:00                 AtomxX...  This driver does not have a valid final certification.
11  1/2/2019  10:15:31 AM -05:00                            Initializing driver Atomx XYZ Purge and Trap Concentrator.
12  1/2/2019  10:15:31 AM -05:00                            Teledyne.CmVulcanDriver - Teledyne.AtomxXYZDriver, Version 1.0.24.0. Copyright © Teledyne Technologies, Inc. 2018. All Rights Reserved.
```

Figure 1. Chromeleon control of the Atomx XYZ P&T

Peaks:
19. tert-butyl alcohol
20. tert-butyl ethyl ether
21. trans-1,2-dichloroethene
22. Bromochloromethane
23. Chloroform
24. Carbon tetrachloride
25. Tetrahydrofuran
26.1,1,1-trichloroethane
27. 1,1-dichloropropene
28. 1-chlorobutane
29. Benzene

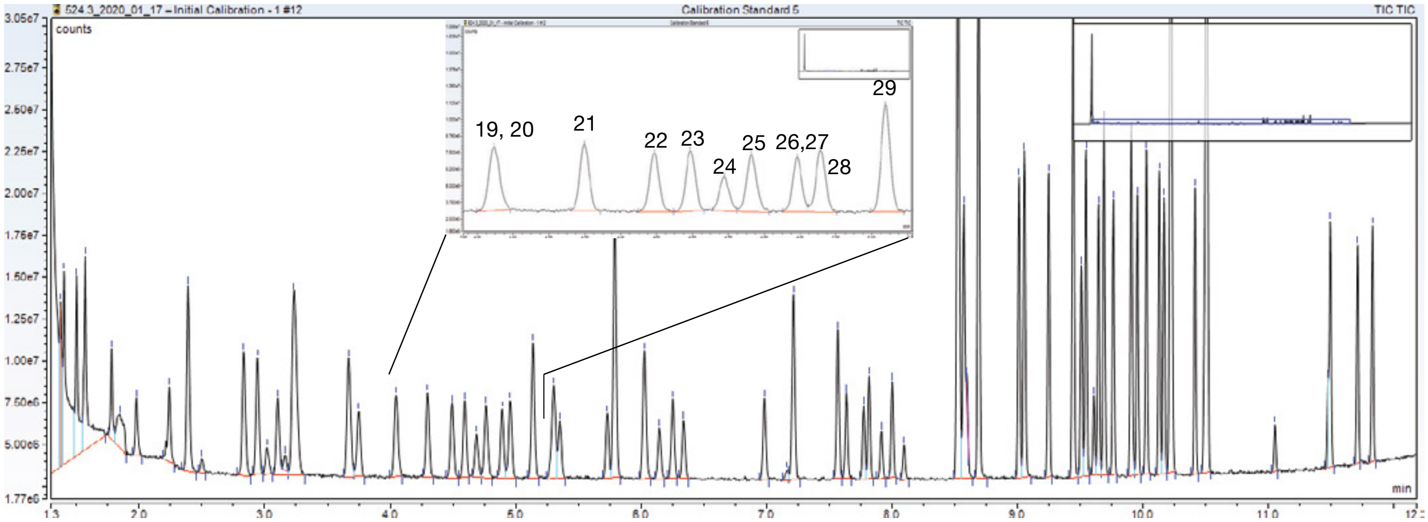


Figure 2. Total ion chromatogram (TIC) of a water method 5 ppb VOC standard with an inset indicating good peak shape and separation with minimal matrix interference

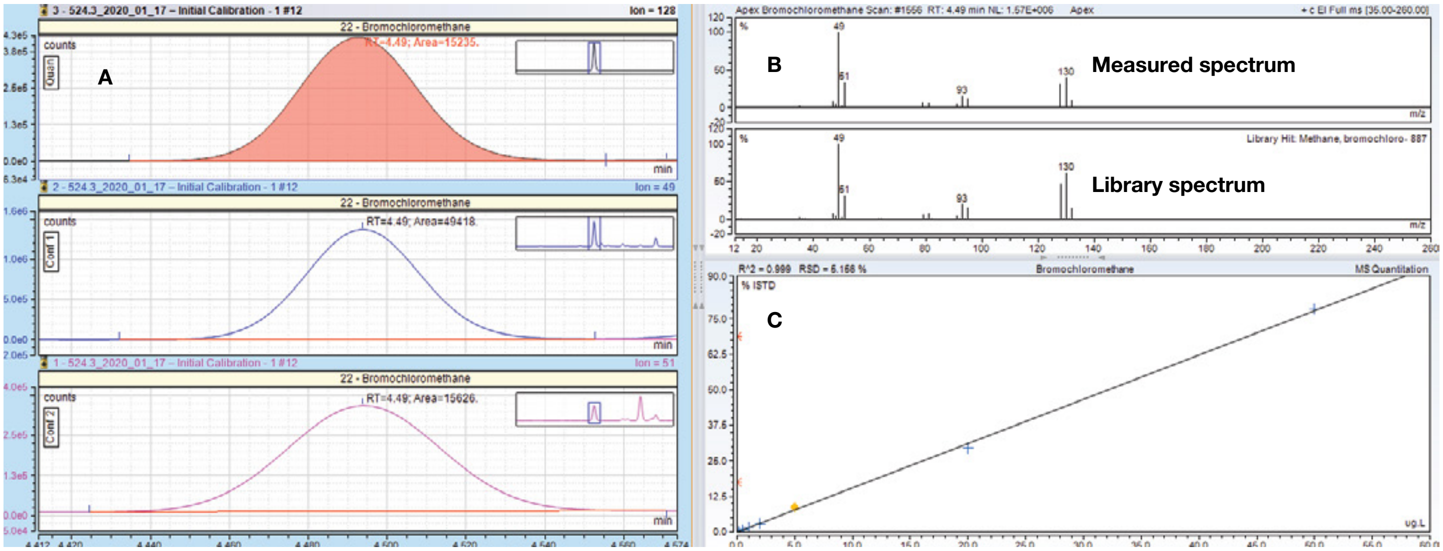


Figure 3. Chromeleon results browser showing extracted ion chromatograms for bromochloromethane, quantitation ion and two confirming ions (A), a matching measured spectrum to the NIST library (B) and a linear calibration over a concentration range of 0.2 ppb to 50 ppb (C)

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Table 3 (part 1). Calibration, detection limit, and minimum reporting limit results

Compound	**Calibration**			**MDL (n=7, 0.5 ppb)**				**IDC (n=7, 5 ppb)**		**MRL confirmation (n=7, 0.5 ppb)**	
	Retention Time	**Linearity (r^2 ≥0.995)**	**Avg. RF**	**Avg. Conc. (ppb)**	**MDL (ppb)**	**Accuracy (±20%)**	**Precision (≤20%)**	**Accuracy (±20%)**	**Precision (≤20%)**	**LPIR (≥50%)**	**UPIR (≤150%)**
Dichlorodifluoromethane[1]	1.38	0.999	0.339	0.49	*0.11*	*89*	*7.9*	*119*	*5.2*	*61*	*117*
Chlorodifluoromethane[3]	1.41	0.998	0.851	0.60	*0.10*	*120*	*5.1*	*120*	*4.0*	*96*	*144*
Chloromethane	1.51	0.999	1.27	0.44	*0.14*	*87*	*9.9*	*119*	*4.6*	*53*	*121*
Vinyl chloride	1.57	0.998	0.470	0.60	*0.11*	*120*	*6.0*	*119*	*4.8*	*91*	*148*
1,3-Butadiene	1.58	0.999	0.415	0.58	*0.13*	*116*	*7.0*	*120*	*7.2*	*84*	*149*
Bromomethane[1]	1.79	0.997	0.416	0.43	*0.13*	*85*	*9.8*	*117*	*6.5*	*52*	*117*
Trichlorofluoromethane	1.99	0.999	0.481	0.58	*0.11*	*117*	*6.3*	*114*	*5.2*	*88*	*146*
Diethyl ether	2.26	0.999	0.337	0.60	*0.10*	*119*	*5.1*	*118*	*5.9*	*95*	*144*
1,1-Dichloroethene	2.4	0.999	0.374	0.59	*0.11*	*117*	*5.8*	*116*	*5.1*	*90*	*144*
Allyl chloride	2.41	0.999	1.51	0.60	*0.09*	*120*	*4.6*	*120*	*6.0*	*98*	*142*
Iodomethane[2,3,5]	2.52	0.999	0.348	5.7	*2.7*	*113*	*14.9*	*113*	*14.9*	*46*	*180*
Carbon disulfide	2.86	0.998	0.284	0.58	*0.13*	*116*	*7.2*	*115*	*4.2*	*83*	*149*
Methylene chloride	2.97	0.997	1.02	0.59	*0.10*	*118*	*5.6*	*120*	*3.6*	*91*	*144*
cis-1,2-Dichloroethene	3.13	0.999	0.403	0.57	*0.09*	*114*	*5.3*	*116*	*4.5*	*90*	*138*
Methyl acetate	3.19	1.000	0.445	0.54	*0.10*	*108*	*5.8*	*108*	*6.9*	*83*	*133*
Methyl-t-butyl ether-d_3 (surr)	3.25	10.7	0.932	12.8		*102*	*6.4*	*105*	*7.9*	*76*	*128*
Methyl tert butyl ether	3.27	0.995	0.878	0.54	*0.10*	*109*	*5.6*	*103*	*7.8*	*85*	*133*
Diisopropyl ether	3.68	0.997	1.71	0.57	*0.05*	*114*	*2.8*	*116*	*3.3*	*101*	*127*
1,1-Dichloroethane	3.77	0.999	0.891	0.60	*0.10*	*120*	*5.5*	*118*	*4.2*	*94*	*146*
t-Butyl alcohol (TBA)	4.07	0.997	1.01	0.56	*0.07*	*112*	*3.7*	*105*	*4.2*	*96*	*129*
t-Butyl ethyl ether (ETBE)	4.07	0.997	1.01	0.56	*0.07*	*113*	*3.8*	*111*	*4.1*	*96*	*129*
trans-1,2-dichloroethene	4.32	0.998	0.658	0.58	*0.06*	*115*	*3.5*	*120*	*3.0*	*99*	*132*
Bromochloromethane	4.52	0.999	0.201	0.60	*0.07*	*119*	*3.7*	*113*	*1.6*	*101*	*137*
Chloroform	4.62	0.999	0.740	0.58	*0.07*	*116*	*3.8*	*118*	*3.1*	*98*	*133*
Carbon tetrachloride	4.71	0.999	0.376	0.52	*0.10*	*104*	*5.9*	*102*	*6.3*	*79*	*128*
1,1,1-Trichloroethane	4.79	0.999	0.492	0.55	*0.10*	*110*	*5.7*	*107*	*5.0*	*85*	*135*
Tetrahydrofuran	4.79	1.000	0.047	0.56	*0.15*	*112*	*8.3*	*119*	*8.9*	*75*	*149*
1,1-Dichloropropene	4.91	0.995	0.432	0.54	*0.07*	*108*	*4.1*	*96*	*6.5*	*91*	*125*
1-Chlorobutane	4.98	0.996	0.704	0.54	*0.06*	*108*	*3.7*	*102*	*5.5*	*92*	*124*
Benzene	5.16	0.996	1.44	0.56	*0.06*	*112*	*3.5*	*105*	*4.2*	*97*	*128*
t-Amyl methyl ether (TAME)	5.33	0.998	0.866	0.57	*0.06*	*115*	*3.3*	*114*	*3.7*	*100*	*130*
1,2-Dichloroethane	5.37	0.999	0.518	0.58	*0.05*	*115*	*2.8*	*116*	*4.1*	*102*	*128*
Trichloroethylene	5.75	0.996	0.309	0.56	*0.11*	*113*	*6.5*	*100*	*5.6*	*84*	*142*
cis-1,3-Dichloropropene	7.65	0.996	0.503	0.55	0.06	111	3.3	99	3.9	96	126
1,1,2-Trichloroethane	7.79	0.996	0.224	0.57	0.07	114	3.9	107	6.4	96	131
Ethyl methacrylate	7.83	0.999	0.463	0.57	0.11	115	6.2	114	4.7	86	143
Dibromochloromethane	7.93	0.996	0.261	0.53	0.10	106	6.1	99	5.8	80	132

1. Calibration curve 0.5 ppb-50 ppb.
2. Calibration curve 1 ppb-50 ppb.
3. Compounds were quadratic regressed.
4. Analyte is a poor purger and broke down after several injections.
5. 5 ppb MDL.

Table 3 (part 2). Calibration, detection limit, and minimum reporting limit results

Compound	Calibration			MDL (n=7, 0.5 ppb)				IDC (n=7, 5 ppb)		MRL confirmation (n=7, 0.5 ppb)	
	Retention Time	Linearity (r^2 ≥0.995)	Avg. RF	Avg. Conc. (ppb)	MDL (ppb)	Accuracy (±20%)	Precision (≤20%)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
1,3-Dichloropropane	8.02	0.996	0.503	0.58	0.04	116	2.2	102	5.2	106	126
1,2-Dibromoethane	8.11	0.997	0.248	0.54	0.08	109	4.5	107	5.4	89	128
Chlorobenzene-d_5 (ISTD)	8.54			12.5							
Chlorobenzene	8.55	0.999	0.920	0.57	0.11	114	5.9	112	4.2	87	140
Ethylbenzene	8.58	0.998	1.72	0.58	0.09	115	4.9	109	5.0	93	138
1,1,1,2-Tetrachloroethane	8.61	0.999	0.239	0.55	0.06	111	3.6	108	5.4	95	127
m,p-Xylene	8.7	0.998	1.50	1.13	0.15	113	4.3	107	5.0	93	132
o-Xylene	9.02	0.997	1.53	0.56	0.08	112	4.4	107	3.8	92	131
Styrene	9.06	0.999	1.15	0.55	0.07	110	4.1	104	4.7	93	128
Bromoform	9.07	0.999	0.211	0.54	0.10	108	6.2	102	5.2	82	134
Isopropylbenzene	9.26	0.999	1.63	0.54	0.09	108	5.0	105	5.5	87	130
4-Bromofluorobenzene (surr)	9.45	4.8	0.863	12.9		103	3.8	99	1.3	88	119
Bromobenzene	9.52	0.998	0.847	0.60	0.06	119	3.2	112	4.1	104	135
n-Propylbenzene	9.55	1.000	3.02	0.54	0.14	109	8.1	111	6.2	74	143
1,1,2,2-Tetrachloroethane	9.62	1.000	0.530	0.58	0.10	116	5.3	116	8.4	92	141
2-Chlorotoluene	9.65	0.999	1.88	0.54	0.12	108	7.2	111	6.0	78	139
1,3,5-Trimethylbenzene	9.7	0.999	1.93	0.56	0.14	112	7.8	106	5.8	77	146
1,2,3-Trichloropropane	9.7	0.999	0.498	0.59	0.10	119	5.5	117	8.2	93	145
4-Chlorotoluene	9.77	0.999	1.96	0.57	0.12	114	6.7	109	5.8	84	144
p-Isopropyltoluene	9.91	0.999	1.75	0.52	0.14	103	8.7	101	5.2	68	139
tert-Butylbenzene	9.91	0.999	1.77	0.52	0.15	104	9.2	101	5.3	66	142
Pentachloroethane[3,4]	9.92	0.995	0.153	0.49	0.18	98	11.9	75	27.7	52	144
1,2,4-Trimethylbenzene	9.96	0.999	1.96	0.56	0.13	112	7.4	108	5.7	79	145
sec-Butylbenzene	10.03	0.999	2.50	0.53	0.13	106	8.0	106	6.2	72	139
1,3-Dichlorobenzene	10.18	0.999	1.44	0.59	0.13	117	6.8	112	5.4	86	149
1,4-Dichlorobenzene-d^4 (ISTD)	10.23			12.5							
1,4-Dichlorobenzene	10.24	0.999	1.47	0.57	0.14	114	7.9	110	6.6	78	150
n-Butylbenzene	10.42	0.999	1.92	0.59	0.13	118	6.9	107	6.0	85	150
Hexachloroethane	10.5	0.998	0.317	0.6	0.13	112	7.1	115	6.2	80	143
1,2-Dichlorobenzene (surr)	10.51	2.0	0.927	12.7		101	1.7	102	2.1	95	108
1,2-Dichlorobenzene	10.52	0.999	1.41	0.56	0.14	112	7.7	110	6.0	77	146
1,2-Dibromo-3-chloropropane	11.06	0.997	0.137	0.55	0.13	109	7.8	118	7.5	76	143
Hexachlorobutadiene	11.48	0.999	0.051	0.58	0.12	115	6.7	112	6.6	84	146
1,2,4-Trichlorobenzene	11.5	0.995	0.922	0.58	0.19	116	10.2	117	2.4	86	147
Naphthalene	11.72	0.996	1.85	0.58	0.12	116	6.6	119	6.4	82	143
1,2,3-Trichlorobenzene	11.84	0.995	0.887	0.56	0.15	112	8.5	120	5.7	74	149

1. Calibration curve 0.5 ppb-50 ppb.
2. Calibration curve 1 ppb-50 ppb.
3. Compounds were quadratic regressed.
4. Analyte is a poor purger and broke down after several injections.
5. 5 ppb MDL.

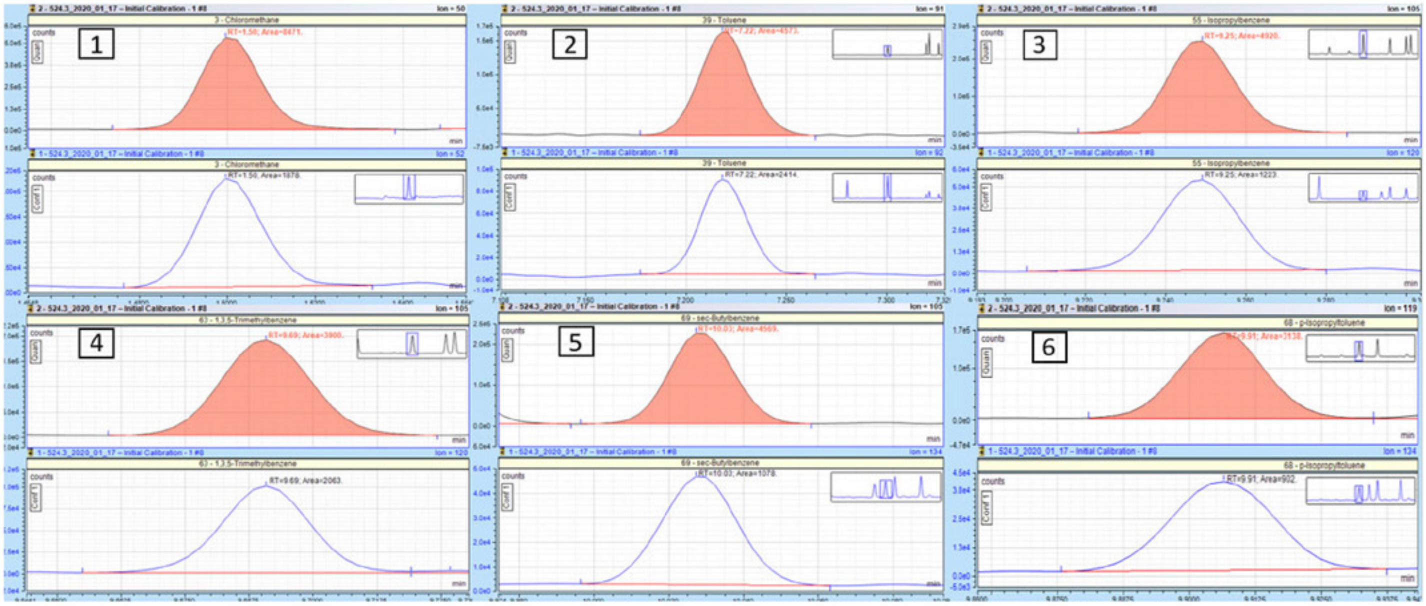

Figure 4. Example of chromatography (extracted quantitation and confirmatory ions) from the calibration level 0.2 ppb for several compounds (1. chloromethane 2. toluene 3. isopropylbenzene 4. 1,3,5-trimethylbenzene 5. sec-butylbenzene 6. p-isopropyltoluene)

Precision and accuracy

Precision and accuracy were assessed by analyzing n=7 replicates of a 5 ppb standard. The results are displayed in Table 3. For all compounds assessed, the %RSD of the calculated concentration is 20% and the mean recovery is within ±20% of the true value meeting the requirements of EPA Method 524.4 for initial demonstration of capability (IDC). Pentachloroethane broke down during the IDC and recovery was just under ±20%.

Method robustness

For use as a routine testing method, it is extremely important that the analytical method is stable and reproducible. In order to demonstrate this, 5 ppb standards (n=20) were injected at intervals over a 120-sample injection sequence. The samples were acquired without user intervention. Figure 5 shows the reproducibility of six of the compounds over 120 injections with excellent percentage RSDs. Accuracy and precision data are displayed in Table 4.

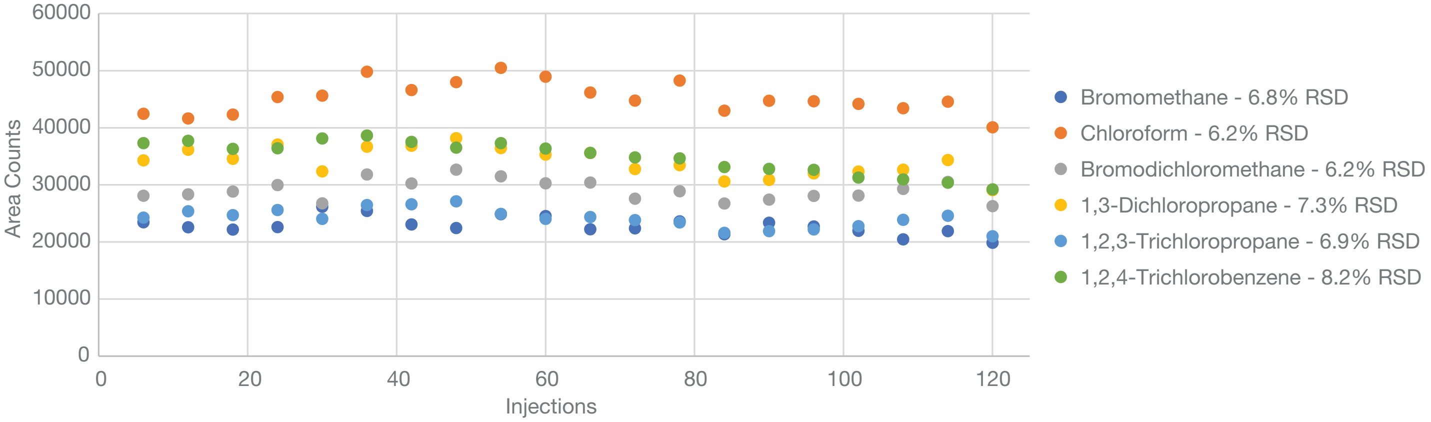

Figure 5. Repeatability of a 5 ppb VOC standard (as absolute peak area counts) assessed over n=120 consecutive injections

Table 4. Accuracy and precision data for n=20 injections of a 5 ppb standard

Compound	Quant. ion	Analyte recovery (n=20)		
		Avg. conc. (ppb)	Accuracy	Precision
Dichlorodifluoromethane	85	5.3	106	17.5
Chlorodifluoromethane	51	6.6	133	18.1
Chloromethane	50	7.0	140	13.8
Vinyl chloride	62	6.1	122	16.0
1,3-Butadiene	54	5.8	117	16.6
Bromomethane	94	6.8	136	8.3
Trichlorofluoromethane	101	5.5	110	16.2
Diethyl ether	59	6.1	121	5.7
1,1-Dichloroethene	96	5.7	113	15.2
Allyl chloride	76	6.1	121	14.4
Iodomethane	142	5.6	112	20.1
Carbon disulfide	76	5.2	105	7.3
Methylene chloride	49	7.1	143	9.0
cis-1,2-Dichloroethene	96	5.6	113	10.5
Methyl acetate	43	6.8	137	7.3
Methyl-t-butyl ether-d$_3$ (surr)	76	12.1	97	6.9
Methyl tert butyl ether	73	4.8	95	5.9
Diisopropyl ether	45	5.7	115	4.4
1,1-Dichloroethane	63	6.4	127	9.3
t-Butyl alcohol (TBA)	59	5.2	103	3.2
t-Butyl ethyl ether (ETBE)	59	5.2	103	3.2
trans-1,2-dichloroethene	61	5.9	118	5.7
Bromochloromethane	128	6.0	119	5.9
Chloroform	83	6.0	120	7.2
Carbon tetrachloride	117	4.6	92	13.9
1,1,1-Trichloroethane	72	5.1	101	11.8
Tetrahydrofuran	97	5.1	103	7.9
1,1-Dichloropropene	75	4.3	85	11.4
1-Chlorobutane	56	4.8	95	11.7
Benzene	78	5.2	103	8.3
t-Amyl methyl ether (TAEE)	73	5.0	100	4.2
1,2-Dichloroethane	62	6.1	122	4.6
Trichloroethylene	95	5.1	101	17.4
1,4-Difluorobenzene (ISTD)	114			
t-Amyl ethyl ether (TMEE)	59	5.1	101	3.5
Dibromomethane	93	5.8	116	4.4
1,2-Dichloropropane	63	5.6	111	7.1
Bromodichloromethane	83	5.3	106	6.4
trans-1,3-Dichloropropene	75	4.2	84	7.3
Toluene	91	4.8	95	6.5
Tetrachloroethylene	164	5.9	118	16.1
cis-1,3-Dichloropropene	75	4.3	86	6.2
1,1,2-Trichloroethane	83	5.5	110	5.8
Ethyl Methacrylate	69	4.6	92	9.5
Dibromochloromethane	129	4.7	94	6.0
1,3-Dichloropropane	76	5.2	104	5.2
1,2-Dibromoethane	107	5.3	105	5.1
Chlorobenzene-d$_5$ (ISTD)	117			
Chlorobenzene	112	5.3	106	5.2
Ethylbenzene	91	4.5	91	7.0
1,1,1,2-Tetrachloroethane	131	5.3	106	5.6
m,p-Xylene	91	8.8	88	6.6
o-Xylene	91	4.3	86	5.6
Styrene	104	4.3	85	5.4
Bromoform	173	4.8	96	5.8
Isopropylbenzene	105	4.2	84	7.2
4-Bromofluorobenzene (surr)	95	11.9	95	3.9
Bromobenzene	77	5.3	106	5.8
n-Propylbenzene	91	4.5	90	8.2
1,1,2,2-Tetrachloroethane	83	6.0	120	15.6
2-Chlorotoluene	91	4.8	96	6.9
1,3,5-Trimethylbenzene	105	4.5	90	7.7
1,2,3-Trichloropropane	75	6.3	125	8.5
4-Chlorotoluene	91	4.7	94	7.3
p-Isopropyltoluene	119	3.9	79	8.0
tert-Butylbenzene	119	3.9	79	8.1
Pentachloroethane[1]	167	2.9	89	35.8
1,2,4-Trimethylbenzene	105	4.6	93	8.0
sec-Butylbenzene	105	4.4	88	9.1
1,3-Dichlorobenzene	146	5.3	106	7.0
1,4-Dichlorobenzene-d$_4$ (ISTD)	152			
1,4-Dichlorobenzene	146	5.3	105	6.9
n-Butylbenzene	91	4.3	86	8.7
Hexachloroethane	201	5.0	101	10.0
1,2-Dichlorobenzene (surr)	152	13.1	105	2.2
1,2-Dichlorobenzene	146	5.4	107	7.0
1,2-Dibromo-3-chloropropane	75	6.0	120	7.8
Hexachlorobutadiene	225	4.8	95	8.6
1,2,4-Trichlorobenzene	180	5.4	107	7.7
Naphthalene	128	4.9	98	10.1

[1] Analyte is a poor purger and broke down after several injections.

Conclusion

The combined solution of the TRACE 1310 GC coupled with the ISQ 7000 system and the Atomx XYZ P&T system provides clear advantages for EPA Method 524.4.

- The ISQ 7000 VPI coupled with the Tekmar Atomx XYZ P&T exceeds all the requirements outlined in EPA Method 524.4 for analysis of purgeable VOCs in water.
- Excellent linearity for all compounds was demonstrated with the R^2 of the calibration response factors passing all method requirements.
- MDL, precision, and MRL confirmation for n=7, 0.5 ppb standards showed no interference from excessive water and produced very reproducible results.
- Precision and accuracy for n=7, 5 ppb standards showed excellent results with average %RSD <9% and recovery values between 96% and 120%.
- The analytical method was demonstrated to be stable and reproducible over 120 injections ensuring consistent results can be obtained.

Further information on VOC analysis using the ISQ 7000 system and the Atomx XYZ P&T can be found in the application note entitled: *Routine Analysis of Volatile Organic Compounds in Drinking Water with ISQ 7000 GC-MS.*[3]

References

1. Method 524.4 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100J7EE.TXT
2. Thermo Fisher Scientific AppsLab Library https://appslab.thermofisher.com/
3. Thermo Scientific Application Note 65632: Routine analysis of volatile organic compounds in drinking water with ISQ 7000 GC-MS https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-65632-gc-ms-volatile-organic-compounds-drinking-water-an65632-en.pdf

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ThermoFisher SCIENTIFIC

EPA Method 624

EPA	624
Matrix	Municipal and Industrial discharges as provided under 40 CFR Part 136.1
Compounds	Volatile Organic Compounds
Number of Compounds	31
Calibration	Calculated response factors <35% RSD
Method Detection Limits (MDLs)	MDLs will vary depending on instrument sensitivity and matrix effect. May range from not determined to 7.2 ppb
BFB Tune Check	Must pass criteria to validate calibration and before daily analysis
QC Check Sample	Must verify calibration curve daily—accuracy interval = 70–110% or determined by average recovery and standard deviation of 4 recovery measurements
Initial Demonstration of Capability	Must pass criteria for each analyst before they run field samples—average percent recovery of n=5 spiked wastewater samples = 70–110%

TECHNICAL NOTE 73762

Analysis of VOCs in wastewater using P&T-single quadrupole GC-MS

Authors: Adam Ladak[1], Terry Jeffers[1], David Lee[2], and Amy Nutter[3]

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Keywords: EPA, VOCs, environmental, trace analysis, gas chromatography, single quadrupole mass spectrometry, selected ion monitoring, environmental testing lab, environmental sample analysis, contract testing labs, wastewater, purge and trap

Goal

Show proof of principle for the major method challenges of U.S. EPA Method 624 for the quantitation of volatile organic compounds (VOCs) in wastewater, using the Teledyne Tekmar Atomx XYZ purge and trap (P&T) system along with a Thermo Scientific™ ISQ™ 7000 Mass Spectrometry (MS) system coupled with a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC) and Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS). Linearity, method detection limit (MDL), precision, accuracy, and Initial Demonstration of Capability (IDC) were assessed to evaluate method performance.

Introduction

It is crucial that environmental analytical testing laboratories monitor wastewater for the presence of volatile organic compounds (VOCs). U.S. EPA Method 624 is used in environmental labs to test wastewater to ensure that it does not contain any pollutants and complies with the Clean Water Act.[1] If VOCs are released into wastewater from industrial activities, they can have an adverse effect on plants, wildlife, and ultimately the public.[2] It is extremely important that analytical testing labs ensure accurate detection and quantitation of VOCs to verify if wastewater samples are not contaminated. Due to technological advances in analytical instrumentation and techniques, EPA Method 624 allows the analyst to modify P&T parameters and GC-MS conditions. This can result in reduced sample run time and increased laboratory throughput in a 12-hour period.

To perform EPA Method 624, method acceptance criteria must be achieved. These criteria include creating a working calibration curve, MDL and IDC accuracy, and precision for target compounds. As the sample matrix is water, it is essential that moisture is not introduced into the analytical column as this could damage the column and affect the results.

The following evaluation describes the use of the ISQ 7000 MS system coupled to the Atomx XYZ P&T for the main criteria of U.S. EPA Method 624.

Experimental

Sample preparation

A working 50 ppm calibration standard was prepared in methanol from Restek™ standards: 624 Calibration Mix #1 and Volatiles MegaMix™ Standard, EPA Method 624. In total, the standard contained 31 compounds.

The calibration curve was prepared from 0.5 to 200 parts per billion (ppb) (µg/L) for all compounds. The relative response factor (RRF) was calculated for each compound using one of the three internal standards: bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane. Surrogate standards consisted of pentafluorobenzene, fluorobenzene, and 1-bromo-4-fluorobenzene. Internal and surrogate standards were prepared together in methanol from Restek standards at a concentration of 30 parts per million (ppm) (mg/L), after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 30 ppb.

Seven 0.5 ppb standards were prepared for MDLs and precision calculations. Also, five 5 ppb standards were prepared for the IDC precision and accuracy calculations. All calibration, MDL, and IDC samples were analyzed with the Atomx XYZ conditions in Table 1.

Table 1. Tekmar Atomx XYZ water method parameters

Purge	Variable
Valve oven temp.	140 °C
Transfer line temp.	140 °C
Sample mount temp.	90 °C
Water heater temp.	90 °C
Sample vial temp.Temp	20 °C
Soil valve temp.	100 °C
Standby flow	10 mL/min
Condensate ready temp.	45 °C
Purge ready temp.	40 °C
Purge	Variable
Sample equilibrate time	0.00 min
Pre-sweep time	0.25 min
Prime sample fill volume	3.00 mL
Sample volume	5.00 mL
Sweep sample time	0.25 min
Sweep sample flow	100 mL/min
Sparge vessel heater	Off
Sparge vessel temp.	20 °C
Pre-purge time	0.00 min
Pre-purge flow	0 mL/min
Purge time	11.00 min
Purge flow	40 mL/min
Purge temp.	20 °C
Condensate purge temp.	20 °C
Dry purge time	0.00 min
Dry purge flow	100 mL/min

Desorb	Variable
Methanol needle rinse	Off
Methanol needle rinse volume	0.00 mL
Water needle rinse volume	7.00 mL
Sweep needle time	0.25 min
Dry purge temp.	20 °C
Desorb preheat temp.	245 °C
GC start signal	Begin Desorb
Desorb time	2.00 min
Drain flow	300 mL/min
Desorb temp.	250 °C
Bake	Variable
Methanol glass rinse	Off
Number of methanol glass rinses	0
Methanol glass rinse volume	0.00 mL
Water bake rinses	1
Water bBake rinse volume	7.00 mL
Bake rinse sweep time	0.25 min
Bake rinse sweep flow	100 mL/min
Bake rinse drain time	0.40 min
Bake time	2.00 min
Bake flow	200 mL/min
Bake temp.	260 °C
Condensate bake temp.	200 °C
Trap	#9
Purge gas	Nitrogen

GC-MS parameters

A TRACE 1310 GC was coupled to the ISQ 7000 MS system equipped with the Thermo Scientific™ NeverVent™ vacuum probe interlock (VPI) and a Thermo Scientific™ ExtractaBrite™ ion source. A Thermo Scientific™ TraceGOLD™ TG-VMS 20 m x 0.18 mm, 1 µm film (P/N 26080-4950) was used for compound separation. The GC run time is under 15 minutes and a 50 to 1 split injection was used. The ISQ 7000 MS system was operated in full-scan mode, which gave enough sensitivity to meet the regulatory requirements. Expanded method parameters for the GC-MS system are displayed in Table 2.

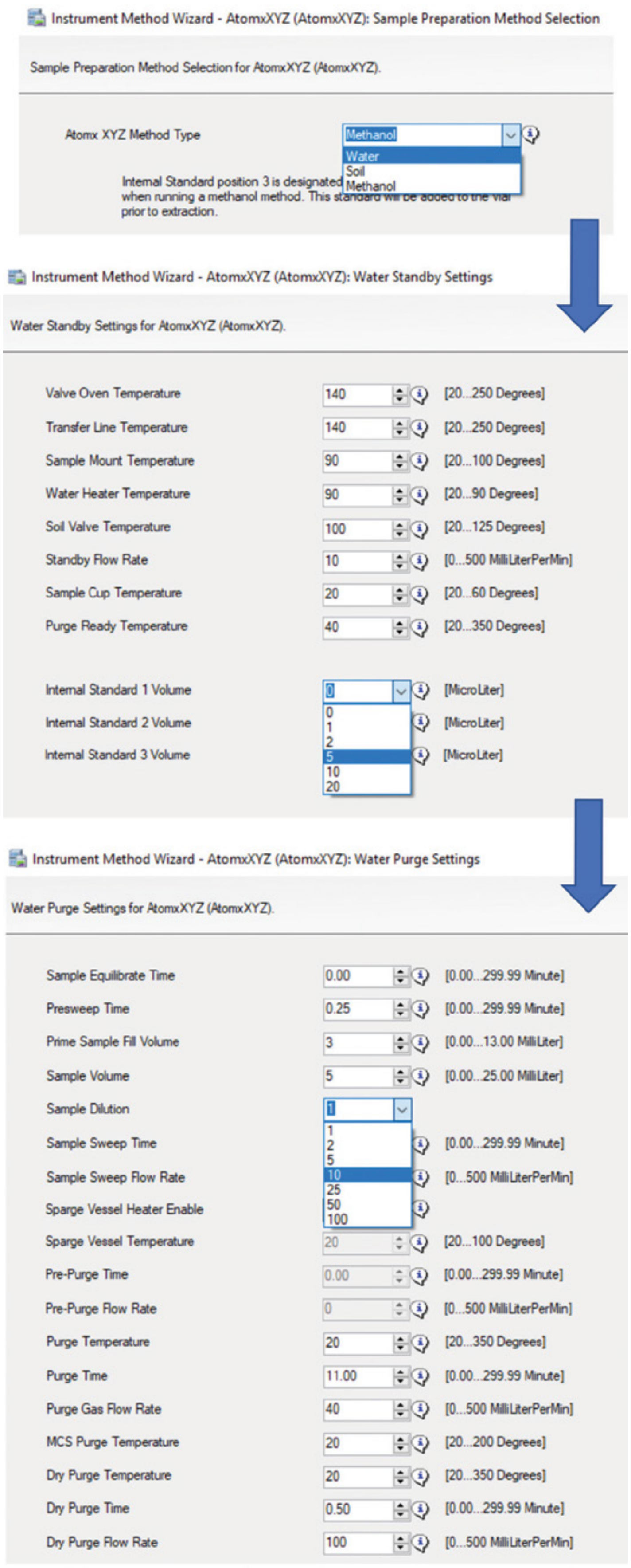
Table 2. GC-MS conditions

TRACE 1310 GC Conditions	
Column	TraceGOLD VMS, 20 m × 0.18 mm, 1 µm film Carrier gas: helium @ 1 mL/min Helium – 0.8 mL/min
Oven temperature program	35 °C, 3 min, 12 °C/min to 85 °C 25 °C/min to 225 °C, 2 min hold Run time: 14.767 min
Inlet	SSL at 200 °C, 50:1 split Purge flow: 0.5 mL/min
ISQ 7000 MS Conditions	
Temperature	Transfer line: 230 °C Ion source: 280 °C
Scan	Range: 35 amu to 260 amu Ionization mode: Electron ionization at 70 eV Solvent delay: 0.50 min Dwell/scan time: 0.15 s
Current	Emission current: 25 µA, Detector gain: 3.00E+005

Instrument control and data processing

Data were acquired, processed, and reported using Chromeleon CDS software, version 7.2. This software can control both the GC-MS system and the Tekmar Atomx XYZ P&T. This allows a single software to be utilized for the full workflow simplifying the instrument operation. Figure 1 shows the Chromeleon control of the Atomx XYZ P&T. The fully optimized method used within this application note is available for download via Thermo Scientific™ AppsLab. AppsLab contains all the parameters needed to acquire, process, and report the analytical data for EPA Method 624.2

Guided instrument setup of Atomx XYZ module within Chromeleon CDS



Instrument Method Wizard - AtomxXYZ (AtomxXYZ): Sample Preparation Method Selection

Sample Preparation Method Selection for AtomxXYZ (AtomxXYZ).

Atomx XYZ Method Type: Methanol

Internal Standard position 3 is designated when running a methanol method. This standard will be added to the vial prior to extraction.

Instrument Method Wizard - AtomxXYZ (AtomxXYZ): Water Standby Settings

Water Standby Settings for AtomxXYZ (AtomxXYZ).

Valve Oven Temperature	140	[20...250 Degrees]
Transfer Line Temperature	140	[20...250 Degrees]
Sample Mount Temperature	90	[20...100 Degrees]
Water Heater Temperature	90	[20...90 Degrees]
Soil Valve Temperature	100	[20...125 Degrees]
Standby Flow Rate	10	[0...500 MilliLiterPerMin]
Sample Cup Temperature	20	[20...60 Degrees]
Purge Ready Temperature	40	[20...350 Degrees]
Internal Standard 1 Volume	0	[MicroLiter]
Internal Standard 2 Volume		[MicroLiter]
Internal Standard 3 Volume		[MicroLiter]

Instrument Method Wizard - AtomxXYZ (AtomxXYZ): Water Purge Settings

Water Purge Settings for AtomxXYZ (AtomxXYZ).

Sample Equilibrate Time	0.00	[0.00...299.99 Minute]
Presweep Time	0.25	[0.00...299.99 Minute]
Prime Sample Fill Volume	3	[0.00...13.00 MilliLiter]
Sample Volume	5	[0.00...25.00 MilliLiter]
Sample Dilution	1	
Sample Sweep Time		[0.00...299.99 Minute]
Sample Sweep Flow Rate		[0...500 MilliLiterPerMin]
Sparge Vessel Heater Enable		
Sparge Vessel Temperature	20	[20...100 Degrees]
Pre-Purge Time	0.00	[0.00...299.99 Minute]
Pre-Purge Flow Rate	0	[0...500 MilliLiterPerMin]
Purge Temperature	20	[20...350 Degrees]
Purge Time	11.00	[0.00...299.99 Minute]
Purge Gas Flow Rate	40	[0...500 MilliLiterPerMin]
MCS Purge Temperature	20	[20...200 Degrees]
Dry Purge Temperature	20	[20...350 Degrees]
Dry Purge Time	0.50	[0.00...299.99 Minute]
Dry Purge Flow Rate	100	[0...500 MilliLiterPerMin]

Figure 1. Chromeleon control of the Atomx XYZ P&T

Results and discussion

Chromatography

Excellent chromatography was achieved using the conditions described in Table 2. The moisture transferred onto the analytical column was minimized using the Atomx XYZ P&T, which limits any damage to the analytical column and increases method robustness. This is achieved by the moisture control system that improves water vapor removal from the samples. Figure 2 displays consistent peak shape and separation of a 10 ppb VOC standard with minimal water interference.

Linearity and sensitivity

A calibration range of 0.5–200 ppb was assessed for all compounds, except for chloroethane (2–200 ppb) and *cis*-1,3-dichloropropene (1–200 ppb). The calibration curves were used to calculate the average and relative standard deviation (%RSD) of the response factor (RF) for the calibration curve. The obtained values are shown in Table 3. To meet the EPA Method 624 criteria, the %RSD of the RF must be <35. The MDL was assessed using n=7 replicates of a 0.5 ppb standard for all compounds, except for *cis*-1,3-dichloropropene, which used n=7 replicates of a 1 ppb standard.

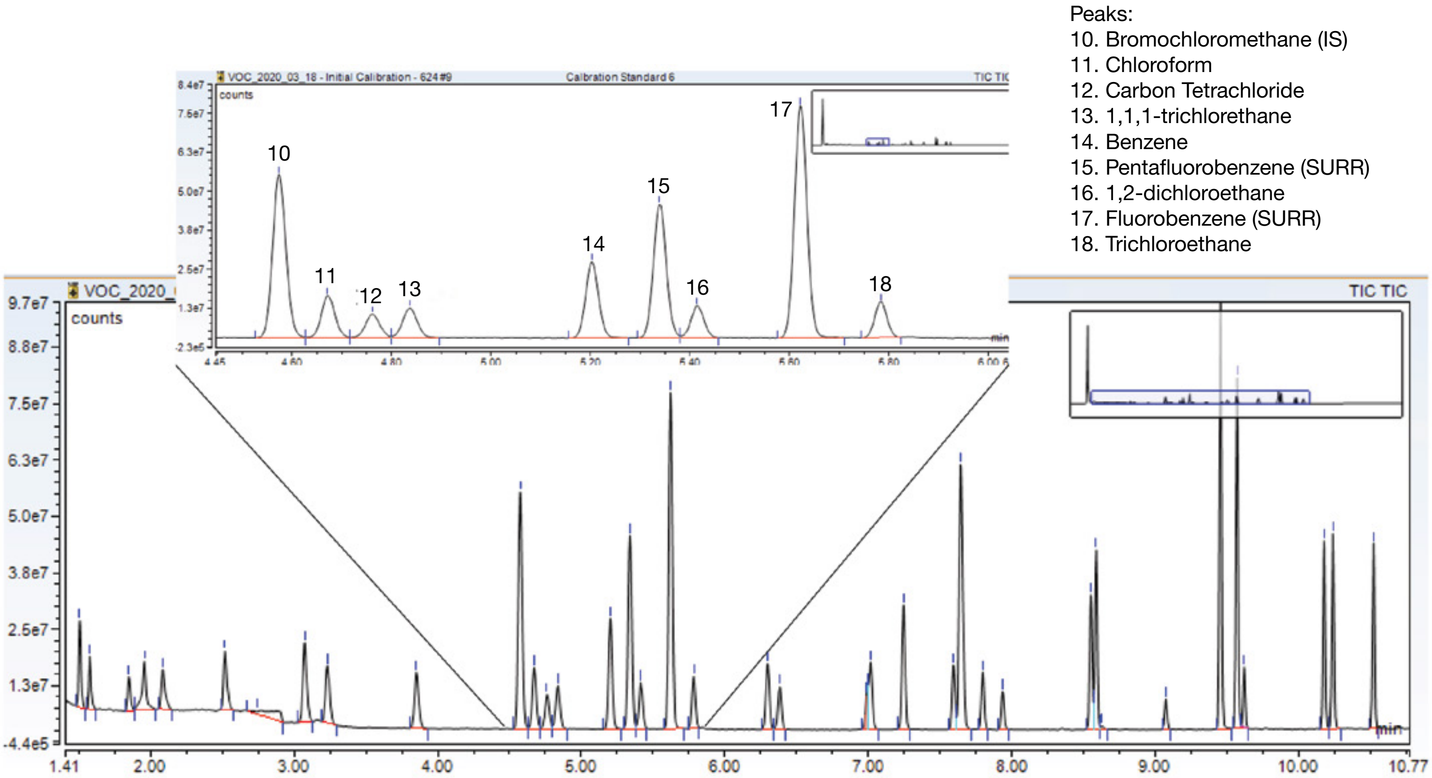


Figure 2. Total ion chromatogram (TIC) of a 10 ppb (equivalent to 10 µg/L in sample) VOC standard with an inset indicating consistent peak shapes and separation with minimal water interference

Table 3. Calibration results showing average and relative standard deviation (%RSD) of the response factor (RF) for each compound

Peak name	Retention time	Quantitation ion	Linearity (RF %RSD)	Average RF
Chloromethane	1.51	50	17.8	1.4
Vinyl chloride	1.58	62	5.61	0.7
Bromomethane	1.85	94	16.7	0.3
Chloroethane	1.96	64	16.2	0.4
Trichlorofluoromethane	2.09	101	5.76	0.6
1,1-Dichloroethene	2.52	96	6.09	0.4
Methylene chloride	3.07	84	14.5	0.6
trans-1,2-Dichloroethene	3.22	96	5.83	0.4
1,1-Dichloroethane	3.84	63	5.41	1.1
Bromochloromethane (ISTD)	4.57	49		
Chloroform	4.67	83	6.42	0.8
Carbon tetrachloride	4.76	117	13.7	1.7
1,1,1-Trichloroethane	4.83	97	8.67	2.2
Benzene	5.20	78	6.55	7.2
Pentafluorobenzene (surr)	5.34	168	8.64	3.8
1,2-Dichloroethane	5.41	98	13.9	0.2
Fluorobenzene (surr)	5.62	96	1.75	7.4
Trichloroethene	5.78	130	10.2	1.4
1,2-Dichloropropane	6.29	112	10.1	0.2
Bromodichloromethane	6.38	127	9.20	0.2
2-Chloroethyl vinyl ether	6.99	106	3.90	0.2
trans-1,3-Dichloropropene	7.02	75	10.4	2.7
Toluene	7.24	92	7.18	3.8
Tetrachloroethylene	7.59	164	6.07	0.3
2-Bromo-1-chloropropane (ISTD)	7.64	79		
cis-1,3-Dichloropropene	7.65	75	17.7	0.7
1,1,2-Trichloroethane	7.80	97	9.54	0.3
Dibromochloromethane	7.93	127	12.2	0.3
Chlorobenzene	8.55	112	8.35	1.1
Ethylbenzene	8.58	106	6.55	0.6
Bromoform	9.07	173	7.80	0.3
4-Bromofluorobenzene (surr)	9.45	95	4.37	0.8
1,4-Dichlorobutane (ISTD)	9.57	55		
1,1,2,2-Tetrachloroethane	9.61	168	9.60	0.0
1,3-Dichlorobenzene	10.17	146	10.9	1.2
1,4-Dichlorobenzene	10.24	146	10.7	1.2
1,2-Dichlorobenzene	10.52	146	10.0	1.2

1. Calibration curve 2–200 ppb (µg/L)
2. Calibration curve 1–200 ppb (µg/L)
3. IDL calculated from n=x repeat injections of a 1 ppb (µg/L) standard

Table 4 displays the MDL values, which are <0.25 ppb for most compounds, and the precision data obtained at the MDL level, which shows %RSD of calculated amount <20 for all compounds. Table 4 also displays the IDC results for all compounds. Using n=5 replicates of a 5 ppb standard, accuracy and precision were assessed.

Table 4. Method detection limits and initial demonstration of capability results

	Method detection limit (n=7, 0.5 ppb)			Initial demonstration of capability (n=5, 5 ppb)	
Peak name	**Average conc.**	**MDL**	**Precision (<20%)**	**Precision (<20%)**	**Accuracy (70–110%)**
Chloromethane	0.54	0.31	18.4	6.0	75
Vinyl chloride	0.43	0.12	8.9	8.6	79
Bromomethane	0.69	0.17	7.6	5.7	90
Chloroethane	0.68	0.28	12.9	6.9	105
Trichlorofluoromethane	0.44	0.15	10.9	7.6	79
1,1-Dichloroethene	0.44	0.11	8.0	7.7	82
Methylene chloride	0.56	0.09	5.0	2.2	88
trans-1,2-Dichloroethene	0.50	0.12	7.3	6.4	87
1,1-Dichloroethane	0.45	0.09	6.1	4.3	87
Bromochloromethane (ISTD)					
Chloroform	0.44	0.08	6.0	3.6	88
Carbon tetrachloride	0.38	0.09	7.7	7.2	87
1,1,1-Trichloroethane	0.41	0.11	8.3	6.2	87
Benzene	0.44	0.09	6.7	3.8	85
Pentafluorobenzene (surr)	30.0		2.2	1.9	97
1,2-Dichloroethane	0.60	0.29	15.4	1.3	96
Fluorobenzene (surr)	29.8		1.0	0.9	99
Trichloroethene	0.44	0.12	8.5	6.2	86
1,2-Dichloropropane	0.50	0.21	13.1	9.4	83
Bromodichloromethane	0.42	0.18	13.7	6.2	91
2-Chloroethyl vinyl ether	0.46	0.17	11.8	1.1	87
trans-1,3-Dichloropropene	0.40	0.10	7.8	1.9	81
Toluene	0.45	0.12	8.4	5.0	84
Tetrachloroethylene	0.44	0.13	9.7	5.9	77
2-Bromo-1-chloropropane (ISTD)					
cis-1,3-Dichloropropene	1.2	0.22	5.7	3.0	77
1,1,2-Trichloroethane	0.43	0.07	4.9	3.5	85
Dibromochloromethane	0.41	0.09	6.7	2.1	82
Chlorobenzene	0.45	0.10	7.0	2.9	80
Ethylbenzene	0.42	0.12	9.1	5.1	76
Bromoform	0.41	0.07	5.3	1.9	78
4-Bromofluorobenzene (surr)	28.5		2.2	2.5	95
1,4-Dichlorobutane (ISTD)					
1,1,2,2-Tetrachloroethane	0.47	0.18	11.9	2.3	85
1,3-Dichlorobenzene	0.50	0.14	9.0	2.5	79
1,4-Dichlorobenzene	0.51	0.13	8.1	3.0	80
1,2-Dichlorobenzene	0.48	0.13	8.5	2.3	82

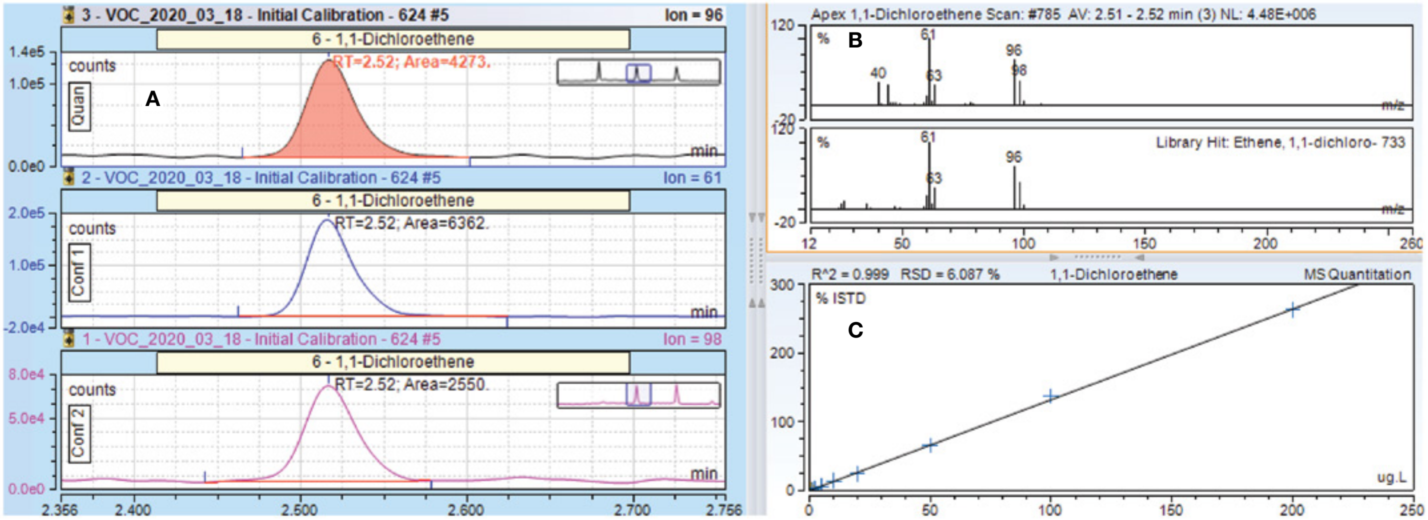


Figure 3. Chromeleon results browser showing extracted ion chromatograms for 1,1-dichloroethene in the 0.5 ppb standard, quantitation ion and two confirming ions (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 0.5 ppb to 200 ppb (C)

To validate the quality control of the calibration curve, this IDC procedure must be completed and continuing calibration checks must be performed with samples to ensure data quality. To meet the IDC criteria the %RSD of the calculated results must be <20 and the accuracy must be within 70–100%. Figure 3 demonstrates the quantitation of 1,1-dichloroethane in the 0.5 ppb standard with excellent library spectral matching and calibration curve.

Conclusion

The combined solution of the TRACE 1310 GC coupled with the ISQ 7000 system and the Atomx XYZ P&T system provides guidance to achieving EPA Method 624 criteria. The Atomx XYZ concentrator's efficient trap cooling design reduces sample cycle time and enables an increase in sample throughput. The moisture control system improves water vapor removal, thereby reducing peak interference and increasing GC column life span. The ISQ 7000 VPI and ExtractaBrite ion source allow users to exchange ionization sources and analytical columns without venting the instrument significantly, reducing instrument downtime and minimizing sample analysis interruptions. Combined, these technologies effectively address the challenges of analytical testing laboratories for the analysis of VOCs and provide a robust, sensitive solution needed for ensuring maximized instrument output and regulatory method compliance.

- The ISQ 7000 VPI GC-MS coupled with the Tekmar Atomx XYZ P&T exceeds all the requirements outlined in EPA Method 624 for analysis of VOCs in wastewater.
- MDLs calculated from n=7 0.5 ppb standards showed no interference from excessive water and resulted in values <0.25 ppb for most compounds.
- Precision and accuracy for n=5 5 ppb standards showed excellent results with %RSD <20% and recovery values between 75% and 105%.

Further information on VOC analysis using the ISQ 7000 GC-MS system and the Atomx XYZ P&T can be found in the Thermo Scientific AppsLab library.[3]

References

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2. United States Environmental Protection Agency, Guideline Series, Control of Volatile Organic Compound Emissions from Industrial Wastewater. https://www3.epa.gov/airquality/ctg_act/199209_voc_epa453_d-93-056_industrial_wastewater(draft).pdf
3. Thermo Scientific AppsLab Library. https://appslab.thermofisher.com/

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Webinar

Dealing with a volatile relationship:

Using purge and trap and GC-MS to improve volatile organic compound workflows

Drinking water testing laboratories face the daily challenge of analyzing large numbers of samples, while maintaining competitive cost per sample and increasing profitability. With restrictive method parameters for volatile organic compound (VOC) analysis, the areas in which purge and trap workflows can be improved for productivity gains are limited. Changes to existing lab methods can improve efficiency, but few changes have the potential for large impact. Additionally, the option of new EPA method adoption provides new opportunities with methodology flexibility, but new methods often interrupt work streams and require additional training among other challenges. Instrument providers offer various solutions that can assist in productivity enhancement. Choosing the best solution that will have the greatest impact should be strategic to ensure the continued success of environmental analysis labs.

In this webcast, our experts will guide you through a review of current regulatory requirements for purge and trap (P&T) analysis. We will also outline the challenges that commonly extend or negatively impact P&T workflows for EPA methods. Tekmar P&T experts will also outline the specific advantages of the Teledyne Tekmar purge and trap system combined with Thermo Scientific GC-MS systems with real sample data examples. Finally, we will review the potential overall impact of our solutions to help guide your lab in choosing the solution that best addresses VOC workflow needs.

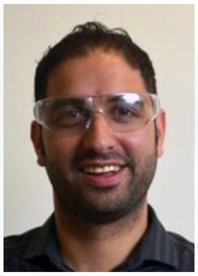
Key learning objectives

- Review of the regulatory requirements for VOC analysis using P&T
- Learn about the challenges of analytical/essential testing laboratories P&T drinking water analysis
- Explore the details and benefits of the Teledyne Tekmar P&T and Thermo Scientific GC–MS systems and their impact on lab productivity and efficiency

The presenters

Amy Nutter, Senior VOC Applications Chemist, Teledyne Tekmar

Amy Nutter is a senior VOC applications chemist at Teledyne Tekmar. Currently, she is focused on applications development and customer application support on the Purge and Trap product line.



Adam Ladak, Global Product Marketing Manager GC–MS, Thermo Fisher Scientific

Adam Ladak is the global product marketing manager for GC quadrupole mass spectrometry at Thermo Fisher Scientific, based in Macclesfield, UK.

Watch the webinar here

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