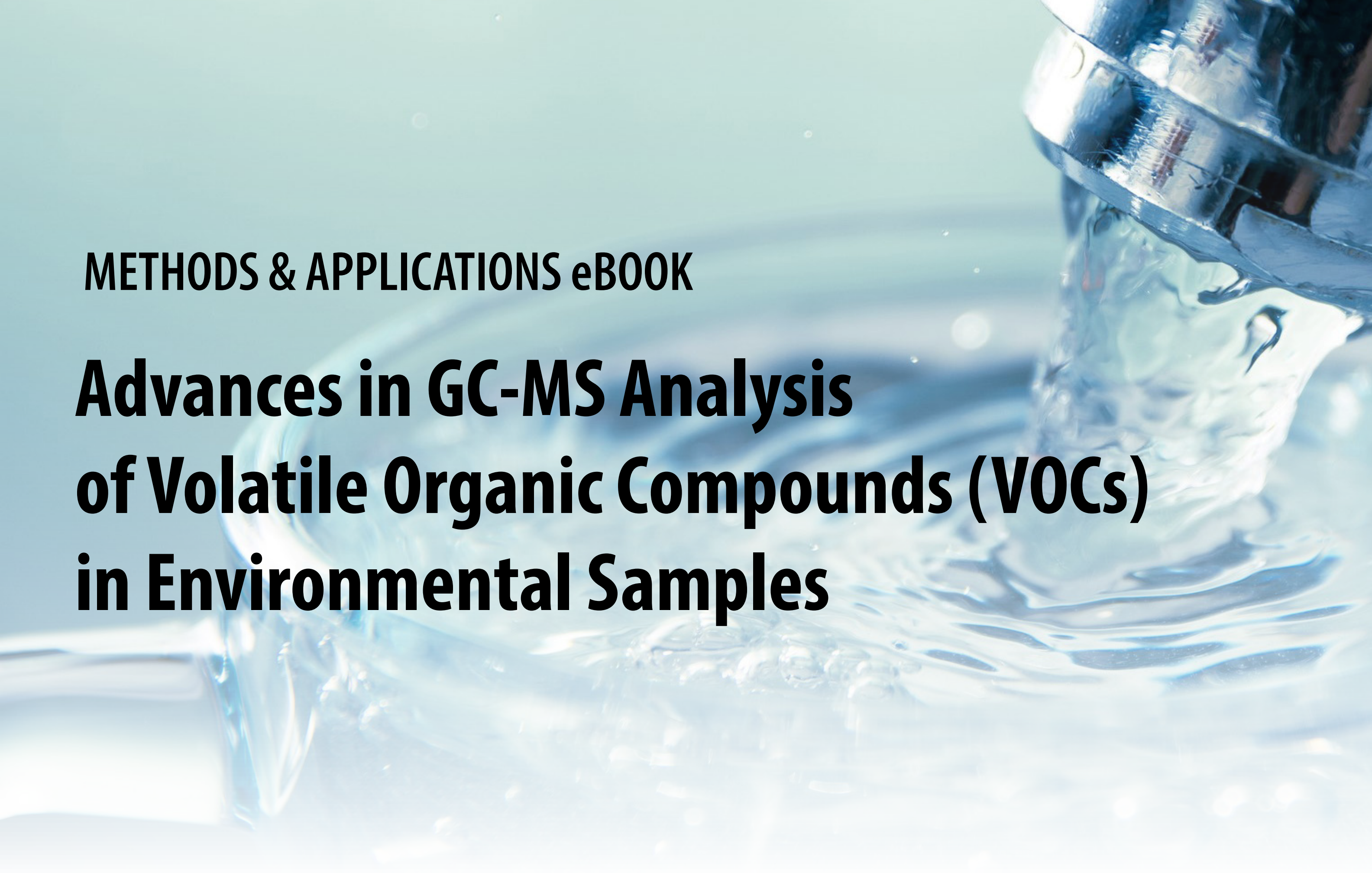

METHODS & APPLICATIONS eBOOK

Advances in GC-MS Analysis of Volatile Organic Compounds (VOCs) in Environmental Samples

VOC analysis in water and soils is a crucial testing for environmental laboratories who work to safeguard the environment and public health, by monitoring contamination levels in compliance with local legislation. Advancements in analytical techniques and technologies drive continuous improvement in environmental monitoring capabilities. Laboratories that invest in state-of-the-art instrumentation and methodologies enhance their capacity to detect regulated and emerging contaminants, improve data accuracy, and meet evolving regulatory requirements.

This eBook covers advanced technology available for VOC analysis, demonstrating features and benefits of different sampling techniques, including:

- Purge & Trap (P&T)
- In-tube extraction (ITEX) with refocusing of very volatile compounds
- Solid Phase Micro Extraction (SPME)
- Static headspace with automated calibration standard dilution and ISTD/Surrogate addition

In combination with highly sensitive GC-MS, new solutions are demonstrated to face growing workload, improve data quality and increase overall laboratory's efficiency.

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ThermoFisher
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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 several challenges when analyzing VOCs. Paramount is meeting all regulation criteria mandated by regulatory authority such as the United States Environmental Protection Agency (EPA), the European Environment Agency, and the European Commission with its associated agencies.

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 unplanned instrument downtime or inaccurate results requiring re-analysis of samples. Additionally, pressure to reduce costs and manage reduced resources forces laboratories to consider systems that provide automated operations and require minimum maintenance. Regulatory methods for analysis of VOCs in environmental samples have recently been updated to allow environmental labs to improve current approaches to VOC analysis. However, although regulations have been updated, many environmental testing laboratories rely on outdated instruments because of their ability to meet regulatory method requirements with minimal interruption. Replacement of aging systems with updated technology provides labs with the ability to increase efficiency and possibly exceed current sample throughput.

This eBook covers different methodology laboratories may employ to meet the challenges of VOC analysis for environmental samples. Different sampling techniques and automated solutions will be showcased including:

- Purge & Trap (P&T)
- In-tube extraction (ITEX) with refocusing of very volatile compounds
- Solid Phase Micro Extraction (SPME)
- Static headspace with automated calibration standard dilution and ISTD/Surrogate addition

The advanced Thermo Scientific™ ISQ™ 7610 Single Quadrupole GC-MS system has been used in combination with the different sampling techniques to support the daily challenges of environmental laboratories with sensitivity that meets and exceeds regulatory requirements.

The ISQ 7610 features NeverVent™ technology to greatly simplify and accelerate maintenance operations. When maintenance is required, downtime is eliminated thanks to vent-free ion source removal and analytical column exchange. This means that the system can be

Introduction (cont.)

up and running again in minutes. The ISQ 7610 can also be operated continuously with little user intervention due to automated system readiness with SmartTune as well as inherent robustness. The entire system is controlled by the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software.

The Chromeleon Environmental Analysis Extension Pack for U.S. EPA-based environmental applications provides a comprehensive set of GC-MS e-workflows for quick sequence set-up and reporting templates to make data review and reporting easier. Moreover, with the ever-evolving compliance requirements for data integrity and data security, Chromeleon CDS provides a secure platform for analytical laboratories to comply with modern regulatory guidelines including FDA 21 CFR Part 11 and European Commission (EU) Annex 11.

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Application Notes

Adhering to U.S. EPA Method 524.2 for the analysis of volatile organic compounds in drinking water

The ISQ 7610 GC-MS system, coupled to the Teledyne Tekmar Lumin P&T with the AQUATek LVA autosampler system offer benefits for executing U.S. EPA Method 524.2, with extended MS linearity, minimized maintenance, sensitivity and precision for high confidence data and consistent method compliance, with full system control through Chromeleon CDS.

Sustainable uncompromised performance: analysis of volatile organic compounds in drinking water with the ISQ 7610 GC-MS using HeSaver-H$_2$Safer technology

Routine robustness for method US EPA 524.4 is demonstrated with the ISQ 7610 GC-MS coupled with the Teledyne Tekmar Atomx XYZ P&T, with significant reduction of helium gas consumption, especially during analysis, offering helium gas savings extending the helium cylinder lifetime four times longer in comparison to standard operations.

Uninterrupted analysis of VOCs according to U.S. EPA Method 8260C using purge and trap and single quadrupole GC-MS technology

VOC analysis in wastewater and solid waste according to the EPA method 8260C is demonstrated with continuous analysis of 240 injections over three days with no user intervention, showing excellent system stability with accuracy (% revcovery) and precision (%RSD) for all the compounds well within the regulatory requirements.

Trace analysis of volatile organic compounds in wastewater according to U.S. EPA Method 624.1

Analysis of VOCs in wastewater using the ISQ 7610 GC-MS system, with helium saver technology coupled with the Teledyne LABS Tekmar Lumin P&T concentrator paired with the AQUATek LVA autosampler, is demonstated to exceed all the requirements outlined in U.S. EPA Method 624.1 while reducing helium usage 4 fold.

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Application Notes

Improvements for the analysis of volatile (VOC) and very volatile (VVOC) organic compounds using In-Tube Extraction-Dynamic Headspace (ITEX-DHS) and cryogen-free refocusing

High sensitivity and selectivity for volatile and very volatile compounds is achieved with the ITEX sampling technique combined with efficient re-focusing into the PTV injector. Extraction and enrichment of analytes at trace levels from complex matrices is achieved minimizing interference from non-volatile matrix, achieving sensitivity in compliance with stringent regulatory limits.

Determination of BTEX and volatile organic compounds (VOCs) in drinking water by GC-MS/MS coupled to static headspace and solid-phase microextraction sampling

Static headspace and solid-phase microextraction using Arrow technology (SPME Arrow) are demonstrated for the determination of benzene, toluene, ethylbenzene, and xylenes (BTEX), chlorinated and brominated volatile compounds in drinking water. GC-MS/MS provides operational flexibility in both single ion monitoring (SIM) acquisition mode for fast screening and selected reaction monitoring (SRM) acquisition mode when higher selectivity is required.

An automated approach for the analysis of VOCs in drinking and surface water by using the TriPlus RSH SMART VOC Sample Prep Station

A dedicated robotic autosampler is used to execute a fully automated workflow for VOC analysis including calibration standard dilution and ISTD/SURR addition with on-line HS extraction and GC-MS analysis, offering enhanced accuracy and precision over H24 unattended operations. The automated addition just before sample incubation and analysis preserve sample integrity in compliance with regulatory requirements.

Case Study

Eurofins South Bend Indiana Lab standardizes on TRACE 1600 Series Gas Chromatograph (GC) Systems for water analysis

At the Eurofins South Bend, GC-ECD, GC-MS and GC-MS/MS techniques are essential to identify and quantify volatile organic compounds (VOCs), pesticides, and synthetic organic compounds (SOCs) in municipal drinking water per the methods U.S. EPA 500 series, analyzing several hundreds of water samples every day.

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Application note | 002952

Environmental

Adhering to U.S. EPA Method 524.2 for the analysis of volatile organic compounds in drinking water

Authors

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[2]Teledyne Tekmar, Mason, OH, USA

Environmental trace analysis, U.S. EPA, U.S. EPA Method 524.2, volatile organic compounds (VOCs), phthalates, gas chromatography, single quadrupole mass spectrometry, selected ion monitoring

Goal

Demonstration of a routine analytical method that meets the requirements outlined in U.S. EPA 524.2 for the quantitation of volatile organic compounds (VOCs) in drinking water, using the Teledyne LABS Tekmar Lumin Purge and Trap (P&T) concentrator paired with the AQUATek LVA autosampler system along with a Thermo Scientific™ ISQ™ 7610 MS system coupled with a Thermo Scientific™ TRACE™ 1610 gas chromatograph (GC) and Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS). Method linearity, method detection limit (MDL), precision, and accuracy were assessed to evaluate method performance.

Introduction

Analytical testing labs play a crucial role in monitoring surface, ground, and drinking water for volatile organic compounds (VOCs). Common by-products in the processing of household and industrial products, VOCs can contaminate water sources, potentially harming the environment and public health. To safeguard against this, labs use the U.S. EPA Method 524.2[1] to test water for the presence of VOCs, including four trihalomethane disinfection by-products. This procedure utilizes Purge and Trap (P&T) procedures to remove VOCs with high volatility and low water solubility from water samples, followed by gas chromatography-mass spectrometry (GC-MS).

U.S. EPA Method 524.2 has mandated criteria that environmental testing labs must adhere to, including detection limits, linearity, and precision. Labs must meet this criteria day in and day out to report their findings, hence having a robust and reproducible system is critical to reporting results on time.

The following evaluation describes the use of the ISQ 7610 MS system coupled coupled with a TRACE 1610 gas chromatograph (GC) and the Tekmar Lumin P&T concentrator paired with the AQUATek LVA autosampler for U.S. EPA Method 524.2.

Experimental

Sample preparation

A 50 µg/mL (parts per million or ppm) calibration working standard was prepared in purge and trap grade methanol (Honeywell/Burdick & Jackson, P/N 232-1L) from the following Restek™ standards: Drinking Water VOA MegaMix™ (P/N 30601), Ketone Mix (P/N 30602), and 502.2 Calibration Mix (P/N 30042). In total, the standards contained 83 compounds.

The calibration curve was prepared from 0.2 µg/L to 40 µg/L (parts per billion or ppb) for all compounds. The relative response factor (RF) was calculated for each compound using one Restek internal standard: fluorobenzene (P/N 30201). Surrogate standards from Restek consisted of 4-bromofluorobenzene and 1,2-dichlorobenzene-d4 (P/N 30201). 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 25 mL sample for a resulting concentration of 10 ppb.

A total of seven standards at a concentration of 0.5 ppb were prepared in deionized water to calculate the MDL and precision calculations for all compounds. Also, seven standards with a concentration of 10 ppb were prepared to determine the accuracy and precision of recovery of each compound. All calibration, MDL, and recovery standards were analyzed with the Tekmar Lumin P&T and AQUATek LVA autosampler conditions in Table 1.

GC-MS conditions

A TRACE 1610 GC was coupled to the ISQ 7610 single quadrupole mass spectrometer equipped with the NeverVent™ vacuum probe interlock (VPI) and a Thermo Scientific™ ExtractaBrite™ ion source. A Thermo Scientific™ TraceGOLD™ TG-VMS, 30 m × 0.25 mm, 1.4 µm film column (P/N 26080-3320) was used for compound separation. The Thermo Scientific™ HeSaver-H_2Safer™ Split/Splitless injector was operated in split mode with a run time under 13 minutes. The ISQ 7610 mass spectrometer 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. Expanded method parameters for the ISQ 7610 mass spectrometer are displayed in Table 2.

Instrument control and data processing

Data were acquired, processed, and reported using Chromeleon CDS, version 7.3. This software can control both the GC-MS system and the Tekmar Lumin P&T and AQUATek LVA autosampler. This allows a single software to be utilized for the full workflow simplifying the instrument operation. Figure 2 shows the Chromeleon CDS control of the Tekmar Lumin P&T and AQUATek LVA autosampler. The fully optimized method used within this application note is available for download in the Thermo Scientific™ AppsLab application note repository, which contains all the parameters needed to acquire, process, and report the analytical data for U.S EPA Method 524.2.[2]

Figure 1. ISQ 7610 GC-MS coupled with the Tekmar Lumin P&T and AQUATek LVA autosampler

Table 1 (part 1). Teledyne Tekmar Lumin AQUATek LVA P&T water method conditions

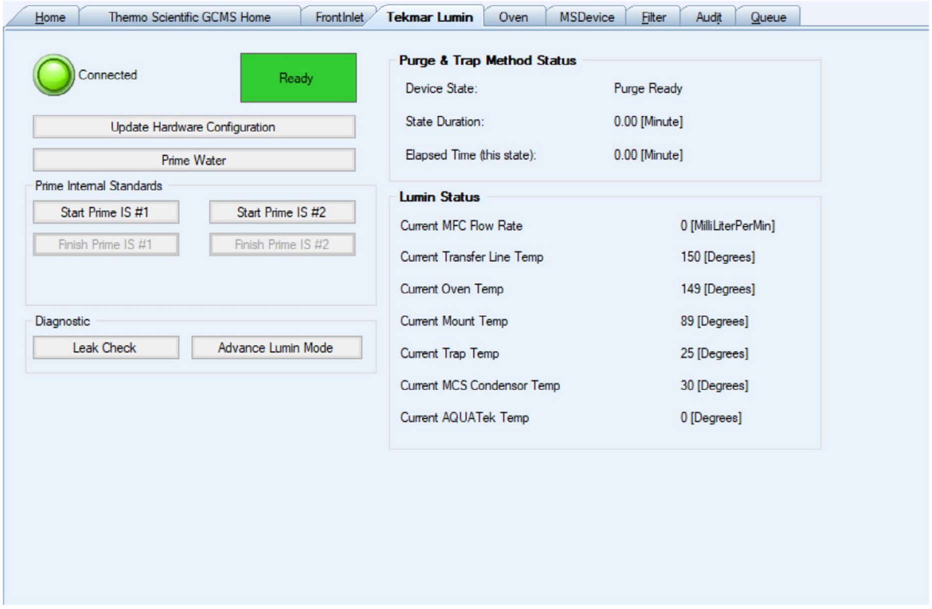
Standby	Variable
Valve oven temp.	150 °C
Transfer line temp.	150 °C
Sample mount temp.	90 °C
Purge ready temp.	35 °C
MCS purge temp.	20 °C
Standby flow	10 mL/min
Purge	**Variable**
Purge temp.	20 °C
Purge time	11.00 min
Purge flow	40 mL/min
Dry purge temp.	20 °C
Dry purge time	1.0 min
Dry purge flow	100 mL/min
Sparge vessel heater	Off
Desorb	**Variable**
Desorb preheat temp.	245 °C
Desorb temp.	250 °C
Desorb time	4.00 min
Desorb flow	300 mL/min
GC start signal	Start_Only
Bake	**Variable**
Bake time	4.00 min
Trap bake temp.	270 °C
MCS bake temp.	180 °C
Bake flow	200 mL/min

Table 1 (part 2). Teledyne Tekmar Lumin AQUATek LVA P&T water method conditions

AQUATek LVA	Variable
Sample loop time	1.10 min
Sample transfer time	1.25 min
Rinse loop time	1.10 min
Sweek needle time	0.30 min
Presweep time	0.35 min
Water temperature	90 °C
Bake rinse cycles	1
Bake rinse drain time	0.60 min
Trap	9
Chiller tray	On
Purge gas	Helium

Table 2. GC-MS conditions

TRACE 1610 GC conditions	
Column	TraceGOLD TG-VMS, 30 m × 0.25 mm, 1.4 µm film (P/N 26080-3320)
Carrier gas	Helium, 1.8 mL/min
Oven profile	35 °C, 2 min; 15 °C/min to 100 °C; 30 °C/min to 225 °C; 2 min hold; Run time 12.5 min
HeSaver-H_2Safer Split/Splitless injector	200 °C, 30:1 split, purge flow 5.0 mL/min, 0.20 min helium delay
ISQ 7610 MS conditions	
Temperature	Transfer line 230 °C; ion source 280 °C
Scan	Range 35 amu to 260 amu, solvent delay 1.43 min, dwell/scan time 0.10 s
Current	Emission current 30 µA, gain 3.00E+005



Purge & Trap Method Status

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

Lumin Status

Current MFC Flow Rate	0 [MilliLiterPerMin]
Current Transfer Line Temp	150 [Degrees]
Current Oven Temp	149 [Degrees]
Current Mount Temp	89 [Degrees]
Current Trap Temp	25 [Degrees]
Current MCS Condensor Temp	30 [Degrees]
Current AQUATek Temp	0 [Degrees]

Figure 2. Chromeleon CDS control and monitoring of the Tekmar Lumin P&T and AQUATek LVA autosampler

Results and discussion

Chromatography

Employing the GC conditions outlined in Table 2, successful chromatographic resolution of all desired compounds was achieved. Minimal moisture entered the analytical column from the water samples, ensuring no adverse effects on peak shape. Consequently, even in lower concentration samples, the chromatography remained optimized. Figure 3 illustrates this consistent peak shape and separation using a 20 ppb VOC standard, showing minimal water interference.

Linearity and sensitivity

The calibration range of 0.2 ppb to 40 ppb was assessed for all compounds. Figure 4 demonstrates the quantitation of bromodichloromethane at 0.5 ppb in a VOC standard with excellent library spectral matching and calibration curve. Figure 5 demonstrates the same information for *trans*-1,3-dichloropropene.

20 ppb

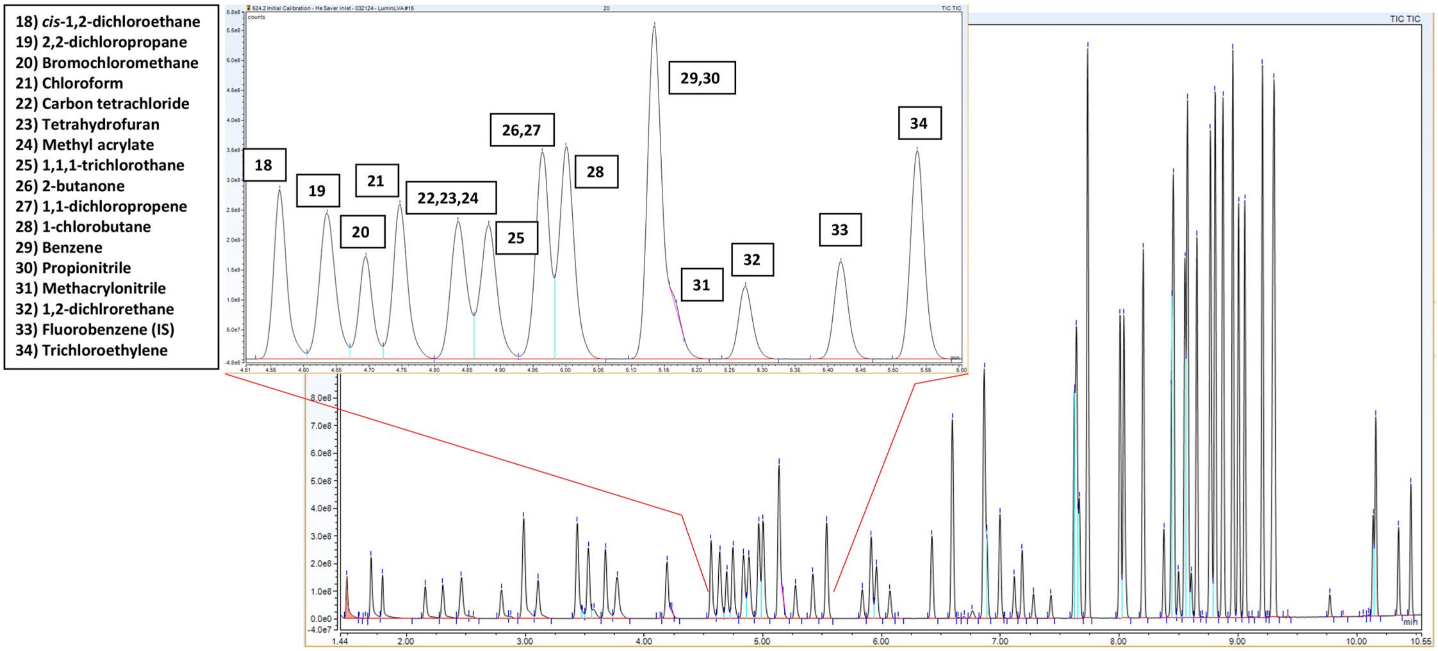


Figure 3. Total ion chromatogram (TIC) of a 20 ppb VOC standard with an inset indicating consistent peak shapes and separation with minimal water interference

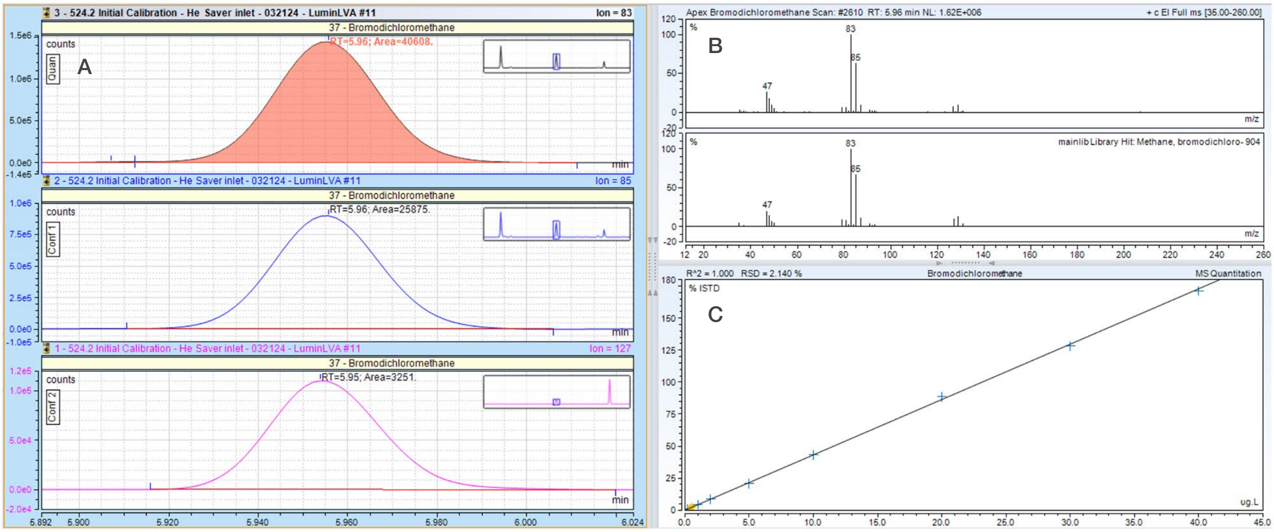


Figure 4. Chromeleon CDS results browser showing extracted ion chromatograms for bromodichloromethane in the 0.5 ppb water standard, quantitation ion (*m/z*= 83) and two confirming ions (*m/z* = 85, 127). (A) A matching measured spectrum to the NIST library and (B) a linear calibration over a concentration range of 0.2 ppb to 40 ppb (C).

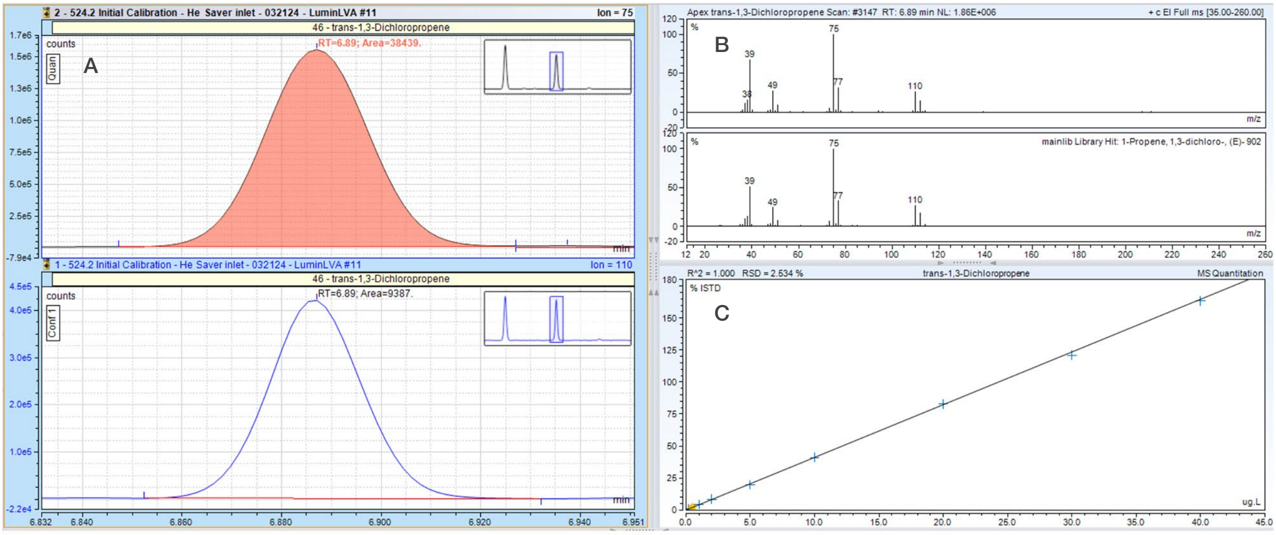


Figure 5. Chromeleon CDS results browser showing extracted ion chromatograms for *trans*-1,3-dichloropropene in the 0.5 ppb water standard, quantitation ion (*m/z*= 75) and one confirming ion (*m/z* = 110). (A) A matching measured spectrum to the NIST library and (B) a linear calibration over a concentration range of 0.2 ppb to 40 ppb (C).

Appendix Table A1 displays the relative standard deviation (%RSD) of the response factors (RFs) which were <20% for all compounds, except for acetone, 1,1,2,2-tetrachloroethane, *trans*-1,4-dichloro-2-butene, and hexachloroethane, which used a quadratic regression calibration with r^2>0.995. The table also shows the MDL for each analyte calculated by injecting n=7 injections of the 0.5 ppb water standard. Figure 6 shows a subset of the MDL data with calculated MDLs and precision for 25 compounds.

Method robustness

To assess the stability of the method, which is essential for environmental testing labs, 10 ppb calibration check standards were injected at intervals 31 times over a sequence of 189 injections. This is equivalent to 3.5 days of uninterrupted analysis with no maintenance performed on the system. Figure 7 shows the reproducibility of 14 of the compounds over 189 injections with excellent percentage RSDs. RSDs for all compounds were under the 30% accuracy method requirements. Appendix Table A2 shows the reproducibility results for all compounds over the 189-injection sequence.

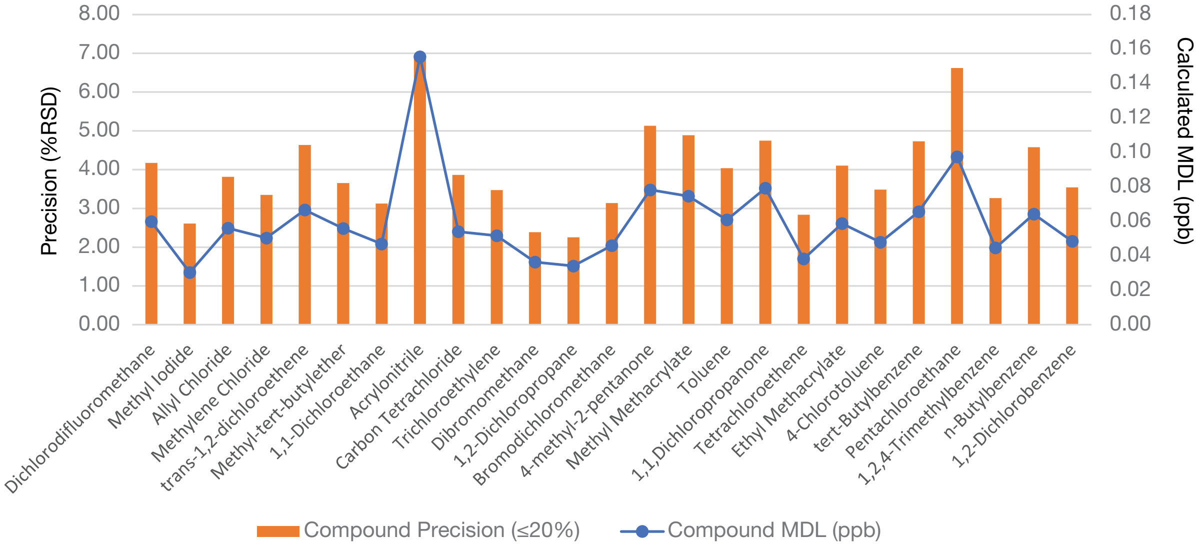


Figure 6. MDL and precision calculated for a subset of compounds (n=25) from n=7 injections of a 0.5 ppb standard

Figure 7. Repeatability of a 10 ppb VOC standard (n=31) (as concentration in ppb) assessed over n=189 consecutive injections. Red lines represent the ±30% accuracy as required by the method.

Conclusion

The TRACE 1610 GC, the ISQ 7610 system, and the Tekmar Lumin P&T with the AQUATek LVA autosampler system together offer benefits for executing U.S. EPA Method 524.2. The Tekmar Lumin P&T concentrator enhances sample throughput through efficient trap cooling and moisture control, thus reducing peak interference and extending GC column life. The ISQ 7610 system's VPI and ExtractaBrite ion source allow ionization source and analytical column replacement without venting the instrument, ensuring minimal downtime, and the XLXR™ detector offers extended linear dynamic range. The collective technology addresses routine VOC analysis challenges, ensuring robust sensitivity, maximized output, and consistent method compliance.

The ISQ 7610 system equipped with the VPI coupled with the Tekmar Lumin P&T and the AQUATek LVA autosampler exceeds all the requirements outlined in U.S. EPA Method 524.2 for analysis of VOCs in drinking water:

- Excellent linearity for all compounds was demonstrated with the %RSD of the calibration response factors passing all method requirements.

- MDL and precision for seven 0.5 ppb standards showed no interference from excessive water and produced very reproducible results. The average MDL result for all 83 target compounds was 0.06 ppb with a precision of 4.06%.

- The precision for n=31 samples over 189 injections displayed <30% RSD accuracy for all compounds as the method requires. The average precision for all 83 target compounds and 2 surrogates gave a %RSD of 6.43% with an accuracy of 98% recovering the compounds. Individually, 4-bromofluorobenzene and 1,2-dichlorobenzene-d4 had a 7.68% RSD with an accuracy of 98% and 4.95% RSD and an accuracy of 95%, respectively, over 189 injections and almost four days of uninterrupted analysis.

References

1. U.S. EPA 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
2. Thermo Scientific AppsLab: https://appslab.thermofisher.com/App/4373/epa-5242-compounds-drinking-water-by-gcms

Appendix

Table A1. U.S. EPA Method 524.2 calibration, accuracy, and precision data (part 1)

Compound	Calibration			Accuracy and precision (n=7, 0.5 ppb)			Mid-point check (n=7, 10 ppb)	
	Retention time	Quant ion	Relative SD (%RSD)	Average RF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±20%)
Dichlorodifluoromethane	1.51	85	14.5	0.447	0.06	4.17	6.11	99
Chloromethane	1.71	50	14.3	1.01	0.06	3.86	6.12	87
Vinyl Chloride	1.81	62	8.16	0.509	0.05	3.34	5.66	92
Bromomethane	2.17	94	14.7	0.343	0.08	4.78	3.89	86
Chloroethane	2.32	64	8.68	0.407	0.05	3.52	5.10	81
Trichlorofluoromethane	2.47	101	10.4	0.487	0.05	3.86	4.45	95
Diethyl Ether	2.81	59	7.33	0.218	0.07	4.59	3.59	93
1,1-Dichloroethene	2.99	96	6.70	0.363	0.07	4.70	3.26	92
Carbon Disulfide	3.00	76	7.07	0.934	0.07	4.82	3.73	84
Methyl Iodide	3.11	142	12.9	0.652	0.03	2.61	2.87	98
Allyl Chloride	3.44	76	4.91	0.272	0.06	3.82	3.66	93
Methylene Chloride	3.54	84	7.16	0.404	0.05	3.35	2.25	90
Acetone[1]	3.60	43	1.00	0.174	0.13	7.37	10.7	98
trans-1,2-dichloroethene	3.68	96	6.88	0.416	0.07	4.64	2.61	89
Methyl-tert-butylether	3.78	73	4.32	0.657	0.06	3.66	2.31	95
1,1-Dichloroethane	4.20	63	6.71	0.853	0.05	3.13	3.30	92
Acrylonitrile	4.24	52	11.6	0.055	0.16	6.92	4.90	110
cis-1,2-Dichloroethene	4.57	96	5.59	0.428	0.05	3.07	2.88	91
2,2-Dichloropropane	4.64	77	7.36	0.560	0.07	4.43	5.96	94
Bromochloromethane	4.70	128	5.01	0.134	0.05	3.37	1.77	93
Chloroform	4.75	83	6.51	0.688	0.05	3.00	3.38	92
Methyl Acrylate	4.84	55	5.21	0.134	0.08	4.78	3.42	104
Carbon Tetrachloride	4.85	117	5.53	0.461	0.05	3.87	3.50	98
Tetrahydrofuran	4.86	71	11.5	0.021	0.09	4.77	4.50	109
1,1,1-Trichloroethane	4.89	97	5.77	0.537	0.05	3.27	3.73	95
2-Butanone	4.97	43	11.5	0.129	0.09	5.49	9.05	107
1,1-Dichloropropene	4.97	75	6.53	0.509	0.05	3.54	4.37	95
1-Chlorobutane	5.01	56	6.48	0.782	0.05	3.30	4.58	95
Benzene	5.14	78	5.95	1.68	0.04	2.87	3.36	93
Propionitrile	5.17	54	7.51	0.029	0.12	7.06	1.91	102
Methacrylonitrile	5.18	67	5.83	0.071	0.05	3.18	3.53	103
1,2-Dichloroethane	5.28	62	6.60	0.317	0.03	2.15	3.36	95
Fluorobenzene (ISTD)	5.43	96						
Trichloroethylene	5.54	95	7.36	0.424	0.05	3.47	2.99	92
Dibromomethane	5.84	93	5.14	0.139	0.04	2.39	1.99	95
1,2-Dichloropropane	5.92	63	5.56	0.423	0.03	2.26	3.11	94
Bromodichloromethane	5.96	83	2.14	0.433	0.05	3.14	2.73	96
4-methyl-2-pentanone	6.08	100	5.40	0.038	0.08	5.13	1.74	101
Methyl Methacrylate	6.08	69	3.54	0.109	0.07	4.89	2.53	102
cis-1,3-Dichloropropene	6.43	75	2.72	0.559	0.04	2.71	3.13	96
Toluene	6.60	92	7.10	1.08	0.06	4.04	2.52	92
Chloroacetonitrile	6.70	48	8.01	0.010	0.19	14.9	9.92	80
2-Nitropropane	6.77	43	7.55	0.110	0.09	5.04	4.28	109

Table A1. U.S. EPA Method 524.2 calibration, accuracy, and precision data (part 2)

	Calibration			Accuracy and precision (n=7, 0.5 ppb)			Mid-point check (n=7, 10 ppb)	
Compound	Retention time	Quant ion	Relative SD (%RSD)	Average RF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±20%)
1,1,Dichloropropanone	6.87	43	8.13	0.233	0.08	4.75	4.96	105
Tetrachloroethene	6.87	166	6.11	0.949	0.04	2.84	4.27	92
trans-1,3-Dichloropropene	6.89	75	2.53	0.412	0.05	3.59	2.93	97
Ethyl Methacrylate	7.00	69	6.22	0.236	0.06	4.11	3.02	103
1,1,2-Trichloroethane	7.01	83	2.94	0.192	0.04	2.33	1.89	98
Dibromochloromethane	7.12	129	4.82	0.236	0.05	3.64	1.52	100
1,3-Dichloropropane	7.19	76	4.15	0.395	0.03	2.17	2.48	97
1,2-Dibromoethane	7.29	107	2.76	0.195	0.05	3.25	1.63	98
2-Hexanone	7.43	43	9.26	0.196	0.12	7.40	9.24	102
Chlorobenzene	7.63	112	3.45	1.17	0.05	3.67	2.09	95
Ethylbenzene	7.65	91	4.84	2.15	0.05	3.50	3.14	94
1,1,1,2-Tetrachloroethane	7.67	131	4.55	0.349	0.05	3.46	1.75	96
m,p-Xylene	7.74	106	3.80	0.905	0.09	3.29	2.84	93
o-Xylene	8.01	106	3.09	0.929	0.04	2.94	2.95	92
Styrene	8.05	104	7.41	1.37	0.05	3.61	2.54	95
Bromoform	8.06	173	16.7	0.168	0.04	3.52	0.76	101
Isopropylbenzene	8.21	105	4.17	2.43	0.06	4.16	3.95	96
4-Bromofluorobenzene (surr)	8.38	95	11.0	0.577		1.71	1.33	97
Bromobenzene	8.45	156	8.37	0.648	0.03	2.27	2.42	92
n-propylbenzene	8.46	91	7.03	3.23	0.05	3.46	3.61	99
1,1,2,2-Tetrachloroethane[1]	8.51	83	1.00	0.232	0.04	2.52	1.97	101
2-Chlorotoluene	8.56	91	4.80	2.20	0.05	3.55	3.43	95
1,3,5-Trimethylbenzene	8.58	105	7.11	2.51	0.05	3.55	3.37	97
1,2,3-Trichloropropane	8.59	75	10.3	0.233	0.05	3.60	3.47	103
trans-1,4-Dichloro-2-butene[1]	8.61	53	1.00	0.072	0.06	4.50	3.46	98
4-Chlorotoluene	8.66	91	7.06	2.10	0.05	3.48	3.31	94
tert-Butylbenzene	8.77	119	8.37	2.35	0.07	4.73	4.41	97
Pentachloroethane	8.79	117	17.8	0.249	0.10	6.62	6.64	99
1,2,4-Trimethylbenzene	8.81	105	6.74	2.62	0.04	3.27	3.42	99
sec-Butylbenzene	8.88	105	8.81	3.28	0.06	3.97	3.54	104
p-Isopropyltoluene	8.96	119	7.47	2.74	0.06	4.12	3.59	103
1,3-Dichlorobenzene	9.01	146	11.3	1.73	0.05	4.04	2.64	95
1,4-Dichlorobenzene	9.06	146	10.2	1.69	0.04	3.14	2.94	96
n-Butylbenzene	9.21	91	7.68	2.67	0.06	4.58	3.70	103
1,2-Dichlorobenzene-d4 (surr)	9.31	152	15.8	0.820		2.00	3.75	96
Hexachloroethane[1]	9.31	117	0.997	1.68	0.13	8.31	2.08	102
1,2-Dichlorobenzene	9.31	146	8.40	1.47	0.05	3.55	2.63	96
1,2-Dibromo-3-chloropropane	9.78	75	10.2	0.046	0.07	4.96	2.95	103
Nitrobenzene	10.11	123	12.9	0.005	0.05	3.44	9.66	84
Hexachlorobutadiene	10.14	225	10.1	0.048	0.08	5.57	3.20	103
1,2,4-Trichlorobenzene	10.17	180	7.42	0.595	0.06	4.21	1.99	101
Naphthalene	10.36	128	8.01	0.596	0.06	3.94	1.50	101
1,2,3-Trichlorobenzene	10.46	180	10.1	0.394	0.06	4.35	2.20	102

[1] Compounds used a quadratic regression calibration

Table A2. Repeatability of a 10 ppb VOC standard (n=31) (as absolute peak area counts) assessed over n=189 consecutive injections

Compound	Analyte recovery (10 ppb n=31, 191 injections)	
	Precision (≤20%RSD)	Accuracy (±30%)
Dichlorodifluoromethane	14.4	120
Chloromethane	8.91	106
Vinyl Chloride	9.48	102
Bromomethane	7.10	98
Chloroethane	9.42	98
Trichlorofluoromethane	11.0	103
Diethyl Ether	5.18	104
1,1-Dichloroethene	10.1	96
Carbon Disulfide	11.3	92
Methyl Iodide	7.40	100
Allyl Chloride	7.80	98
Methylene Chloride	5.38	97
Acetone[1]	8.69	70
trans-1,2-dichloroethene	7.85	93
Methyl-tert-butylether	4.30	104
1,1-Dichloroethane	6.32	100
Acrylonitrile	6.17	124
cis-1,2-Dichloroethene	4.28	92
2,2-Dichloropropane	16.5	87
Bromochloromethane	3.21	93
Chloroform	3.78	97
Methyl Acrylate	4.35	109
Carbon Tetrachloride	7.82	97
Tetrahydrofuran	5.56	117
1,1,1-Trichloroethane	6.82	97
2-Butanone	5.36	74
1,1-Dichloropropene	7.59	96
1-Chlorobutane	7.38	97
Benzene	4.73	94
Propionitrile	4.05	112
Methacrylonitrile	4.07	108
1,2-Dichloroethane	2.42	102
Fluorobenzene (ISTD)		
Trichloroethylene	8.13	97
Dibromomethane	2.52	98
1,2-Dichloropropane	3.08	99
Bromodichloromethane	2.76	100
4-methyl-2-pentanone	4.59	99
Methyl Methacrylate	4.00	103
cis-1,3-Dichloropropene	4.16	96
Toluene	5.05	92
Chloroacetonitrile	9.16	81
2-Nitropropane	11.1	103
1,1,Dichloropropanone	4.83	86
Tetrachloroethene	7.24	93
trans-1,3-Dichloropropene	3.72	98
Ethyl Methacrylate	3.50	104
1,1,2-Trichloroethane	2.71	102
Dibromochloromethane	2.92	101
1,3-Dichloropropane	2.73	101
1,2-Dibromoethane	3.41	100
2-Hexanone	5.06	76
Chlorobenzene	4.20	94
Ethylbenzene	5.38	95
1,1,1,2-Tetrachloroethane	3.54	96
m,p-Xylene	5.92	91
o-Xylene	4.91	91
Styrene	4.42	93
Bromoform	3.63	103
Isopropylbenzene	6.13	94
4-Bromofluorobenzene (surr)	3.24	98
Bromobenzene	3.96	90
n-propylbenzene	7.15	99
1,1,2,2-Tetrachloro ethane[1]	9.19	94
2-Chlorotoluene	8.10	96
1,3,5-Trimethylbenzene	12.9	104
1,2,3-Trichloropropane	8.15	114
trans-1,4-Dichloro-2-butene[1]	6.39	99
4-Chlorotoluene	5.59	96
tert-Butylbenzene	7.87	94
Pentachloroethane	16.7	87
1,2,4-Trimethylbenzene	6.22	99
sec-Butylbenzene	8.56	103
p-Isopropyltoluene	8.17	102
1,3-Dichlorobenzene	5.81	95
1,4-Dichlorobenzene	5.18	95
n-Butylbenzene	9.08	106
1,2-Dichlorobenzene-d4 (surr)	7.52	99
Hexachloroethane[1]	4.11	101
1,2-Dichlorobenzene	4.80	96
1,2-Dibromo-3-chloropropane	4.71	110
Nitrobenzene	10.6	86
Hexachlorobutadiene	9.83	103
1,2,4-Trichlorobenzene	5.57	104
Naphthalene	4.09	107
1,2,3-Trichlorobenzene	5.20	107

[1] Compounds used a quadratic regression calibration

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Application note | 001773

Environmental

Sustainable uncompromised performance: analysis of volatile organic compounds in drinking water with the ISQ 7610 GC-MS using HeSaver-H_2Safer technology

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Keywords

Helium, HeSaver-H_2Safer, EPA, EPA Method 524.4, VOCs, trace analysis, gas chromatography, single quadrupole mass spectrometry, volatiles, environmental sample analysis, analytical testing laboratories, ISQ 7610 GC-MS, TRACE 1610 GC

Goal

Demonstration of a routine analytical method that meets the requirements outlined in U.S. EPA Method 524.4 for the quantitation of volatile organic compounds (VOCs) in drinking water, using the Teledyne Tekmar Atomx XYZ Purge and Trap (P&T) system along with a Thermo Scientific™ ISQ™ 7610 MS system coupled with a Thermo Scientific™ TRACE™ 1610 gas chromatograph (GC), equipped with the Thermo Scientific™ HeSaver-H_2Safer™ technology for split splitless (SSL) injector, and Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software. Method linearity, method detection limit (MDL), precision, and MRL were assessed to evaluate method performance. A long-term study was performed to ensure the stability of this analytical method.

Introduction

VOCs are analyzed widely in environmental laboratories that follow strict EPA regulations, including U.S. EPA Methods 524.2, 524.4, and 8260. VOCs are human-made contaminants, used and produced in the processing of, or as, paints, adhesives, petroleum products, pharmaceuticals, and refrigerants. When released into surface or ground water, they can have an adverse effect on the ecosystem. It is extremely important that analytical laboratories ensure both accurate and rapid detection and quantitation of VOCs to ensure public safety.

In a previous application note, the use of the ISQ 7610 MS system coupled with a TRACE 1610 GC and the Teledyne Tekmar Atomx XYZ P&T for U.S. EPA Method 524.4[1] was demonstrated. The method targets 75 VOCs and differs from U.S. EPA Method 524.2 as nitrogen is required as a purge gas and the method allows more flexibility with the parameters. Although the parameters are more flexible, U.S. EPA Method 524.4 has stricter QC requirements to ensure the method is fit for purpose. These QC requirements include the minimum reporting level (MRL), which is determining the upper and lower limits used to evaluate the continuing calibration checks. This is intended to minimize the occurrence of reporting false positive results. U.S. EPA Method 524.4 requires a linear or quadratic regression (r^2) of 0.995 or better, where weighting of the individual calibration points may be used but forcing the calibration curve through zero cannot be applied. The lowest concentration in the curve must be within ±50% of its true value, whereas all other points must be within ±30%. The samples must also be chilled, which involves using the chiller tray upgrade for the Atomx XYZ P&T.

Helium is used as the carrier gas of choice for GC-MS analysis of VOCs; however, recently there have been several challenges in obtaining the helium supply for the analysis. Switching to alternative carrier gases, such as hydrogen, is a possible solution, but MS vacuum and detection performance are reduced, which may lead to issues with regulatory compliance. This highlights the need for helium conservation to maintain current system performance. The Thermo Scientific HeSaver-H_2Safer carrier gas saving technology[2] offers an innovative approach to significantly reduce carrier gas consumption, even during GC operation. It consists of a modified Split Splitless (SSL) injector body connected to two gas lines: an inexpensive gas (e.g., nitrogen or argon) is used for inlet pressurization, analyte vaporization, and transfer to the analytical column, while the selected carrier gas (e.g., helium or hydrogen) is used only to supply the chromatographic column for the separation process, with a limited maximum flow rate. When used with helium as the carrier gas, the limited consumption allows mitigation of shortage issues while maintaining GC-MS performance without the need for method re-optimization, typically required when switching to a different carrier gas.

The following evaluation describes the use of the ISQ 7610 GC-MS system equipped with the HeSaver-H_2Safer SSL inlet and the Atomx XYZ P&T for U.S. EPA Method 524.4.

Experimental

Sample preparation

A 50 µg/mL (equivalent to parts per million or ppm) calibration working standard was prepared in purge and trap grade methanol (Honeywell/Burdick & Jackson, P/N 232-1L) from the following Restek™ standards: 524.3 VOA MegaMix™ (P/N 30013) and 524.3 Gas Calibration Mix (P/N 30014). In total, the standard contained 75 compounds.

The calibration curve was prepared to contain 0.2 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 three Restek internal standard: 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4 (P/N 30017). Surrogate standards from Restek consisted of methyl-*t*-butyl ether-d_3, 4-bromofluorobenzene, and 1,2-dichlorobenzene (P/N 30017). Internal and surrogate standards were prepared in methanol at a concentration of 12.5 ppm, after which 5 µL was then mixed with each 5 mL water sample for a resulting concentration of 12.5 ppb.

A total of seven standards at a concentration of 0.5 ppb were prepared in deionized water to determine the MDL and precision calculations for all compounds. Also, ten standards with a concentration of 10 ppb 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 using the conditions summarized in Table 1. Seven individual standards with a concentration of 1 ppb of each compound were prepared to determine the MRL.

GC-MS conditions

A TRACE 1610 GC was coupled to the ISQ 7610 single quadrupole mass spectrometer equipped with the Thermo Scientific™ NeverVent™ vacuum probe interlock (VPI) and a Thermo Scientific™ ExtractaBrite™ ion source. A Thermo Scientific™ TraceGOLD™ TG-VMS column, 20 m x 0.18 mm, 1 µm film (P/N 26080-4950) was used for compound separation. The injector was operated in split mode, and a sample turnover time of under 16 minutes was achieved. The HeSaver-H_2Safer SSL inlet allows for most previous method parameters to remain the same, with the addition of new parameters to optimize the performance of the inlet. For example, the helium delay and nitrogen as the pressurizing gas allow for extended helium tank life. The ISQ 7610 single quadrupole mass spectrometer was operated in full scan mode, offering sufficient sensitivity to achieve the required limits of detection. The instrument can also be operated in Selected Ion Monitoring (SIM) mode to increase selectivity. Expanded method parameters for the ISQ 7610 GC-MS are displayed in Table 2.

Table 1. Teledyne Tekmar Atomx XYZ water method conditions

Standby	**Variable**
Valve oven temperature	140 °C
Transfer line temperature	140 °C
Sample mount temperature	90 °C
Water heater temperature	90 °C
Sample cup temperature	20 °C
Soil valve temperature	50 °C
Standby flow	10 mL/min
Purge ready temperature	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
Purge time	8.00 min
Purge flow	55 mL/min
Purge temperature	20 °C
MCS purge temperature	20 °C
Dry purge time	0.5 min
Dry purge flow	100 mL/min
Dry purge temperature	20 °C
Desorb	**Variable**
Methanol needle rinse	Off
Water needle rinse volume	7.00 mL
Sweep needle time	0.25 min
Desorb preheat temperature	245 °C
GC start signal	Begin Desorb
Desorb time	1.00 min
Drain flow	300 mL/min
Desorb temperature	250 °C
Bake	**Variable**
Methanol glass rinse	Off
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
Trap bake temperature	270 °C
MCS bake temperature	200 °C
Bake flow	200 mL/min

Trap	Teledyne Tekmar #9 Proprietary U-shaped trap
Chiller tray	On
Purge gas	Nitrogen

Table 2. GC-MS conditions

TRACE 1610 GC conditions	
Column	TraceGOLD TG-VMS, 20 m × 0.18 mm, 1 µm film (P/N 26080-4950)
Carrier gas	Helium, 0.3 mL/min
Oven profile	35 °C, 4 min, 12 °C /min to 85 °C, 25 °C/min to 225 °C, 2 min hold, run time 15.767 min
Inlet	200 °C, 50:1 split, purge flow 5.0 mL/min, 0.40 min helium delay
ISQ 7610 MS conditions	
Temperature	Transfer line 230 °C; ion source 280 °C
Scan	Range 35 amu to 260 amu, solvent delay 1.55 min, dwell/scan time 0.10 s
Current	Emission current 25 µA, gain 3.00E+005

Instrument control and data processing

Data were acquired, processed, and reported using Chromeleon CDS software, version 7.3. The software can control both the GC-MS system and the Atomx XYZ P&T. This allows a single software to be utilized for the full workflow simplifying the instrument operation. The fully optimized method used within this application note is available for download in the Thermo Scientific™ AppsLab application note repository, which contains all the parameters needed to acquire, process, and report the analytical data for EPA Method 524.4.[3]

Results and discussion

Chromatography

Using the GC conditions described in Table 2, all compounds of interest were chromatographically well resolved. The chromatography was consistent with the results obtained with the standard split/splitless injector. The HeSaver-H_2Safer inlet produces excellent results without any impact on chromatography. Figure 1 displays consistent peak shape and separation of a 10 ppb VOC standard with minimal water interference.

Linearity and sensitivity

The calibration range of 0.2 ppb to 50 ppb was assessed for all compounds. Figure 2 demonstrates the quantitation of 4-chlorotoluene at 5 ppb in a VOC standard with excellent library spectral matching and calibration curve. Figure 3 shows the MDL and precision calculated for a subset of compounds and Appendix 1 displays the linear correlation (r^2) and the MDL for each analyte calculated by injecting n=7 injections of the 0.5 ppb water standard. Also included is the MRL data, which was calculated by injecting n=7 of a 1 ppb standard.

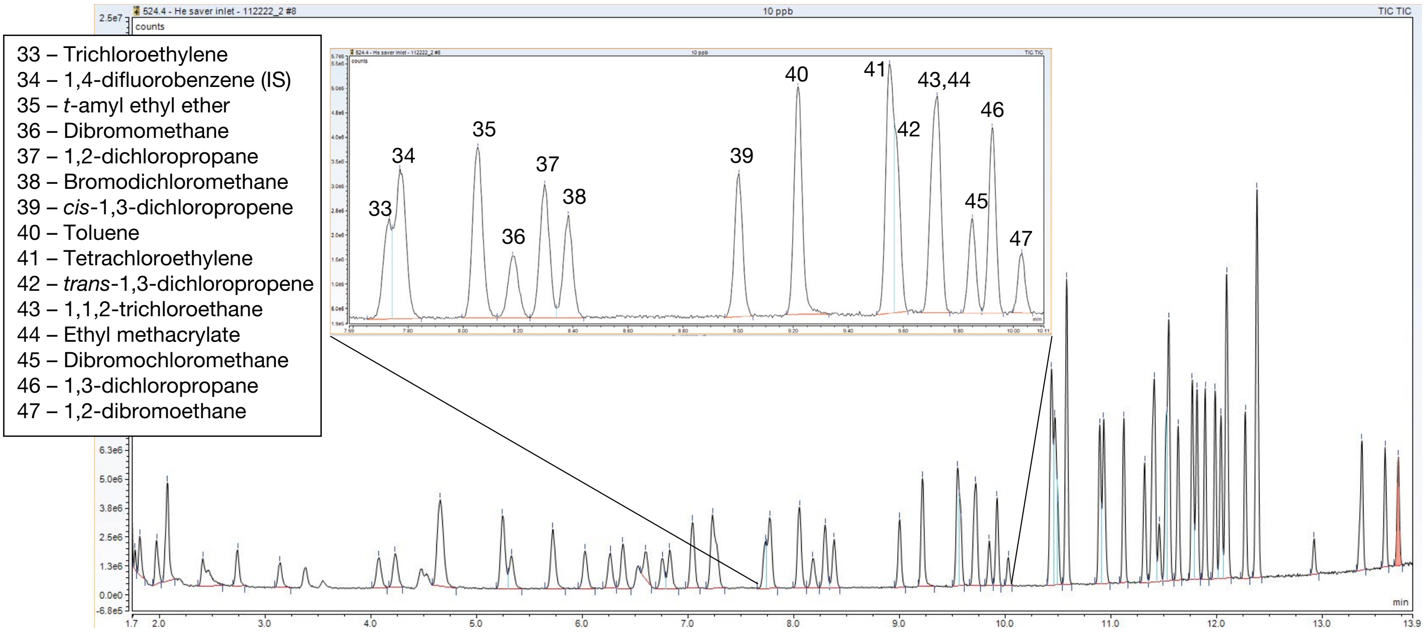


Figure 1. Total ion chromatogram (TIC) of a water method 10 ppb VOC standard with an inset indicating consistent peak shapes and separation with minimal water interference

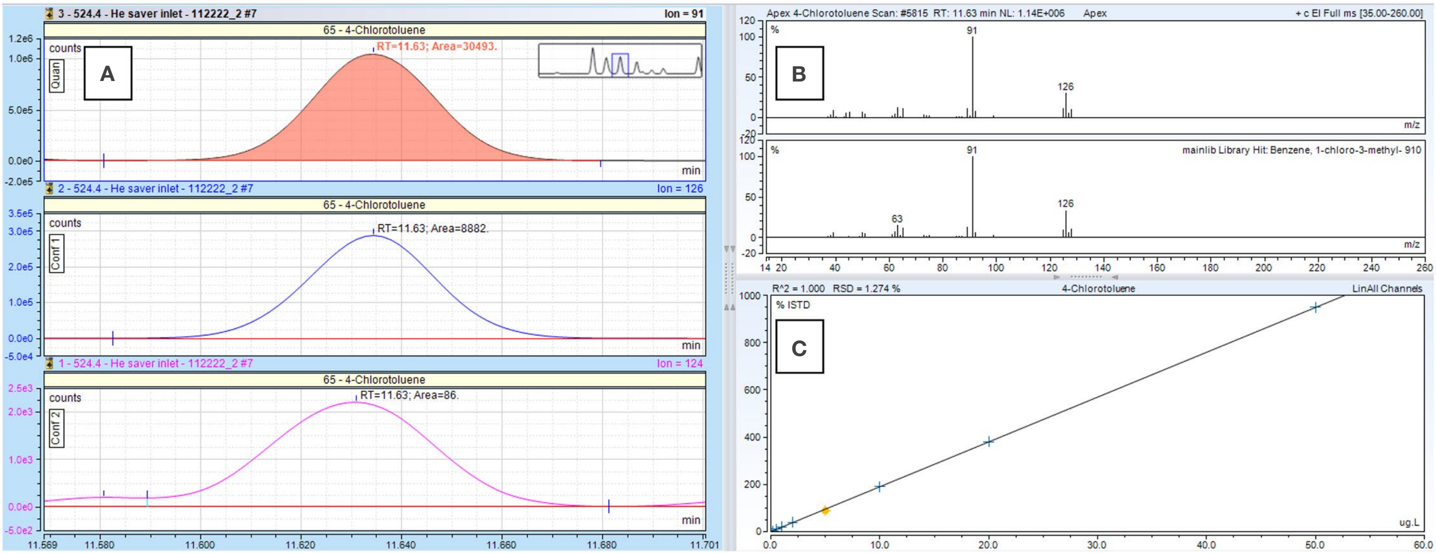


Figure 2. Chromeleon CDS results browser showing extracted ion chromatograms for 4-chlorotoluene in the 5 ppb water standard, quantitation ion (m/z = 91) and two confirming ions (m/z = 126, 124) (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 0.2 ppb to 50 ppb (C)

Method robustness

Analytical testing labs must maximize the utilization of their GC-MS system to ensure results are delivered to customers in a timely manner. To assess the stability of the method, 10 ppb calibration check standards were injected at intervals 26 times over a sequence of 160 injections. This extended sequence is equivalent to two days of uninterrupted analysis. No maintenance was performed on any part of the system during this extended test. Figure 4 shows the reproducibility of 12 of the compounds over 160 injections with excellent percentage RSDs. RSDs for all compounds were under the 30% method requirements. Appendix 2 shows the reproducibility results for all compounds over the 160-injection sequence.

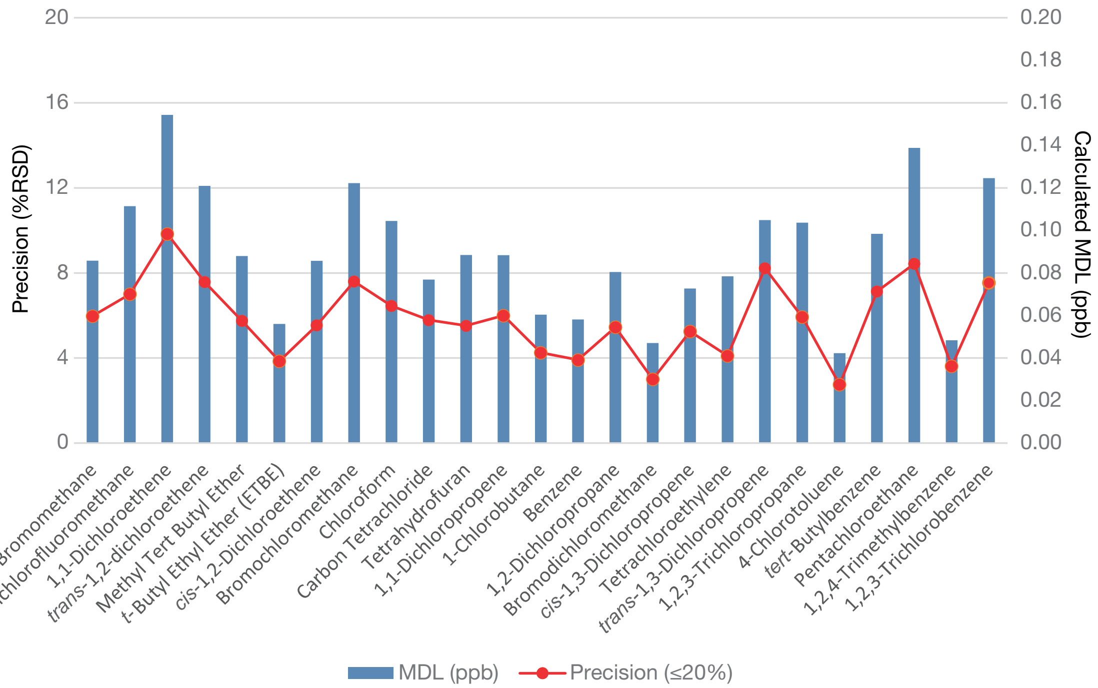


Figure 3. MDL and precision calculated for a subset of compounds (n=25) from n=7 injections of a 0.5 ppb water standard

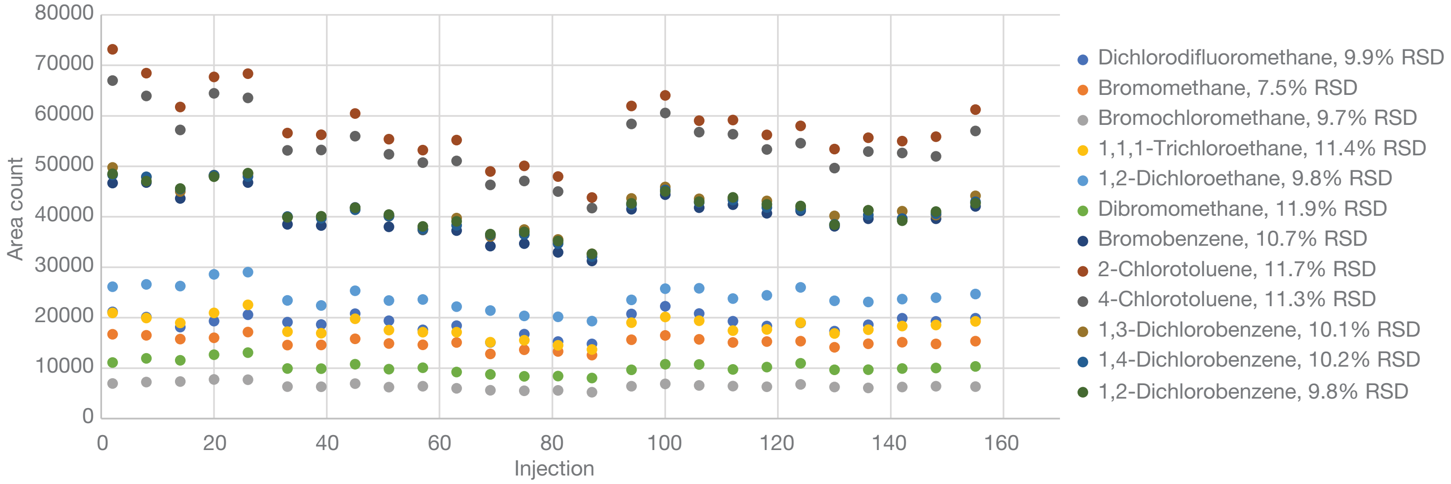
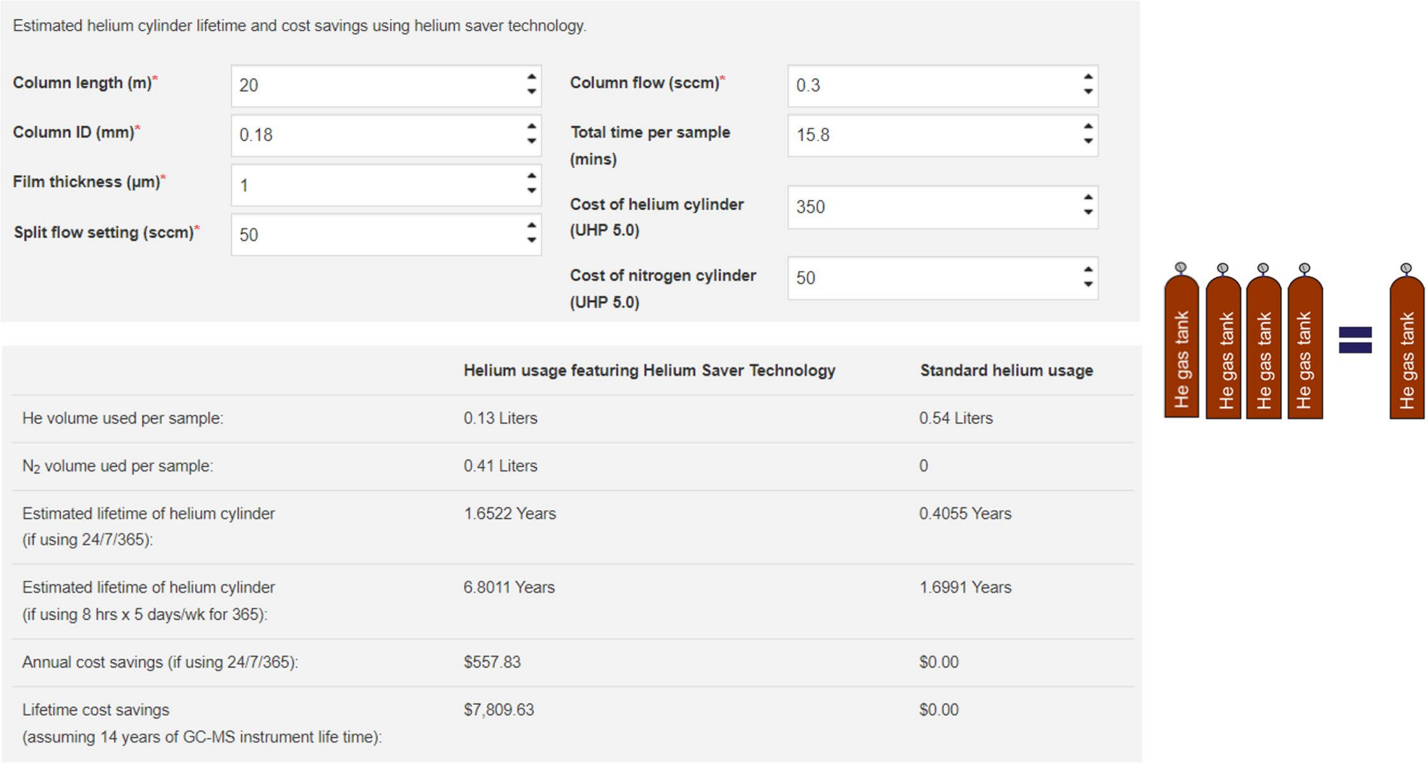


Figure 4. Repeatability of a 10 ppb VOC standard (n=26) (as absolute peak area counts) assessed over n=160 consecutive injections

Reduced helium consumption and cost savings

The HeSaver-H_2Safer technology offers significant gas savings not only when the GC is idle but during operation. This technology can extend helium/hydrogen cylinder lifetime from months to years, depending on instrument method parameters, usage, and the number of GCs supported by a given gas cylinder. The Thermo Scientific™ Helium Saver Calculator tool[4] offers an easy-to-use and intuitive interface to estimate helium consumption and cost impact on an individual laboratory's activities. GC parameters regarding column dimensions, carrier gas and split flow settings, as well as helium and nitrogen costs are adjustable to reflect a given laboratory's methodology and regional gas cost to provide estimates on helium cylinder lifetime and cost savings (Figure 5). The usage of the HeSaver-H_2Safer technology for the analysis of VOCs according to U.S. EPA Method 524.4 would allow the helium cylinder to last four times longer in comparison to the usage of a standard SSL injector.



Estimated helium cylinder lifetime and cost savings using helium saver technology.

Column length (m)* 20

Column ID (mm)* 0.18

Film thickness (µm)* 1

Split flow setting (sccm)* 50

Column flow (sccm)* 0.3

Total time per sample (mins) 15.8

Cost of helium cylinder (UHP 5.0) 350

Cost of nitrogen cylinder (UHP 5.0) 50

	Helium usage featuring Helium Saver Technology	Standard helium usage
He volume used per sample:	0.13 Liters	0.54 Liters
N_2 volume ued per sample:	0.41 Liters	0
Estimated lifetime of helium cylinder (if using 24/7/365):	1.6522 Years	0.4055 Years
Estimated lifetime of helium cylinder (if using 8 hrs x 5 days/wk for 365):	6.8011 Years	1.6991 Years
Annual cost savings (if using 24/7/365):	$557.83	$0.00
Lifetime cost savings (assuming 14 years of GC-MS instrument life time):	$7,809.63	$0.00

Figure 5. Helium saving calculator for U.S. EPA Method 524.4

Conclusion

The combined solution of the TRACE 1610 GC equipped with HeSaver-H_2Safer technology coupled with the ISQ 7610 MS and the Atomx XYZ P&T system provides clear advantages for EPA Method 524.4. Combined, these 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 for EPA Method 524.4.

- The ISQ 7610 VPI coupled with the Teledyne Tekmar Atomx XYZ P&T exceeds all the requirements outlined in EPA Method 524.4 for analysis of VOCs in water.
- Excellent linearity for all compounds was demonstrated with the $r^2 > 0.995$, passing all method requirements.
- MDL, precision, and accuracy for seven 0.5 ppb standards showed no interference from excessive water and produced very reproducible results.
- MRL passed all method requirements of the lower Prediction Interval of Results (PIR) ≥50% and the upper PIR ≤150%.
- Calibration standards meet the required ±50% of the true value for first calibration standard and ±30% of the true value for the rest of the calibration standards.
- The precision for n=26 samples over 160 injections displayed <30% RSD for all compounds as the method requires and an average recovery of 92%.
- The helium consumption was reduced by a factor of 4 compared to a standard SSL inlet configuration, offering a concrete solution to support more sustainable operations and mitigate helium gas shortage issues.

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Appendix 1 (part 1). U.S. EPA Method 524.4 calibration, accuracy, and precision data

		Calibration			MDL (n=7, 0.5 ppb)		IDC (n=10, 10 ppb)		MRL confirmation (n=7, 1 ppb)	
Compound	Retention time	Cal type	Linearity (r^2 ≥0.995)	Avg. RF	MDL (ppb)	Precision (≤20% RSD)	Accuracy (±20%)	Precision (≤20% RSD)	LPIR (≥50%)	UPIR (≤150%)
Dichlorodifluoromethane	1.77	Lin	0.998	0.600	0.13	8.05	8.52	97	66	123
Chlorodifluoromethane	1.8	Lin	0.997	1.446	0.09	5.17	9.25	113	96	128
Chloromethane	1.97	Lin	0.997	1.369	0.07	3.83	9.01	111	88	129
Vinyl chloride	2.05	Lin	0.999	0.777	0.05	2.83	9.31	112	82	133
1,3-Butadiene	2.07	Lin	0.998	1.041	0.16	9.27	9.62	111	78	142
Bromomethane	2.4	Lin, WithOffset, 1/A	0.996	0.557	0.09	5.97	7.41	107	77	127
Trichlorofluoromethane	2.73	Lin	0.999	0.750	0.11	7.01	8.75	106	85	122
Diethyl ether	3.14	Lin	1.000	0.326	0.12	8.20	3.14	104	76	122
1,1-Dichloroethene	3.37	Lin	0.999	0.186	0.15	9.84	8.70	107	81	133
Carbon disulfide	3.39	Lin, WithOffset, 1/A	0.998	0.172	0.14	9.92	9.16	101	91	102
Methyl iodide[1]	3.55	Lin, WithOffset, 1/A	0.995	0.244	0.07	3.28	6.96	81	82	116
Allyl chloride	4.06	Lin	0.999	0.183	0.16	10.3	7.24	103	92	123
Methylene chloride	4.23	Lin, WithOffset, 1/A	0.997	0.952	0.12	8.35	5.71	110	87	114
trans-1,2-dichloroethene	4.47	Lin	0.999	0.408	0.12	7.58	7.21	108	78	128
Methyl acetate	4.55	Lin	0.998	0.582	0.16	9.38	3.97	105	78	136
Methyl-*t*-butyl ether-d_3 (surr)	4.64	AvgCalFact	2.11	1.195	-	4.33	2.15	100	97	105
Methyl tert butyl ether	4.67	Lin	1.000	1.320	0.09	5.75	4.02	99	88	117
t-Butyl alcohol (TBA)	5.24	Lin	1.000	0.158	0.12	8.13	4.10	103	88	127
Diisopropyl ether	5.25	Lin	1.000	1.978	0.09	5.98	4.98	99	88	117
1,1-Dichloroethane	5.33	Lin	0.999	0.871	0.11	6.68	6.75	111	92	124
t-Butyl ethyl ether (ETBE)	5.72	Lin	1.000	1.316	0.06	3.86	4.72	96	86	111
cis-1,2-Dichloroethene	6.03	Lin	1.000	0.432	0.09	5.54	6.11	105	87	120
Bromochloromethane	6.25	Lin	0.999	0.207	0.12	7.60	5.38	108	82	119
Chloroform	6.38	Lin	0.999	0.905	0.10	6.46	5.54	110	91	121
Carbon tetrachloride	6.53	Lin	0.999	0.404	0.08	5.79	7.22	107	73	119
1,1,1-Trichloroethane	6.6	Lin	0.999	0.546	0.27	17.6	8.18	107	95	112
Tetrahydrofuran	6.61	Lin	0.998	0.072	0.09	5.52	4.98	105	66	147
1,1-Dichloropropene	6.76	Lin	1.000	0.388	0.09	6.00	7.66	96	79	107
1-Chlorobutane	6.82	Lin	1.000	0.648	0.06	4.25	7.91	99	90	102
Benzene	7.04	Lin	1.000	1.411	0.06	3.91	5.99	99	85	113
t-Amyl methyl ether (TAME)	7.23	Lin	1.000	1.149	0.04	2.68	5.11	96	87	112
1,2-Dichloroethane	7.27	Lin	0.999	0.725	0.07	4.52	3.88	109	88	123
Trichloroethylene	7.73	Lin	0.997	0.429	0.22	14.0	6.00	116	71	147
1,4-Difluorobenzene (ISTD)	7.77	AvgCalFact	-	-	-	-	-	-	-	-
t-Amyl ethyl ether (TMEE)	8.05	Lin	1.000	1.065	0.06	4.14	4.98	101	92	112
Dibromomethane	8.18	Lin	0.999	0.317	0.11	7.39	4.61	107	82	121
1,2-Dichloropropane	8.29	Lin	1.000	0.552	0.08	5.45	5.13	102	83	116
Bromodichloromethane	8.38	Lin	0.999	0.722	0.05	3.00	4.92	107	79	121
cis-1,3-Dichloropropene	9	Lin	1.000	0.754	0.07	5.25	4.79	94	83	98
Toluene	9.22	Lin	1.000	1.683	0.24	12.5	5.97	100	104	141
Tetrachloroethylene	9.55	Lin	0.997	0.613	0.08	4.11	5.80	119	112	143

[1] Calibration from 0.5–50 ppb

Appendix 1 (part 2). U.S. EPA Method 524.4 calibration, accuracy, and precision data

		Calibration			MDL (n=7, 0.5 ppb)		IDC (n=10, 10 ppb)		MRL confirmation (n=7, 1 ppb)	
Compound	**Retention time**	**Cal type**	**Linearity (r^2 ≥0.995)**	**Avg. RF**	**MDL (ppb)**	**Precision (≤20% RSD)**	**Accuracy (±20%)**	**Precision (≤20% RSD)**	**LPIR (≥50%)**	**UPIR (≤150%)**
trans-1,3-Dichloropropene	9.57	Lin	0.999	0.690	0.10	8.23	4.05	90	69	109
1,1,2-Trichloroethane	9.7	Lin	1.000	0.388	0.08	5.44	4.20	97	83	116
Ethyl methacrylate	9.72	Lin	1.000	0.624	0.12	8.48	4.07	96	85	116
Dibromochloromethane	9.85	Lin	0.999	0.404	0.06	4.63	4.28	93	66	111
1,3-Dichloropropane	9.92	Lin	0.999	0.816	0.05	3.87	3.38	96	86	106
1,2-Dibromoethane	10.03	Lin	1.000	0.400	0.11	7.71	4.69	94	80	104
Chlorobenzene-d_5 (ISTD)	10.43	AvgCalFact	–	–	–	–	–	–	–	–
Chlorobenzene	10.44	Lin	1.000	1.141	0.07	4.75	5.17	99	84	119
Ethylbenzene	10.47	Lin	1.000	1.861	0.06	3.78	5.97	95	82	111
1,1,1,2-Tetrachloroethane	10.49	Lin	0.999	0.361	0.07	5.06	5.08	95	83	101
m,p-Xylene	10.58	Lin	1.000	1.545	0.13	4.99	5.91	92	74	102
o-Xylene	10.89	Lin	1.000	1.649	0.06	4.09	5.74	93	74	105
Styrene	10.93	Lin	0.999	1.165	0.04	3.18	5.73	89	70	96
Bromoform	10.94	Lin	0.999	0.310	0.05	4.18	5.64	96	81	100
Isopropylbenzene	11.12	Lin	1.000	1.756	0.04	2.89	7.28	93	74	98
4-Bromofluorobenzene (surr)	11.31	AvgCalFact	3.57	0.904	–	2.80	2.08	97	93	108
Bromobenzene	11.39	Lin	1.000	1.766	0.06	3.59	5.31	104	91	126
n-Propylbenzene	11.41	Lin	1.000	3.408	0.06	3.88	7.35	97	84	114
1,1,2,2-Tetrachloroethane	11.45	Lin	0.998	0.716	0.09	6.80	5.16	91	70	107
2-Chlorotoluene	11.52	Lin	1.000	2.525	0.07	4.65	6.75	99	81	121
1,3,5-Trimethylbenzene	11.54	Lin	1.000	2.370	0.07	4.78	6.82	92	76	98
1,2,3-Trichloropropane	11.54	Lin	1.000	0.982	0.10	5.93	5.11	106	99	137
4-Chlorotoluene	11.63	Lin	1.000	2.394	0.04	2.75	6.80	98	80	113
tert-Butylbenzene	11.76	Lin	0.999	2.125	0.10	7.13	7.41	91	75	98
Pentachloroethane	11.76	Lin	1.000	0.294	0.14	8.44	8.09	99	66	131
1,2,4-Trimethylbenzene	11.81	Lin	0.999	2.456	0.05	3.62	5.67	92	72	99
sec-Butylbenzene	11.89	Lin	1.000	2.825	0.06	3.99	7.29	96	68	105
p-Isopropyltoluene	11.98	Lin	0.999	2.202	0.06	4.39	7.24	91	65	97
1,3-Dichlorobenzene	12.04	Lin	1.000	1.814	0.08	4.75	5.50	103	86	118
1,4-Dichlorobenzene-d_4 (ISTD)	12.08	AvgCalFact	-	-	-	-	-	-	-	-
1,4-Dichlorobenzene	12.09	Lin	1.000	1.799	0.10	6.07	5.46	102	82	124
n-Butylbenzene	12.26	Lin	0.998	2.252	0.08	5.42	7.38	90	69	102
Hexachloroethane	12.37	Lin	0.999	0.260	0.09	7.80	7.75	98	77	94
1,2-Dichlorobenzene (surr)	12.37	AvgCalFact	1.29	0.976	-	1.77	2.22	100	90	112
1,2-Dichlorobenzene	12.38	Lin	0.999	1.789	0.04	2.33	5.94	106	80	135
1,2-Dibromo-3-chloropropane	12.91	Lin	1.000	0.213	0.12	7.67	6.12	105	65	138
Hexachlorobutadiene	13.34	Lin	1.000	0.038	0.17	10.1	9.39	109	82	149
1,2,4-Trichlorobenzene	13.37	Lin	1.000	0.959	0.11	6.25	5.81	104	77	133
Naphthalene	13.59	Lin	0.999	2.143	0.07	4.52	4.73	94	77	119
1,2,3-Trichlorobenzene	13.71	Lin	1.000	0.813	0.12	7.54	5.84	104	78	123

[1] Calibration from 0.5–50 ppb

Appendix 2. Repeatability of a 10 ppb VOC standard (n=26) (as absolute peak area counts) assessed over n=160 consecutive injections

Compound	Analyte recovery (10 ppb n=26, 160 injections)	
	Precision (≤20% RSD)	Accuracy (±30% RSD)
Dichlorodifluoromethane	9.1	104
Chlorodifluoromethane	9.3	116
Chloromethane	8.8	104
Vinyl chloride	8.7	105
1,3-Butadiene	8.8	102
Bromomethane	7.0	104
Trichlorofluoromethane	7.8	101
Diethyl ether	6.0	92
1,1-Dichloroethene	6.4	92
Carbon disulfide	8.1	70
Methyl iodide[1]	13.2	56
Allyl chloride	6.0	96
Methylene chloride	6.6	111
trans-1,2-dichloroethene	5.5	99
Methyl acetate	10.3	99
Methyl-t-butyl ether-d$_3$ (surr)	5.7	95
Methyl *tert* butyl ether	8.4	91
Diisopropyl ether	5.2	92
t-Butyl alcohol (TBA)	6.1	98
1,1-Dichloroethane	8.2	109
t-Butyl ethyl ether (ETBE)	7.8	87
cis-1,2-Dichloroethene	5.1	102
Bromochloromethane	4.5	107
Chloroform	5.6	114
Carbon tetrachloride	9.1	98
Tetrahydrofuran	15.7	93
1,1,1-Trichloroethane	5.2	105

Compound	Analyte recovery (10 ppb n=26, 160 injections)	
	Precision (≤20% RSD)	Accuracy (±30% RSD)
1,1-Dichloropropene	6.4	86
1-Chlorobutane	5.4	89
Benzene	4.3	94
t-Amyl methyl ether (TAME)	10.3	85
1,2-Dichloroethane	4.1	111
Trichloroethylene	6.1	110
1,4-Difluorobenzene (ISTD)	-	-
t-Amyl ethyl ether (TMEE)	7.3	90
Dibromomethane	3.2	108
1,2-Dichloropropane	3.7	103
Bromodichloromethane	5.1	108
cis-1,3-Dichloropropene	5.6	92
Toluene	10.7	90
Tetrachloroethylene	7.1	109
trans-1,3-Dichloropropene	9.6	82
1,1,2-Trichloroethane	8.3	91
Ethyl methacrylate	17.1	79
Dibromochloromethane	8.9	87
1,3-Dichloropropane	8.1	88
1,2-Dibromoethane	10.7	86
Chlorobenzene-d$_5$ (ISTD)	-	-
Chlorobenzene	6.7	91
Ethylbenzene	7.4	86
1,1,1,2-Tetrachloroethane	7.6	89
m,p-Xylene	7.3	84
o-Xylene	6.5	86
Styrene	7.8	81

Compound	Analyte recovery (10 ppb n=26, 160 injections)	
	Precision (≤20% RSD)	Accuracy (±30% RSD)
Bromoform	11.7	86
Isopropylbenzene	7.5	84
4-Bromofluorobenzene (surr)	3.6	94
Bromobenzene	6.5	95
n-Propylbenzene	8.1	86
1,1,2,2-Tetrachloroethane	15.0	77
2-Chlorotoluene	7.9	89
1,3,5-Trimethylbenzene	12.5	76
1,2,3-Trichloropropane	12.2	92
4-Chlorotoluene	7.4	87
Pentachloroethane	7.1	89
tert-Butylbenzene	9.4	80
1,2,4-Trimethylbenzene	13.3	74
sec-Butylbenzene	8.0	84
p-Isopropyltoluene	10.4	76
1,3-Dichlorobenzene	6.0	95
1,4-Dichlorobenzene-d$_4$ (ISTD)	-	-
1,4-Dichlorobenzene	6.4	92
n-Butylbenzene	10.4	75
Hexachloroethane	6.7	89
1,2-Dichlorobenzene (surr)	2.0	100
1,2-Dichlorobenzene	6.3	96
1,2-Dibromo-3-chloropropane	16.1	86
Hexachlorobutadiene	11.4	92
1,2,4-Trichlorobenzene	11.4	86
Naphthalene	19.0	73
1,2,3-Trichlorobenzene	13.4	85

[1] Reactive compound, compound degraded during analysis

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Application note | 001018

Uninterrupted analysis of VOCs according to U.S. EPA Method 8260C using purge and trap and single quadrupole GC-MS technology

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Keywords

EPA, VOCs, phthalates, trace analysis, gas chromatography, single quadrupole mass spectrometry, selected ion monitoring, sensitivity, GRO, THM, environmental laboratories, analytical testing laboratories

Goal

Demonstration of an analytical method that meets the requirements outlined in U.S. EPA Method 8260C 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™ 7610 Mass Spectrometry (MS) system coupled with a Thermo Scientific™ TRACE™ 1610 Gas Chromatograph (GC) and Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS). Method linearity, method detection limit (MDL), and a long-term robustness study were performed to demonstrate the method's capabilities.

Introduction

Volatile organic compounds, or VOCs, are human-made contaminants used and produced in the processing of, or as, paints, adhesives, petroleum products, pharmaceuticals, and refrigerants. Many of these compounds contaminate our environment and may cause negative health effects in humans and other living beings. Analytical laboratories must monitor a variety of sample types from the environment to ensure the public are not exposed to elevated levels of VOCs. The latest version of applicable method in the United States, U.S. EPA Method 8260C, is applicable when monitoring a variety of solid waste matrices for the presence of VOCs.

To perform U.S. EPA Method 8260C, all method acceptance criteria must be achieved. These criteria include calculating the mean response factor and the relative standard deviation (RSD) of the response factors for target analytes. The RSD should be <20%, with minimum response factors (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 run. 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 7610 GC-MS coupled to the Atomx XYZ P&T for U.S. EPA Method 8260C.

Experimental

Sample preparation

A working calibration standard (at a concentration level of 50 parts per million (ppm) was prepared in methanol using 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 calibration curve for water-based samples was prepared from 0.2 ppb to 200 parts per billion (ppb) or µg/L for most compounds, while the calibration curve for soils was prepared from 0.5 ppb to 200 ppb or µg/kg. The relative response factor (RRF) was calculated for each compound using one of the four internal standards: pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, or 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 purge and trap grade 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 final concentration of 25 ppb.

To calculate the achievable method detection limits (MDL) and precision, seven water standards (containing a concentration of 0.2 ppb of each compound) and seven soil standards (containing 0.5 ppb of each compound) were prepared. Seven water and soil standards (containing 20 ppb of each compound) were prepared as a mid-point check and as an assessment of the Initial Demonstration of Capability (IDC), precision, and accuracy. A further forty water standards with the same concentration 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. To preserve helium usage, nitrogen was utilized as a purge gas for the Atomx XYZ.

Table 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 cup temp.	20 °C
Soil valve temp.	50 °C
Standby flow	10 mL/min
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
Purge time	11.00 min
Purge flow	40 mL/min
Purge temp.	20 °C
MCS purge temp.	20 °C
Dry purge time	1.00 min
Dry purge flow	100 mL/min
Dry purge temp.	20 °C
Desorb	**Variable**
Methanol needle rinse	Off
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**
Methanol glass rinse	Off
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
Trap bake temp.	260 °C
MCS bake temp.	200 °C
Bake flow	200 mL/min
Trap	9
Chiller tray	Off
Purge gas	Nitrogen

Table 2. 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 cup temp.	40 °C
Soil valve temp.	100 °C
Standby flow	10 mL/min
Purge ready temp.	40 °C
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 temp.	20 °C
Purge flow	40 mL/min
MCS 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
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	200 mL/min
Bake temp.	260 °C
MCS bake temp.	180 °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 enables a single software solution to support the full workflow, simplifying the instrument operation. The optimized method used within this application note is available for download via the Thermo Scientific™ AppsLab library. AppsLab contains all the parameters needed to acquire, process, and report the analytical data for U.S. EPA Method 8260C.[2]

GC-MS parameters

A TRACE 1610 GC was coupled to the ISQ 7610 MS equipped with the Thermo Scientific™ NeverVent™ vacuum probe interlock (VPI) and an ExtractaBrite™ ion source. Expanded method parameters for the GC-MS system are displayed in Table 3.

Table 3. GC-MS conditions

	TRACE 1610 GC conditions
Column	Thermo Scientific™ TraceGOLD™ TG-VMS, 20 m × 0.18 mm, 1 µm film (P/N 26080-4950)
Carrier gas	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, purge flow 0.5 mL/min
	ISQ 7610 MS conditions
Temp.	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
Current	Emission current 25 µA, Gain 3.00E+005

Results and discussion

Chromatography

Excellent chromatographic separation was achieved using the conditions described above. The chromatography was consistent and unaffected by matrix type, showing consistent peak shape and separation. Figures 1 and 2 display examples of chromatography for a 10 ppb VOC standard in water and soil samples, respectively.

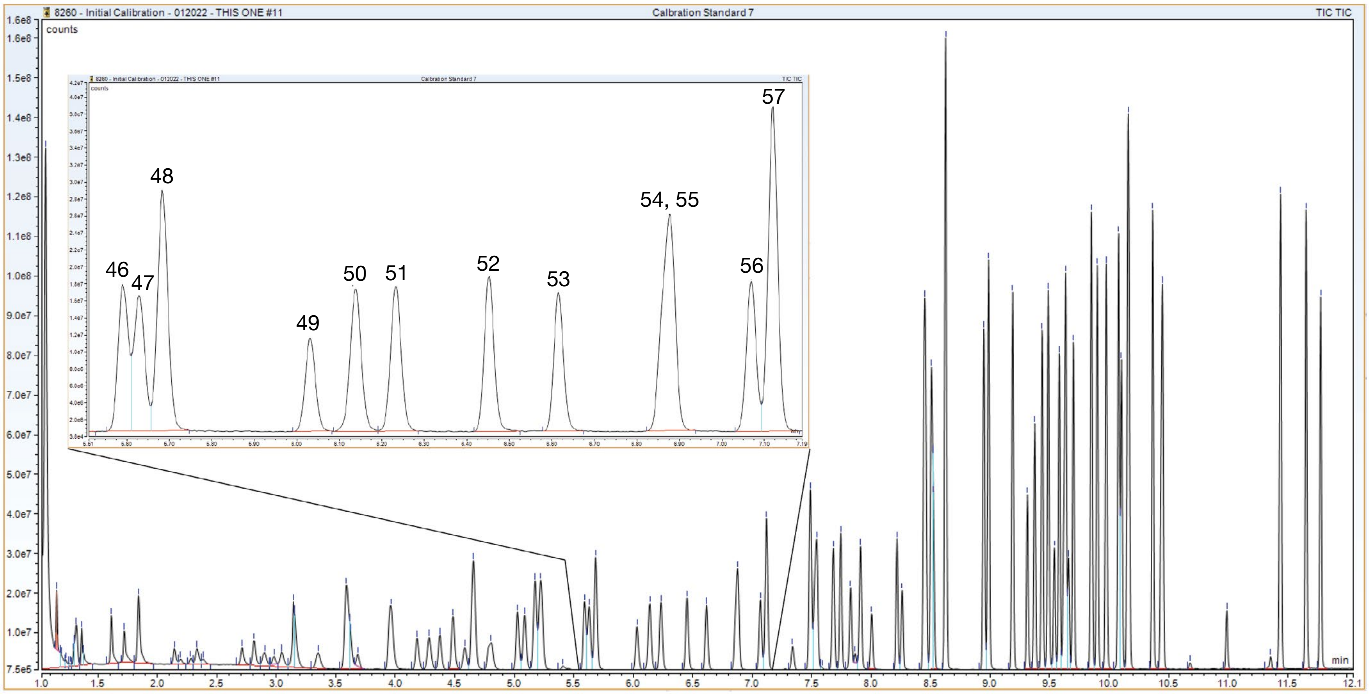

Figure 1. Total ion chromatogram (TIC) of a water method 10 ppb VOC standard with an inset indicating consistent peak shapes and separation with minimal water interference

Peaks:
46. Isopropyl acetate
47. Trichloroethene
48. 1,4-Difluorobenzene (IS)
49. Dibromomethane
50. 1,2-Dichloropropane
51. Bromodichloromethane
52. Methyl methacrylate
53. Propyl acetate
54. 1-Chloroethyl vinyl ether
55. *cis*-1,3-Dichloropropene
56. Toluene-d_8
57. Toluene

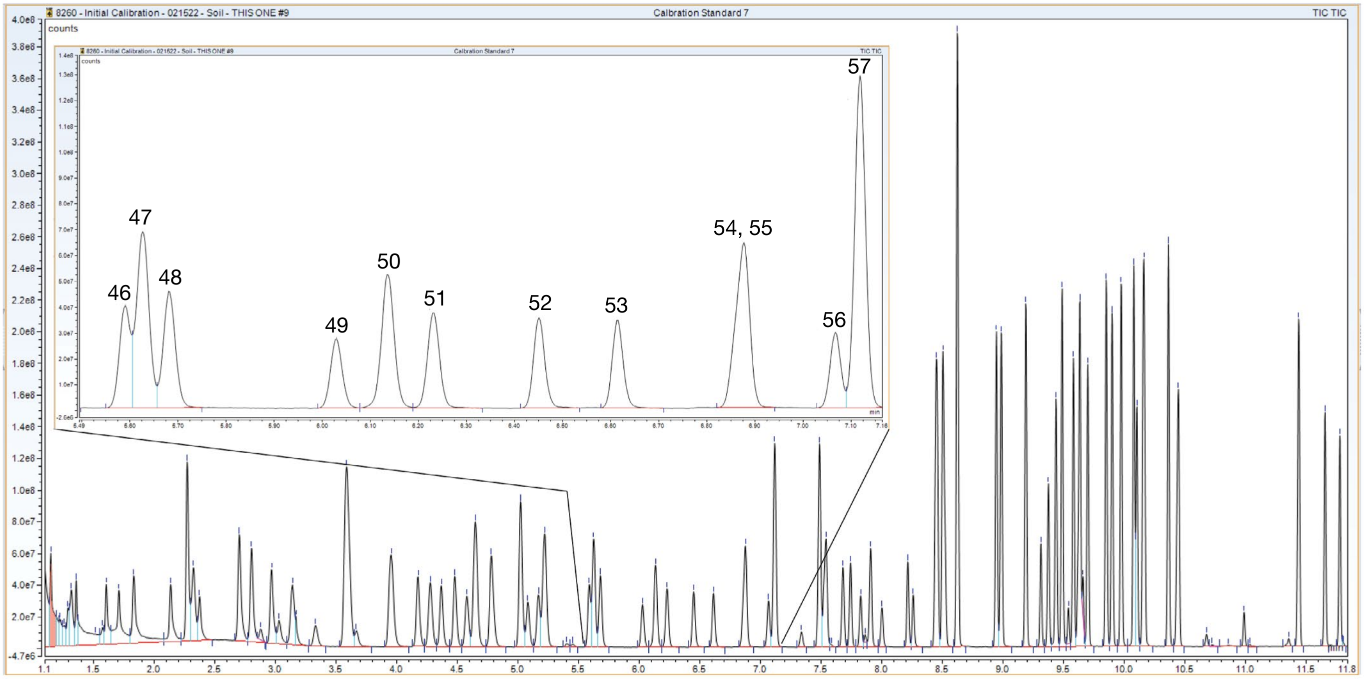

Figure 2. Total ion chromatogram (TIC) of a soil method 10 ppb VOC standard with an inset indicating consistent peak shapes and separation with minimal water interference

Peaks:
46. Isopropyl acetate
47. Trichloroethene
48. 1,4-Difluorobenzene (IS)
49. Dibromomethane
50. 1,2-Dichloropropane
51. Bromodichloromethane
52. Methyl methacrylate
53. Propyl acetate
54. 1-Chloroethyl vinyl ether
55. *cis*-1,3-Dichloropropene
56. Toluene-d_8
57. Toluene

Linearity and sensitivity

The water calibration curve was prepared from 0.2 ppb to 200 ppb (µg/L) for all compounds, while the soil calibration curve was prepared from 0.5 ppb to 200 ppb (µg/kg). The average response factor RSD for the calibration solutions was <20% and typical correlation coefficients $R^2 \geq 0.99$ were achieved for all compounds, indicating linearity across the specified concentration range in the water and soil calibration curves. The MDL and precision were assessed using n=7 replicates of a 0.2 ppb water standard and n=7 replicates of a 0.5 ppb soil standard. Calculated MDLs were <0.2 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.

Examples of the linearity for the water calibration curve for *o*-xylene is shown in Figure 3. This figure shows the 0.5 ppb calibration point and the linearity of the curve giving an R^2 value above 0.99 and average response factor RSD <20%. Figure 4 shows similar data for the soil calibration for 1,3-dichlorobenzene. The lowest point of the curve was 0.5 ppb, and even in a low level standard the peak response meets the regulatory requirements.

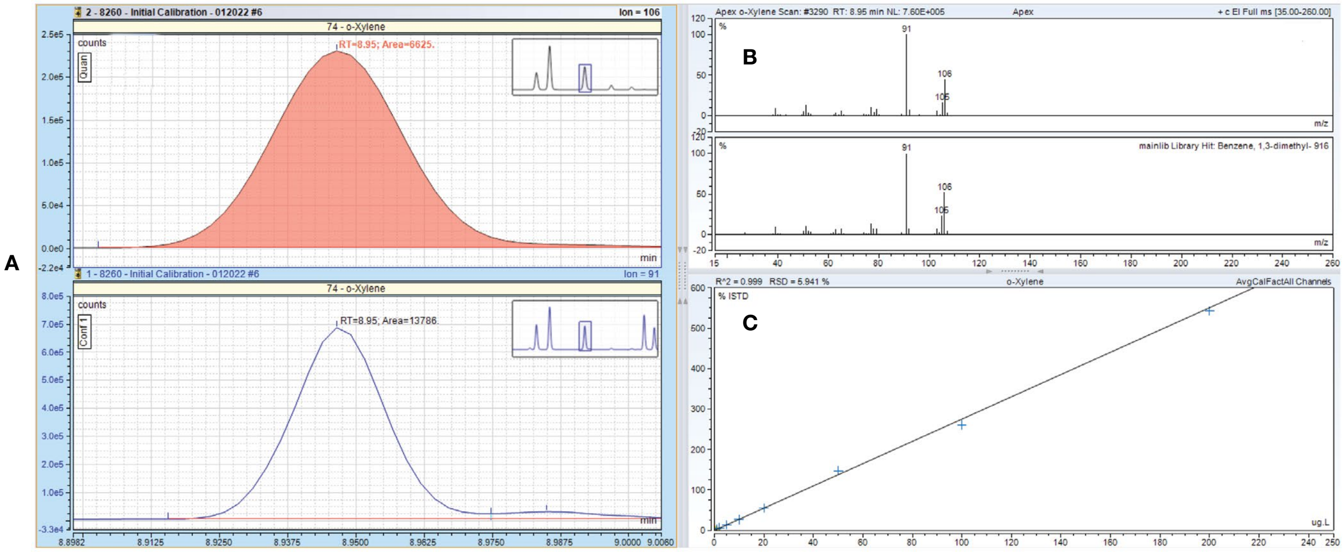

Figure 3. Chromeleon results browser showing extracted ion chromatograms for *o*-xylene in the 0.5 ppb water standard, quantitation ion (mass 106) and one confirming ion (mass 91) (A), an excellent measured spectrum match to the NIST library (B), and a linear calibration over a concentration range of 0.2 ppb to 200 ppb (C)

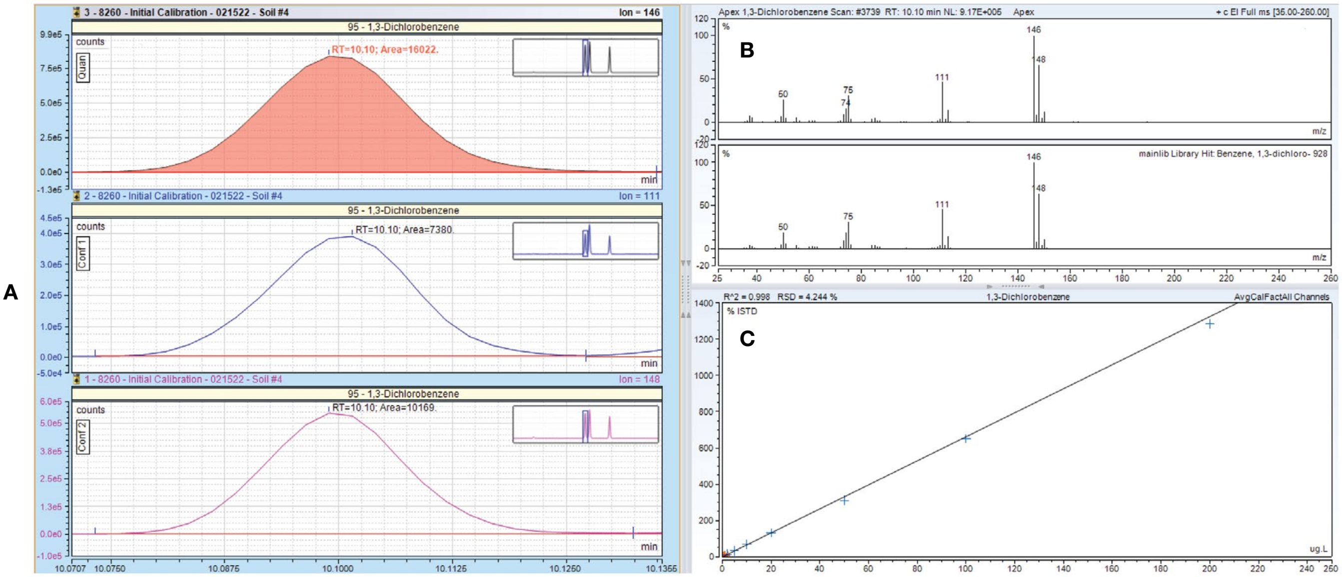

Figure 4. Chromeleon results browser showing extracted ion chromatograms for 1,3-dichlorobenzene in the 0.5 ppb soil standard, quantitation ion (mass 149) and two confirming ions (mass 111, 148) (A), an excellent measured spectrum match to the NIST library (B), and a linear calibration over a concentration range of 0.5 ppb to 200 ppb (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 Appendixes I and 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 U.S. EPA Method 8260C for IDC. Figure 5 shows a cross section of compounds in the soil standard at 20 ppb, demonstrating the accuracy and precision.

Method robustness

For analytical testing laboratories, it is extremely important that the analytical method is stable and reproducible. To demonstrate this, 20 ppb standards (n=40) in water were injected at intervals over a 240-sample injection sequence over 3 days. The samples were acquired with no user intervention on the P&T, GC, or MS system, and the absolute peak areas were plotted to demonstrate the stability of the results. Figure 6 shows the reproducibility of seven of the compounds over 240 injections with excellent percentage RSDs. The accuracy and precision for all compounds in the injection series are shown in Appendices I and II.

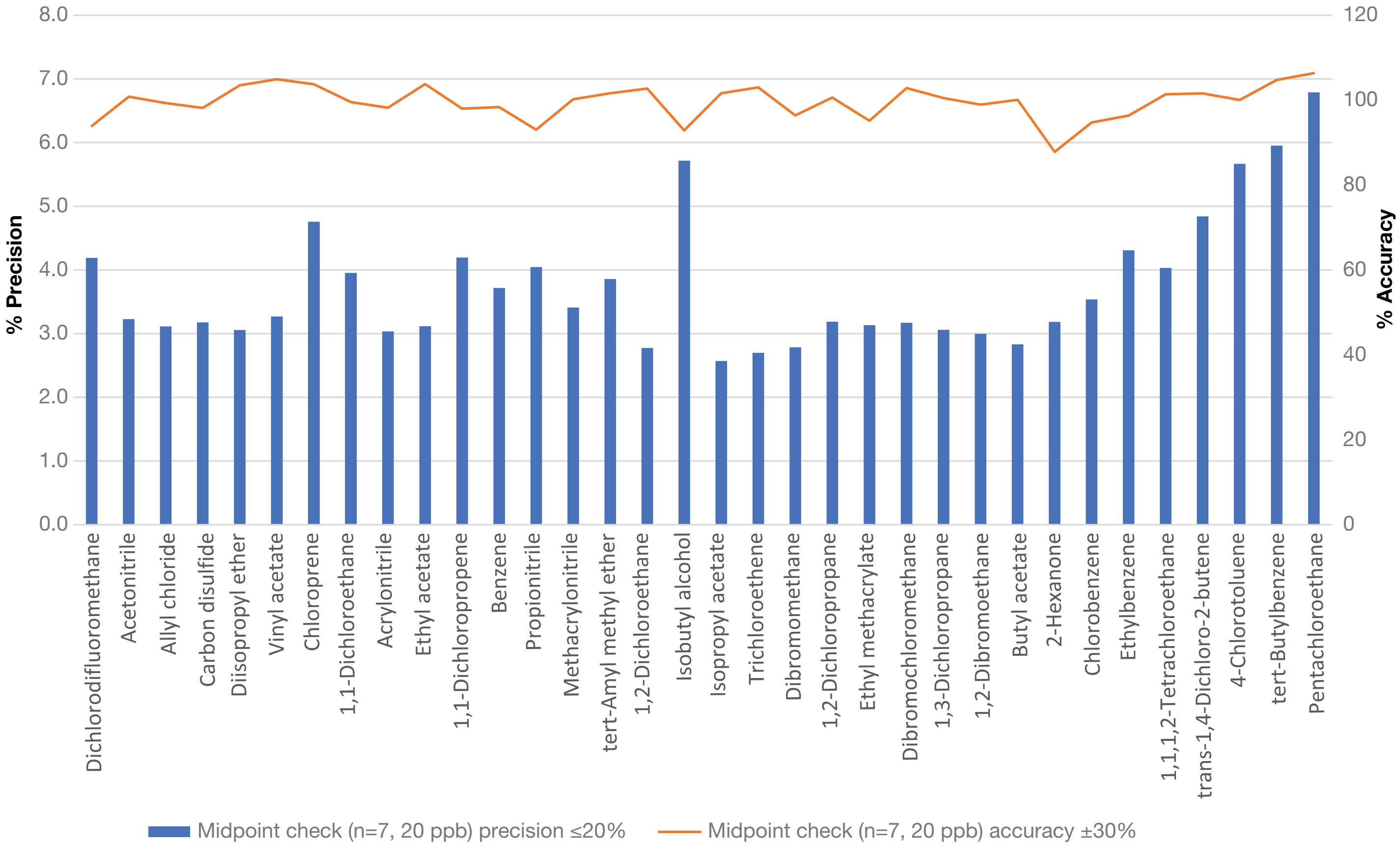

Figure 5. Demonstration of accuracy (% recovery) and precision (calculated concentration) by analyzing n=7 replicates of a 20 ppb soil standard

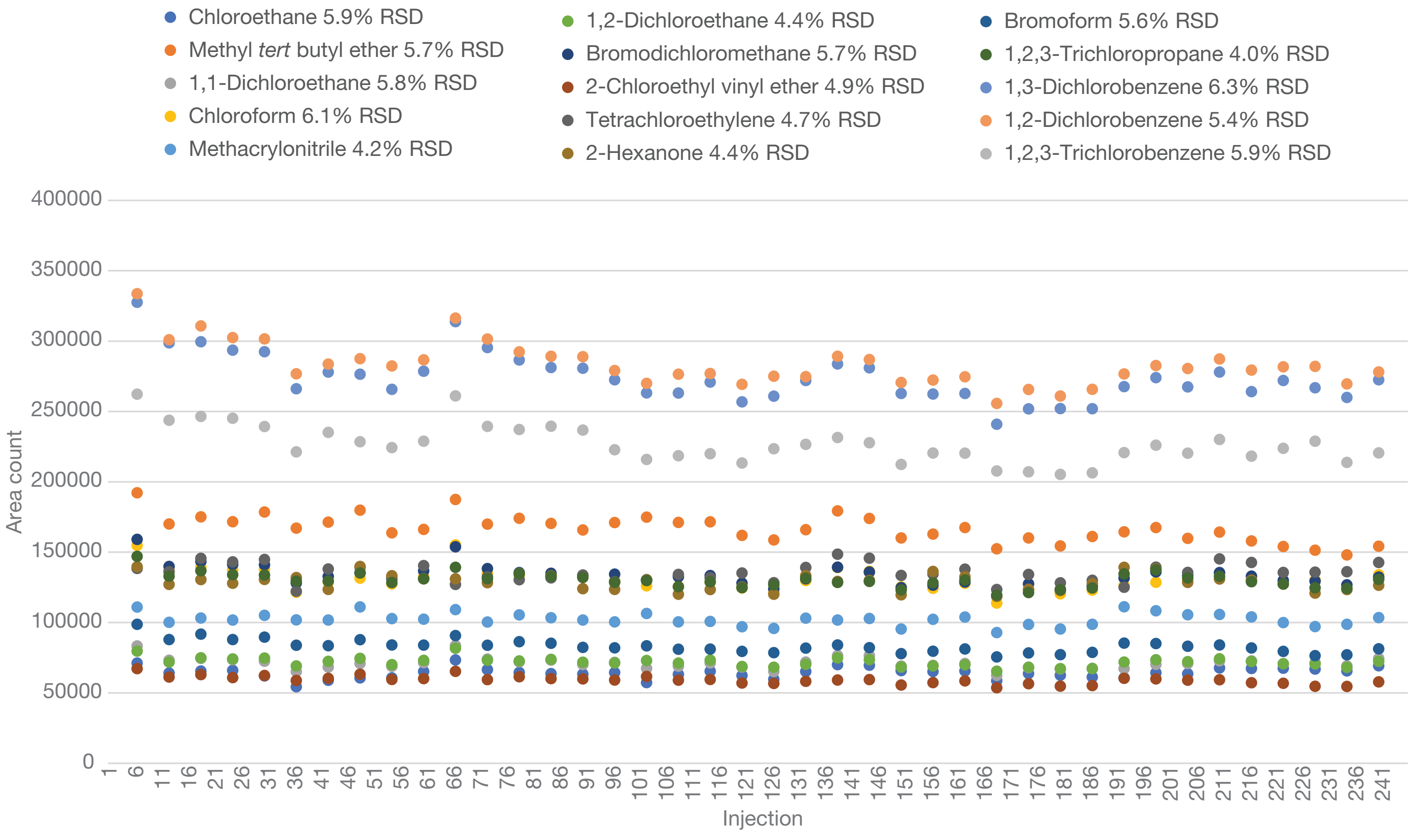

Figure 6. Repeatability (absolute peak area) of a 20 ppb water standard assessed over n=240 consecutive injections corresponding to 3 days of analysis (equivalent to 18 min/sample)

Conclusion

The combined analytical solution with the TRACE 1610 GC coupled with the ISQ 7610 system and the Atomx XYZ P&T system provides clear advantages for analytical testing laboratories that analyze environmental samples following the U.S. EPA Method 8260C requirements. The modularity of the TRACE 1610 GC as well as the ISQ 7610 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, significantly reducing instrument downtime and minimizing 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 GC column life span.

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

- The ISQ 7610 VPI coupled with the Tekmar Atomx XYZ P&T exceeds all the requirements outlined in U.S. EPA Method 8260C for analysis of VOCs in wastewater and solid waste.
- Linearity was achieved with <20% relative standard deviation for both water and soil calibration curves for the majority of compounds.
- The MDL and precision were assessed using n=7 replicates of a 0.2 ppb water standard and n=7 replicates of a 0.5 ppb soil standard. Calculated MDLs were <0.2 ppb and RSDs of calculated results were <10% for most compounds in both the soil and water matrices.
- 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%.

References

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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 I. Calibration, MDL, and IDC results for wastewater

Appendix 1, part 1

	Calibration (0.2 ppb–200 ppb)				Method detection limit (n=7, 0.2 ppb)		Mid-point check (n=7, 20 ppb)	
Compound	Retention time	Quant. ion	RRF (≤20% RSD r^2 ≥0.99)	Avg. RRF	MDL	Precision ≤20%	Precision ≤20%	Accuracy ±30%
Dichlorodifluoromethane	1.17	85	8.6	0.868	0.03	6.5	3.6	93
Chloromethane	1.32	50	5.4	1.37	0.07	6.9	4.1	85
Vinyl chloride	1.38	62	7.7	0.565	0.04	7.3	3.4	96
Bromomethane	1.63	94	6.2	0.622	0.04	7.7	0.8	88
Chloroethane	1.72	64	18.8	0.438	0.05	6.9	2.3	113
Trichlorofluoromethane	1.85	101	7.2	1.25	0.03	5.7	2.9	101
Diethyl ether	2.14	74	11.1	0.133	0.04	6.4	1.9	104
1,1-Dichloroethene[1]	2.28	61	0.999	0.082	0.11	7.8	2.6	121
1,1,2-Trichlorotrifluoroethane	2.33	101	5.3	0.191	0.06	11.2	2.6	100
Iodomethane[2]	2.38	142	11.5	0.156	0.06	8.9	9.0	40
Carbon disulfide	2.71	76	6.7	0.081	0.07	8.3	2.0	104
Acetonitrile	2.72	41	11.2	0.331	0.07	9.1	1.8	115
Allyl chloride	2.73	76	15.9	0.078	0.06	7.5	1.6	108
Methylene chloride	2.81	49	15.0	0.393	0.07	7.0	1.9	109
Acetone[3]	2.88	58	18.5	0.046	0.67	6.4	4.7	76
trans-1,2-dichloroethene	2.97	96	7.1	0.131	0.05	8.0	3.1	95
Methyl acetate	3.04	43	12.9	0.433	0.06	8.5	2.9	126
Methyl *tert* butyl ether	3.14	73	6.3	0.757	0.05	7.5	2.6	107
tert-Butyl alcohol[4]	3.34	59	15.1	0.039	0.32	8.6	6.4	129
Diisopropyl ether	3.59	45	6.4	1.25	0.02	3.5	3.0	111
1,1-Dichloroethane	3.61	63	6.7	0.321	0.03	5.0	3.3	105
Vinyl acetate	3.63	43	5.4	0.541	0.06	7.8	3.2	112
Acrylonitrile	3.69	53	7.3	0.141	0.08	11.4	2.4	108
Chloroprene	3.69	53	6.22	0.141	0.06	8.7	2.3	107
tert-Butyl ethyl ether	3.96	59	6.8	0.657	0.04	6.3	2.7	113
Ethyl acetate	3.97	88	12.8	0.021	0.10	16.4	3.4	95
cis-1,2-Dichloroethene	4.18	96	6.3	0.247	0.06	10.0	3.4	92
2,2-Dichloropropane	4.28	77	6.7	0.303	0.05	7.2	5.1	108
Bromochloromethane	4.37	128	6.5	0.118	0.05	7.9	2.1	96
Chloroform	4.48	83	6.5	0.630	0.04	6.2	2.8	100
Carbon tetrachloride	4.58	117	3.7	0.226	0.05	9.0	3.7	99
Tetrahydrofuran	4.62	42	9.4	0.249	0.06	10.5	8.8	102
Methyl acrylate	4.64	55	10.9	0.242	0.03	4.2	3.2	106
1,1,1-Trichloroethane	4.67	97	5.4	0.355	0.03	5.8	3.6	100
Dibromofluoromethane (surr)	4.66	111	5.1	0.427		4.9	1.7	107

[1] Compound used a linear calibration

[2] Calibration curve from 0.5–200 ppb

[3] Calibration curve from 2.5–500 ppb

[4] Calibration curve from 1–1000 ppb

[5] Calibration curve from 0.5–500 ppb

[6] Calibration curve from 0.4–400 ppb

[7] Calibration curve from 0.25–100 ppb

Appendix 1, part 2

	Calibration (0.2 ppb–200 ppb)				Method detection limit (n=7, 0.2 ppb)		Mid-point check (n=7, 20 ppb)	
Compound	Retention time	Quant. ion	RRF (≤20% RSD r^2 ≥0.99)	Avg. RRF	MDL	Precision ≤20%	Precision ≤20%	Accuracy ±30%
1,1-Dichloropropene	4.78	75	9.1	0.819	0.08	5.3	4.2	98
2-Butanone[2]	4.80	72	4.8	0.045	0.42	8.3	3.9	94
Benzene	5.03	78	5.1	2.38	0.05	3.1	3.7	98
Propionitrile	5.06	54	13.1	0.099	0.17	8.6	4.0	93
Methacrylonitrile	5.09	41	4.5	0.594	0.12	6.3	3.4	100
1,2-Dichloroethane-d_4 (surr)	5.16	65	12.2	0.140		3.3	1.4	104
Pentafluorobenzene (ISTD)	5.17	168						
tert-Amyl methyl ether	5.22	73	10.5	1.27	0.11	7.3	3.9	102
1,2-Dichloroethane	5.24	62	9.4	0.704	0.06	3.0	2.8	103
Isobutyl alcohol	5.40	43	7.6	0.058	0.18	14.0	5.7	93
Isopropyl acetate	5.58	43	6.9	1.56	0.07	4.8	2.6	102
Trichloroethene	5.62	95	9.0	1.45	0.09	6.0	2.7	103
1,4-Difluorobenzene (ISTD)	5.68	114						
Dibromomethane	6.03	93	9.4	0.388	0.04	2.3	2.8	96
1,2-Dichloropropane	6.15	63	5.1	0.626	0.08	5.3	3.2	101
Bromodichloromethane	6.23	83	6.1	0.812	0.05	3.3	2.8	101
Methyl methacrylate	6.45	69	10.3	0.343	0.12	7.8	3.2	92
Propyl acetate	6.62	43	8.2	1.25	0.10	6.0	2.8	97
2-Chloroethyl vinyl ether	6.87	63	11.3	0.272	0.05	3.8	2.7	100
cis-1,3-Dichloropropene	6.88	75	9.7	0.905	0.05	3.9	3.0	103
Toluene-d_8 (surr)	7.06	98	1.9	0.386		1.8	1.2	98
Toluene	7.12	92	4.5	1.28	0.07	4.9	4.4	93
2-Nitropropane	7.33	43	4.4	0.151	0.16	9.9	4.9	102
Tetrachloroethylene	7.49	164	5.4	0.675	0.08	5.0	4.7	93
4-Methyl-2-pentanone[2]	7.53	100	7.9	0.024	0.30	7.6	3.5	88
trans-1,3-Dichloropropene	7.55	75	9.4	0.552	0.06	4.5	3.5	102
1,1,2-Trichloroethane	7.69	83	9.1	0.319	0.08	5.3	3.6	101
Ethyl methacrylate	7.75	69	6.9	0.450	0.07	4.8	3.1	95
Dibromochloromethane	7.83	129	13.2	0.340	0.07	5.4	3.2	103
1,3-Dichloropropane	7.91	76	8.4	0.573	0.07	5.1	3.1	101
1,2-Dibromoethane	8.00	107	9.2	0.360	0.06	4.2	3.0	99
Butyl acetate	8.22	43	11.1	0.898	0.04	2.8	2.8	100
2-Hexanone[2]	8.26	43	13.1	0.202	0.16	3.1	3.2	88
Chlorobenzene-d_5 (ISTD)	8.45	117						

[1] Compound used a linear calibration

[2] Calibration curve from 0.5–200 ppb

[3] Calibration curve from 2.5–500 ppb

[4] Calibration curve from 1–1000 ppb

[5] Calibration curve from 0.5–500 ppb

[6] Calibration curve from 0.4–400 ppb

[7] Calibration curve from 0.25–100 ppb

Appendix 1, part 3

	Calibration (0.2 ppb–200 ppb)				Method detection limit (n=7, 0.2 ppb)		Mid-point check (n=7, 20 ppb)	
Compound	Retention time	Quant. ion	RRF (≤20% RSD r^2 ≥0.99)	Avg. RRF	MDL	Precision ≤20%	Precision ≤20%	Accuracy ±30%
Chlorobenzene	8.46	112	5.0	1.33	0.05	2.9	3.5	95
Ethylbenzene	8.51	91	7.2	2.33	0.06	3.5	4.3	96
1,1,1,2-Tetrachloroethane	8.52	131	16.0	0.347	0.10	7.5	4.0	101
m,p-Xylene[4]	8.63	106	9.3	0.947	0.12	3.9	4.1	98
o-Xylene	8.95	106	6.2	0.919	0.04	2.9	3.6	99
Bromoform	8.98	173	17.2	0.224	0.06	5.1	3.7	99
Styrene	8.99	104	4.3	1.46	0.05	3.1	3.3	98
Isopropylbenzene	9.19	105	8.8	2.25	0.08	5.7	4.2	102
Amyl acetate[1]	9.31	43	0.997	0.766	0.04	4.1	3.9	79
4-Bromofluorobenzene (surr)	9.37	95	3.4	0.892		1.1	1.8	101
cis-1,4-Dichloro-2-butene	9.44	75	6.3	0.567	0.12	6.2	3.0	102
Bromobenzene	9.44	156	3.8	0.830	0.04	2.5	4.5	96
n-Propylbenzene	9.49	91	15.1	4.64	0.06	4.0	6.4	100
1,1,2,2-Tetrachloroethane	9.55	83	5.9	0.434	0.08	4.6	4.7	108
2-Chlorotoluene	9.58	91	6.0	2.69	0.05	3.2	5.7	102
1,2,3-Trichloropropane	9.62	75	4.1	0.606	0.04	2.3	4.9	96
1,3,5-Trimethylbenzene	9.64	105	5.3	3.03	0.12	7.8	6.8	97
trans-1,4-Dichloro-2-butene	9.66	53	6.2	0.288	0.06	4.3	4.8	102
4-Chlorotoluene	9.71	91	5.1	2.84	0.05	3.3	5.7	100
tert-Butylbenzene	9.85	119	7.5	2.56	0.11	7.8	6.0	105
Pentachloroethane	9.85	77	8.1	0.281	0.13	8.6	6.8	106
1,2,4-Trimethylbenzene	9.90	105	7.9	3.08	0.09	5.7	5.8	96
sec-Butylbenzene	9.98	105	8.7	3.97	0.09	6.4	5.9	104
p-Isopropyltoluene	10.08	119	6.5	3.18	0.09	5.9	6.6	102
1,3-Dichlorobenzene	10.11	146	4.2	1.66	0.06	3.3	5.1	97
1,4-Dichlorobenzene-d_4 (ISTD)	10.16	152						
1,4-Dichlorobenzene	10.17	146	8.2	1.72	0.07	3.7	5.3	96
n-Butylbenzene	10.36	91	10.5	3.45	0.06	4.0	6.8	102
Hexachloroethane[5]	10.44	117	17.5	0.842	0.05	7.0	5.9	92
1,2-Dichlorobenzene	10.45	146	5.5	1.50	0.05	3.2	4.6	100
1,2-Dibromo-3-chloropropane	10.99	157	9.7	0.146	0.07	5.5	6.0	97
Nitrobenzene[6]	11.36	123	6.0	0.026	0.35	13.4	5.8	93
Hexachlorobutadiene	11.43	225	9.0	0.470	0.07	4.5	6.9	104
1,2,4-Trichlorobenzene	11.45	180	18.7	1.19	0.10	5.5	6.0	95
Naphthalene[6]	11.66	128	11.1	2.74	0.12	5.8	4.4	105
1,2,3-Trichlorobenzene	11.78	180	18.0	1.13	0.11	6.1	4.6	95

[1] Compound used a linear calibration

[2] Calibration curve from 0.5–200 ppb

[3] Calibration curve from 2.5–500 ppb

[4] Calibration curve from 1–1000 ppb

[5] Calibration curve from 0.5–500 ppb

[6] Calibration curve from 0.4–400 ppb

[7] Calibration curve from 0.25–100 ppb

Appendix II. Calibration, MDL, and IDC results for solid waste

Appendix 2, part 1

	Calibration (0.5 ppb–200 ppb)				Method detection limit (n=7, 0.5 ppb)		Mid-point check (n=7, 20 ppb)	
Compound	Retention time	Quant. ion	RRF (≤20% RSD r^2 ≥0.99)	Avg. RRF	MDL	Precision ≤20%	Precision ≤20%	Accuracy ±30%
Dichlorodifluoromethane	1.17	85	13.5	1.40	0.05	3.2	4.2	94
Chloromethane	1.31	50	13.4	2.66	0.16	7.2	3.4	87
Vinyl chloride	1.36	62	11.2	1.38	0.07	4.3	3.8	94
Bromomethane[1]	1.61	94	0.999	1.32	0.17	5.2	1.9	108
Chloroethane	1.71	64	8.6	0.868	0.10	5.6	3.8	76
Trichlorofluoromethane	1.84	101	13.2	1.96	0.05	3.1	3.7	100
Diethyl ether	2.14	74	7.0	0.684	0.07	3.8	2.4	105
1,1-Dichloroethene	2.27	61	15.0	1.81	0.11	5.2	3.2	97
1,1,2-Trichlorotrifluoroethane	2.33	101	13.8	1.30	0.06	3.8	3.5	102
Iodomethane[1]	2.38	142	0.998	1.10	0.02	5.5	6.9	95
Carbon disulfide	2.70	41	12.2	3.68	0.11	5.6	3.2	101
Acetonitrile	2.71	76	12.0	0.764	0.11	5.8	3.1	99
Allyl chloride	2.71	76	13.3	0.768	0.11	5.7	3.2	98
Methylene chloride[1]	2.81	49	0.999	2.80	0.14	4.3	2.6	121
Acetone[1,2]	2.90	58	0.997	0.138	2.32	6.4	3.1	128
trans-1,2-dichloroethene	2.99	96	10.3	1.51	0.09	4.7	3.2	96
Methyl acetate[1]	3.05	43	0.999	1.81	0.12	5.2	2.6	110
Methyl *tert* butyl ether	3.15	73	6.0	1.41	0.09	5.7	3.3	111
tert-Butyl alcohol[3]	3.35	59	14.0	0.087	0.43	3.8	3.6	91
Diisopropyl ether	3.59	45	10.2	3.00	0.06	3.9	3.1	103
1,1-Dichloroethane	3.59	43	10.5	1.32	0.08	5.0	3.3	105
Vinyl acetate	3.60	53	12.0	0.962	0.08	5.4	4.8	104
Acrylonitrile	3.62	63	11.0	1.26	0.08	4.5	4.0	100
Chloroprene	3.67	53	11.5	0.253	0.12	6.2	3.0	98
tert-Butyl ethyl ether	3.96	88	16.7	0.038	0.19	15.3	3.1	104
Ethyl acetate	3.97	59	13.1	1.55	0.09	6.8	3.6	101
cis-1,2-Dichloroethene	4.18	96	8.5	0.796	0.08	4.6	3.9	94
2,2-Dichloropropane	4.28	77	9.8	0.869	0.07	4.5	4.2	98
Bromochloromethane	4.37	128	11.0	0.327	0.08	4.3	3.7	95
Chloroform	4.48	83	10.4	1.23	0.08	4.1	3.7	97
Carbon tetrachloride	4.58	117	13.9	0.786	0.09	6.8	4.0	99
Tetrahydrofuran	4.65	42	4.7	0.518	0.06	4.0	6.5	95
Methyl acrylate	4.65	55	9.3	0.452	0.05	3.3	2.7	97
1,1,1-Trichloroethane	4.65	97	9.9	0.975	0.04	2.9	4.8	99
Dibromofluoromethane (surr)	4.66	111	5.1	0.427		4.9	1.7	107

[1] Compound used linear calibration

[2] Calibration from 1.25–500 ppb

[3] Calibration from 2.5–1000 ppb

[4] Calibration from 1–400 ppb

[5] Calibration from 0.25–100 ppb

[6] Calibration from 1–200 ppb

Appendix 2, part 2

Compound	Calibration (0.5 ppb–200 ppb)				Method detection limit (n=7, 0.5 ppb)		Mid-point check (n=7, 20 ppb)	
	Retention time	Quant. ion	RRF (≤20% RSD r^2 ≥0.99)	Avg. RRF	MDL	Precision ≤20%	Precision ≤20%	Accuracy ±30%
1,1-Dichloropropene	4.78	75	9.1	0.819	0.08	5.3	4.2	98
2-Butanone[2]	4.80	72	4.8	0.045	0.42	8.3	3.9	94
Benzene	5.03	78	5.1	2.38	0.05	3.1	3.7	98
Propionitrile	5.06	54	13.1	0.099	0.17	8.6	4.0	93
Methacrylonitrile	5.09	41	4.5	0.594	0.12	6.3	3.4	100
1,2-Dichloroethane-d$_4$ (surr)	5.16	65	12.2	0.140		3.3	1.4	104
Pentafluorobenzene (ISTD)	5.17	168						
tert-Amyl methyl ether	5.22	73	10.5	1.27	0.11	7.3	3.9	102
1,2-Dichloroethane	5.24	62	9.4	0.704	0.06	3.0	2.8	103
Isobutyl alcohol	5.40	43	7.6	0.058	0.18	14.0	5.7	93
Isopropyl acetate	5.58	43	6.9	1.56	0.07	4.8	2.6	102
Trichloroethene	5.62	95	9.0	1.45	0.09	6.0	2.7	103
1,4-Difluorobenzene (ISTD)	5.68	114						
Dibromomethane	6.03	93	9.4	0.388	0.04	2.3	2.8	96
1,2-Dichloropropane	6.15	63	5.1	0.626	0.08	5.3	3.2	101
Bromodichloromethane	6.23	83	6.1	0.812	0.05	3.3	2.8	101
Methyl methacrylate	6.45	69	10.3	0.343	0.12	7.8	3.2	92
Propyl acetate	6.62	43	8.2	1.25	0.10	6.0	2.8	97
2-Chloroethyl vinyl ether	6.87	63	11.3	0.272	0.05	3.8	2.7	100
cis-1,3-Dichloropropene	6.88	75	9.7	0.905	0.05	3.9	3.0	103
Toluene-d$_8$ (surr)	7.06	98	1.9	0.386		1.8	1.2	98
Toluene	7.12	92	4.5	1.28	0.07	4.9	4.4	93
2-Nitropropane	7.33	43	4.4	0.151	0.16	9.9	4.9	102
Tetrachloroethylene	7.49	164	5.4	0.675	0.08	5.0	4.7	93
4-Methyl-2-pentanone[2]	7.53	100	7.9	0.024	0.30	7.6	3.5	88
trans-1,3-Dichloropropene	7.55	75	9.4	0.552	0.06	4.5	3.5	102
1,1,2-Trichloroethane	7.69	83	9.1	0.319	0.08	5.3	3.6	101
Ethyl methacrylate	7.75	69	6.9	0.450	0.07	4.8	3.1	95
Dibromochloromethane	7.83	129	13.2	0.340	0.07	5.4	3.2	103
1,3-Dichloropropane	7.91	76	8.4	0.573	0.07	5.1	3.1	101
1,2-Dibromoethane	8.00	107	9.2	0.360	0.06	4.2	3.0	99
Butyl acetate	8.22	43	11.1	0.898	0.04	2.8	2.8	100
2-Hexanone[2]	8.26	43	13.1	0.202	0.16	3.1	3.2	88
Chlorobenzene-d$_5$ (ISTD)	8.45	117						
Chlorobenzene	8.46	112	5.0	1.33	0.05	2.9	3.5	95
Ethylbenzene	8.51	91	7.2	2.33	0.06	3.5	4.3	96
1,1,1,2-Tetrachloroethane	8.52	131	16.0	0.347	0.10	7.5	4.0	101
m,p-Xylene[4]	8.63	106	9.3	0.947	0.12	3.9	4.1	98
o-Xylene	8.95	106	6.2	0.919	0.04	2.9	3.6	99
Bromoform	8.98	173	17.2	0.224	0.06	5.1	3.7	99

[1] Compound used linear calibration

[2] Calibration from 1.25–500 ppb

[3] Calibration from 2.5–1000 ppb

[4] Calibration from 1–400 ppb

[5] Calibration from 0.25–100 ppb

[6] Calibration from 1–200 ppb

Appendix 2, part 3

Compound	Calibration (0.5 ppb–200 ppb)				Method detection limit (n=7, 0.5 ppb)		Mid-point check (n=7, 20 ppb)	
	Retention time	Quant. ion	RRF (≤20% RSD r^2 ≥0.99)	Avg. RRF	MDL	Precision ≤20%	Precision ≤20%	Accuracy ±30%
Styrene	8.99	104	4.3	1.46	0.05	3.1	3.3	98
Isopropylbenzene	9.19	105	8.8	2.25	0.08	5.7	4.2	102
Amyl acetate[1]	9.31	43	0.997	0.766	0.04	4.1	3.9	79
4-Bromofluorobenzene (surr)	9.37	95	3.4	0.892		1.1	1.8	101
cis-1,4-Dichloro-2-butene	9.44	75	6.3	0.567	0.12	6.2	3.0	102
Bromobenzene	9.44	156	3.8	0.830	0.04	2.5	4.5	96
n-Propylbenzene	9.49	91	15.1	4.64	0.06	4.0	6.4	100
1,1,2,2-Tetrachloroethane	9.55	83	5.9	0.434	0.08	4.6	4.7	108
2-Chlorotoluene	9.58	91	6.0	2.69	0.05	3.2	5.7	102
1,2,3-Trichloropropane	9.62	75	4.1	0.606	0.04	2.3	4.9	96
1,3,5-Trimethylbenzene	9.64	105	5.3	3.03	0.12	7.8	6.8	97
trans-1,4-Dichloro-2-butene	9.66	53	6.2	0.288	0.06	4.3	4.8	102
4-Chlorotoluene	9.71	91	5.1	2.84	0.05	3.3	5.7	100
tert-Butylbenzene	9.85	119	7.5	2.56	0.11	7.8	6.0	105
Pentachloroethane	9.85	77	8.1	0.281	0.13	8.6	6.8	106
1,2,4-Trimethylbenzene	9.90	105	7.9	3.08	0.09	5.7	5.8	96
sec-Butylbenzene	9.98	105	8.7	3.97	0.09	6.4	5.9	104
p-Isopropyltoluene	10.08	119	6.5	3.18	0.09	5.9	6.6	102
1,3-Dichlorobenzene	10.11	146	4.2	1.66	0.06	3.3	5.1	97
1,4-Dichlorobenzene-d_4 (ISTD)	10.16	152						
1,4-Dichlorobenzene	10.17	146	8.2	1.72	0.07	3.7	5.3	96
n-Butylbenzene	10.36	91	10.5	3.45	0.06	4.0	6.8	102
Hexachloroethane[5]	10.44	117	17.5	0.842	0.05	7.0	5.9	92
1,2-Dichlorobenzene	10.45	146	5.5	1.50	0.05	3.2	4.6	100
1,2-Dibromo-3-chloropropane	10.99	157	9.7	0.146	0.07	5.5	6.0	97
Nitrobenzene[6]	11.36	123	6.0	0.026	0.35	13.4	5.8	93
Hexachlorobutadiene	11.43	225	9.0	0.470	0.07	4.5	6.9	104
1,2,4-Trichlorobenzene	11.45	180	18.7	1.19	0.10	5.5	6.0	95
Naphthalene[6]	11.66	128	11.1	2.74	0.12	5.8	4.4	105
1,2,3-Trichlorobenzene	11.78	180	18.0	1.13	0.11	6.1	4.6	95

[1] Compound used linear calibration

[2] Calibration from 1.25–500 ppb

[3] Calibration from 2.5–1000 ppb

[4] Calibration from 1–400 ppb

[5] Calibration from 0.25–100 ppb

[6] Calibration from 1–200 ppb

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Environmental

Trace analysis of volatile organic compounds in wastewater according to U.S. EPA Method 624.1

Authors

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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 lab

Goal

Demonstration of an analytical method that meets the requirements outlined in U.S. EPA Method 624.1 for the quantitation of volatile organic compounds (VOCs) in wastewater, using the Teledyne LABS Tekmar Lumin Purge and Trap (P&T) concentrator paired with the AQUATek LVA autosampler system along with a Thermo Scientific™ ISQ™ 7610 mass spectrometry (MS) system coupled with a Thermo Scientific™ TRACE™ 1610 gas chromatograph (GC) and Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS). Method linearity, method detection limit (MDL), precision, and mid-point calibration check were assessed to evaluate method performance.

Introduction

It is crucial that analytical testing laboratories monitor wastewater for the presence of volatile organic compounds (VOCs). VOCs are human-made contaminants used and produced in the processing of paints, adhesives, petroleum products, pharmaceuticals, and refrigerants. If they are released into wastewater from industrial activities, they can have an adverse effect on the natural environment and, ultimately, the public.[1] U.S. EPA Method 624.1 is an approved test method under the Clean Water Act[2] for determination of purgeable organic pollutants in industrial discharges and other environmental samples. The accurate detection and quantitation of VOCs via this method help ensure wastewater is not contaminated. Due to technological advances in analytical instrumentation and techniques, U.S. EPA Method 624.1 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 U.S. EPA Method 624.1, method acceptance criteria must be achieved. These criteria include creating a working calibration curve, method detection limits (MDLs), and Initial Demonstration of Capability (IDC) of accuracy and precision for target compounds. As the sample matrix is water, it is essential that moisture is reduced, limiting the impact on the analytical column as this could damage the column and affect the results.

The following evaluation describes the use of the ISQ 7610 GC-MS system coupled with a TRACE 1610 GC equipped with the Thermo Scientific™ HeSaver-H_2Safer™ split/splitless injector and a Teledyne LABS Tekmar Lumin P&T concentrator paired with the AQUATek LVA autosampler for U.S. EPA Method 624.1 for the analysis of wastewater.

Experimental

Sample preparation

A working 50 ppm calibration standard was prepared in methanol from Restek™ standards: 624.1 Calibration Mix #1 Gases (P/N 30020) and Volatiles MegaMix™ Standard, EPA Method 624.1 (P/N 30497). In total, the standard contained 31 compounds.

The seven-point calibration curve was prepared from 0.5 ppb to 100 ppb for all compounds. The relative response factor (RF) 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 (624.1 Internal Standard Mix, P/N 30023 and 624.1 Surrogate Standard Mix, P/N 30243) at a concentration of 25 ppm, after which 5 µL was mixed with each 5 mL sample for a resulting concentration of 25 ppb.

Seven 0.5 ppb standards were prepared for MDLs and precision calculations. Also, seven 20 ppb standards were prepared for the mid-point calibration check precision and accuracy calculations. All calibration, MDL, and mid-point calibration check samples were analyzed with the Teledyne LABS Tekmar Lumin P&T concentrator paired with the AQUATek LVA autosampler using the parameters described in Table 1.

Table 1. Tekmar Lumin P&T concentrator and AQUATek LVA autosampler parameters

Standby	Variable
Valve oven temp.	140 °C
Transfer line temp.	140 °C
Sample mount temp.	90 °C
Purge ready temp.	35 °C
MCS purge temp.	20 °C
Standby flow	10 mL/min
Purge	**Variable**
Purge temp.	20 °C
Purge time	8.00 min
Purge flow	50 mL/min
Dry purge temp.	20 °C
Dry purge time	1.0 min
Dry purge flow	100 mL/min
Sparge vessel heater	Off
Desorb	**Variable**
Desorb preheat temp.	245 °C
Desorb temp.	250 °C
Desorb time	1.00 min
Desorb flow	300 mL/min
GC start signal	Start_Only
Bake	**Variable**
Bake time	3.00 min
Trap bake temp.	270 °C
MCS bake temp.	180 °C
Bake flow	200 mL/min
AQUATek LVA	**Variable**
Sample loop time	0.35 min
Sample transfer time	0.35 min
Rinse loop time	0.30 min
Sweek needle time	0.30 min
Presweep time	0.25 min
Water temperature	90 °C
Bake rinse cycles	1
Bake rinse drain time	0.35 min
Trap	9
Chiller tray	Off
Purge gas	Nitrogen

GC-MS parameters

A TRACE 1610 GC was coupled to the ISQ 7610 MS equipped with a Thermo Scientific™ NeverVent™ vacuum probe interlock (VPI) and a Thermo Scientific™ ExtractaBrite™ ion source. A Thermo Scientific™ TraceGOLD™ TG-VMS, 30 m × 0.25 mm, 1.4 µm film column (P/N 26080-3320) was used for compound separation. The HeSaver-H_2Safer injector was utilized which reduces the carrier gas consumption by decoupling the gas used for the chromatographic separation from the gas used to pressurize the inlet and maintain split and purge flows. The critical separations were maintained with a run time of under 13 minutes.

For this analysis, the ISQ 7610 MS was operated in full scan mode, ensuring the sensitivity needed for required the method detection limits. Nevertheless, the instrument could operate in Selected Ion Monitoring (SIM) mode for increased selectivity, if needed. Extended method parameters for the ISQ 7610 MS are shown in Table 2.

Table 2. GC-MS conditions

TRACE 1610 GC conditions	
Column	TraceGOLD TG-VMS, 30 m × 0.25 mm, 1.4 µm film (P/N 26080-3320)
Carrier gas	Helium, 1.5 mL/min
Oven profile	35 °C, 2 min; 15 °C/min to 100 °C; 30 °C /min to 225 °C; 2 min hold; run time 12.5 min
HeSaver H_2Safer SSL	200 °C, 30:1 Split, purge flow 5.0 mL/min, 0.30 min helium delay
ISQ 7610 MS conditions	
Temp.	Transfer line 230 °C; ion source 280 °C
Scan range	35 amu to 260 amu
Solvent delay	1.54 min
Dwell/scan time	0.10 s
Emission current	25 µA
Gain	3.00E+005

Instrument control and data processing

Data were acquired, processed, and reported using Chromeleon CDS software, version 7.3. This software can control both the GC-MS system and the Tekmar Lumin P&T and AQUATek LVA. This allows a single software to be utilized for the full workflow, simplifying the instrument operation.

This application note is available for download via Thermo Scientific™ AppsLab library. The AppsLab library contains all the parameters needed to acquire, process, and report the analytical data for U.S. EPA Method 624.1.[3]

Results and discussion

Chromatography

Using the parameters described in Table 2, excellent chromatography was achieved. The Tekmar Lumin P&T reduced the moisture transferred onto the analytical column, thus limiting any damage to the analytical column and increasing system robustness. Figure 1 displays consistent peak shape and separation of a 20 ppb VOC standard with minimal water interference.

Linearity and sensitivity

A calibration range of 0.5–100 ppb was evaluated for all compounds. Calibration curves were used to calculate the response factor's average and relative standard deviation (%RSD), aiming for a %RSD of <20 to meet U.S. EPA Method 624.1 criteria. The XLXR™ detection system of the ISQ 7610 mass spectrometer, with its extended linear dynamic range

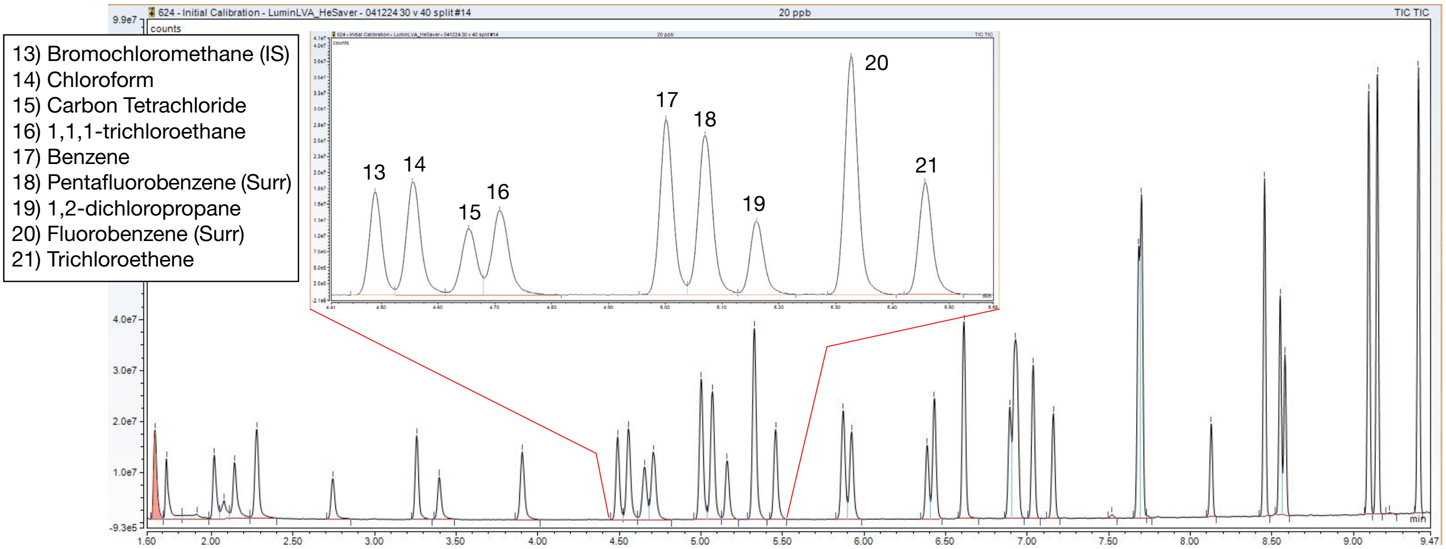


Figure 1. Total ion chromatogram (TIC) of a 20 ppb VOC standard with an inset indicating consistent peak shapes and separation with minimal water interference

and lifespan, enabled extended calibration curves and reduce replacement needs. The MDL was assessed using seven replicates of specific standard levels. The results and precision data are displayed in Appendix Table A1. To ensure data quality, initial and continuing calibration checks were performed, with the mid-point check results also shown in Appendix Table A2. The midpoint check criteria required a %RSD of <20 and accuracy within 80–120%. Figure 2 illustrates excellent library spectral matching and calibration curve for 1-chloromethane quantitation in the 2 ppb standard.

Method robustness

For use as a routine testing method, it is extremely important that the analytical method is stable and reproducible. To demonstrate this, 20 ppb standards (n=34) in water were injected at intervals over a 209-sample injection sequence over 3 days. The samples were acquired with no user intervention at all on the P&T, GC, or MS system and their concentrations were plotted to demonstrate the stability of the results. Figure 3 shows the reproducibility of nine of the compounds over 209 injections with excellent percentage RSDs. The accuracy and precision for all the compounds in the 209-injection series are shown in Appendix Table A2.

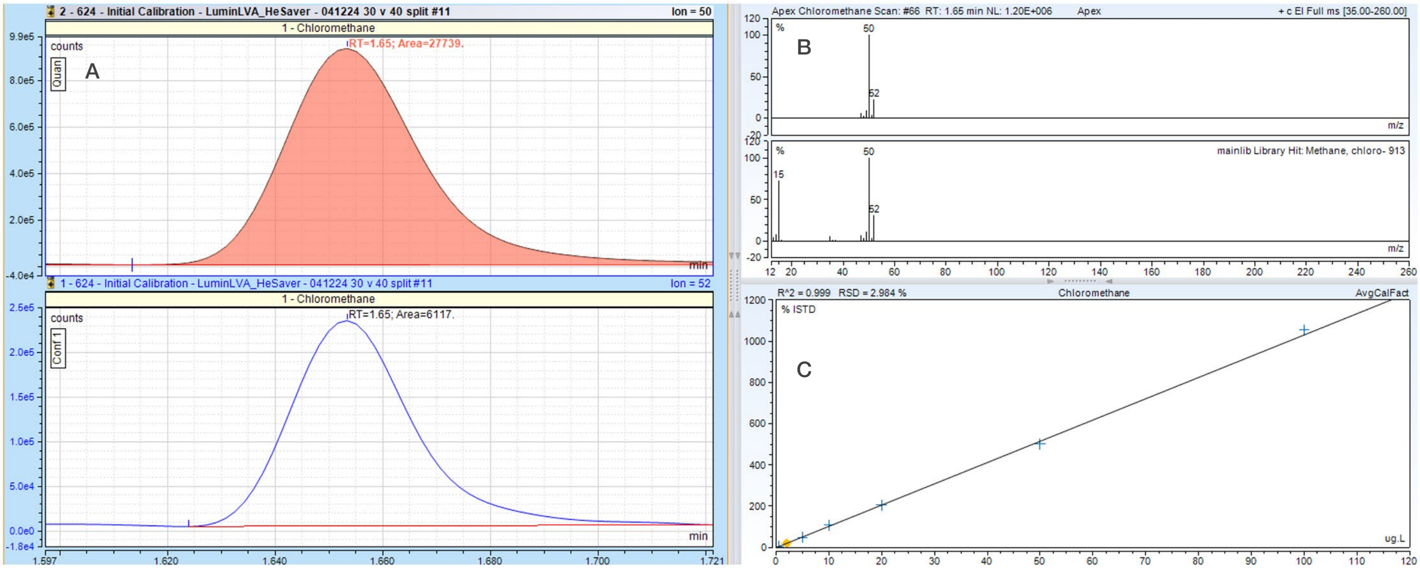


Figure 2. Chromeleon CDS results browser showing extracted ion chromatograms for 1-chloromethane in the 2 ppb standard, quantitation ion (50), and one confirming ion (52) (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 0.5 ppb to 100 ppb (C)

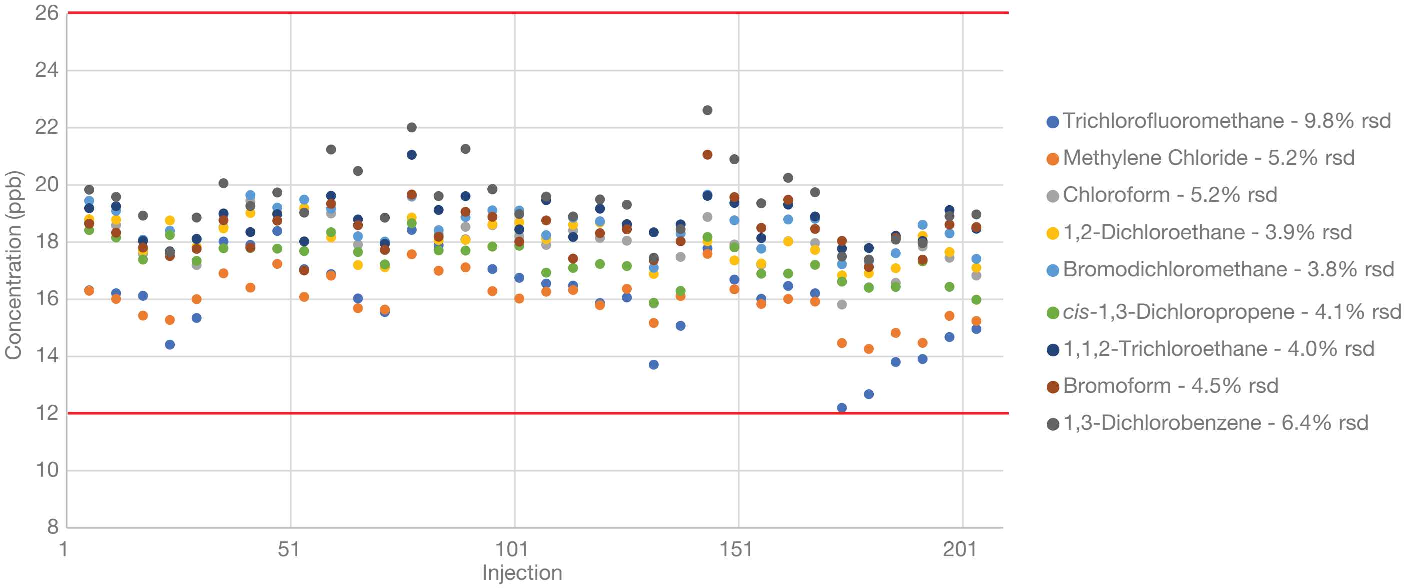
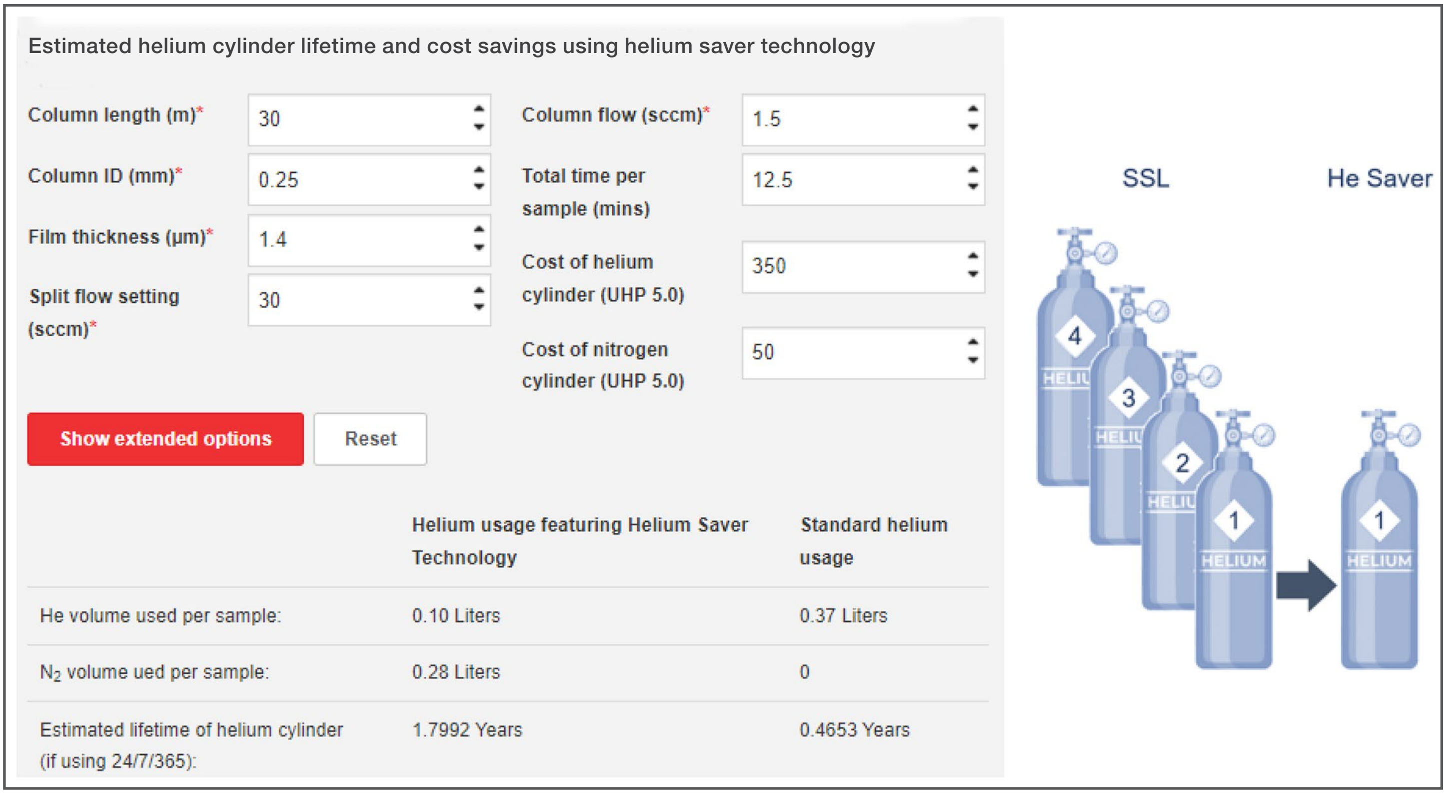


Figure 3. Reproducibility of nine compounds in 20 ppb water standards (n=34) over 209 sample injections



Estimated helium cylinder lifetime and cost savings using helium saver technology

Column length (m)*	30	Column flow (sccm)*	1.5
Column ID (mm)*	0.25	Total time per sample (mins)	12.5
Film thickness (µm)*	1.4	Cost of helium cylinder (UHP 5.0)	350
Split flow setting (sccm)*	30	Cost of nitrogen cylinder (UHP 5.0)	50

	Helium usage featuring Helium Saver Technology	Standard helium usage
He volume used per sample:	0.10 Liters	0.37 Liters
N_2 volume ued per sample:	0.28 Liters	0
Estimated lifetime of helium cylinder (if using 24/7/365):	1.7992 Years	0.4653 Years

Figure 4. Helium Saver Calculator tool showing 4× savings of carrier gas

Reduced helium consumption and cost savings

The HeSaver-H_2Safer technology significantly extends helium cylinder lifetimes and offers substantial gas savings during idle periods and sample injection/analysis. Users can estimate its impact on helium consumption, cost, and cylinder lifetime using the Thermo Scientific™ Gas Saver Calculator tool.[4] By using this technology for U.S. EPA Method 624.1 analysis, the helium cylinder lifespan can potentially quadruple compared to a standard SSL injector, making it a prime choice for helium conservation (Figure 4).

Conclusion

The ISQ 7610 MS system with the VPI coupled with the Teledyne LABS Tekmar Lumin P&T concentrator paired with the AQUATek LVA autosampler exceeds all the requirements outlined in U.S. EPA Method 624.1 for analysis of VOCs in wastewater:

- MDLs calculated from n=7 repeat injections of 0.5 ppb water standards showed no interference from unwanted water entering the system and resulted in values <0.15 ppb for most compounds.
- Precision and accuracy for n=7 20 ppb water standards showed excellent results with %RSD <20% and mean recovery of 93% for the compounds.
- System robustness was tested by continuously acquiring 209 injections of water samples over two days with no user intervention at all. The average %RSD of the calculated concentration was 6.5% over this robustness study.
- Utilizing the HeSaver-H_2Safer technology reduced helium consumption for the method by 4 times, reducing laboratory overheads.

Further information on VOC analysis using the ISQ 7610 system and the Tekmar Lumin P&T paired with the AQUATek LVA can be found in the Thermo Fisher Scientific AppsLab library.[3]

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Appendix

Table A1. Full details for calibration curves, method detection limits, and mid-point check

	Calibration				Method detection limit (n=7, 0.5 ppb)		Mid-point check (n=7, 20 ppb)	
Compound	**Retention Time**	**Quant ion**	**Relative SD (%RSD)**	**Average RF**	**MDL (ppb)**	**Precision (≤20%)**	**Precision (≤20%)**	**Accuracy (±20%)**
Chloromethane	1.65	50	2.98	2.58	0.07	4.67	4.43	93
Vinyl chloride	1.72	62	5.97	1.43	0.05	3.00	3.95	86
Bromomethane	2.01	94	5.38	1.09	0.11	6.70	2.62	88
Chloroethane	2.14	64	5.47	1.23	0.13	9.25	2.68	81
Trichlorofluoromethane	2.27	101	4.91	2.05	0.08	5.36	3.80	88
1,1-Dichloroethene	2.74	61	4.24	0.699	0.11	7.58	4.20	87
Methylene chloride	3.25	84	6.91	0.830	0.12	7.53	2.67	87
trans-1,2-Dichloroethene	3.39	61	6.68	0.689	0.13	8.48	3.87	88
1,1-Dichloroethane	3.9	63	5.96	1.94	0.09	5.67	1.76	91
Bromochloromethane (ISTD)	4.48	49						
Chloroform	4.55	83	9.59	1.23	0.06	3.52	1.75	92
Carbon tetrachloride	4.65	117	7.68	0.613	0.07	4.28	2.75	91
1,1,1-Trichloroethane	4.7	97	9.24	0.857	0.12	7.06	2.2	92
Benzene	4.99	78	7.58	2.01	0.05	3.28	2.05	92
Pentafluorobenzene (surr)	5.06	168	3.13	2.36		1.32	1.40	100
1,2-Dichloroethane	5.16	62	10.0	0.774	0.06	3.49	1.24	92
Fluorobenzene (surr)	5.32	96	6.42	2.33		1.31	1.47	99
Trichloroethene	5.45	130	10.3	0.546	0.10	5.54	1.54	94
1,2-Dichloropropane	5.87	63	8.28	0.728	0.08	5.12	1.73	91
Bromodichloromethane	5.92	83	7.40	0.952	0.05	2.96	1.57	94
2-Chloroethyl vinyl ether	6.38	63	7.52	0.469	0.10	6.62	1.59	93
Toluene	6.61	91	11.1	2.26	0.09	5.75	2.07	90
Tetrachloroethene	6.89	164	10.7	0.461	0.10	6.01	2.33	91
cis-1,3-Dichloropropene	6.91	75	8.17	1.07	0.09	3.21	1.48	93
2-Bromo-1-chloropropane (ISTD)	6.92	77						
1,1,2-Trichloroethane	7.03	97	4.11	0.566	0.06	3.85	1.61	94
Dibromochloromethane	7.15	127	6.86	0.468	0.04	2.63	1.99	94
Chlorobenzene	7.68	112	6.28	1.38	0.06	3.68	3.03	94
trans-1,3-Dichloropropene	7.68	77	5.89	1.05	0.06	3.53	3.35	92
Ethylbenzene	7.69	106	6.22	0.735	0.05	3.45	3.91	96
Bromoform	8.12	173	9.32	0.504	0.08	5.66	2.19	95
4-Bromofluorobenzene (surr)	8.45	95	1.21	0.828		0.78	1.06	103
1,4-Dichlorobutane (ISTD)	8.55	55						
1,1,2,2-Tetrachloroethane	8.58	83	3.91	0.809	0.08	5.86	1.71	91
1,3-Dichlorobenzene	9.09	146	4.20	1.78	0.06	3.45	2.72	100
1,4-Dichlorobenzene	9.14	146	4.66	1.84	0.07	3.97	2.89	100
1,2-Dichlorobenzene	9.39	146	4.97	1.82	0.05	2.87	2.71	102

Table A2. Reproducibility of compounds in 20 ppb water standards (n=34) over 209-sample injections

Compound	Analyte recovery (20 ppb n=34, 209 injections)	
	Precision (≤20%RSD)	Accuracy (±30%)
Chloromethane	11.6	78
Vinyl chloride	10.6	76
Bromomethane	9.06	72
Chloroethane	9.27	74
Trichlorofluoromethane	9.83	80
1,1-Dichloroethene	9.31	79
Methylene chloride	5.20	80
trans-1,2-Dichloroethene	7.97	79
1,1-Dichloroethane	5.86	85
Bromochloromethane (ISTD)		
Chloroform	5.16	90
Carbon tetrachloride	8.64	86
1,1,1-Trichloroethane	7.46	88
Benzene	6.69	85
Pentafluorobenzene (surr)	6.70	94
1,2-Dichloroethane	3.93	90
Fluorobenzene (surr)	3.98	96
Trichloroethene	6.25	99
1,2-Dichloropropane	4.79	90
Bromodichloromethane	3.84	93
2-Chloroethyl vinyl ether	3.51	89
Toluene	6.37	83
Tetrachloroethene	8.30	82
cis-1,3-Dichloropropene	4.11	87
2-Bromo-1-chloropropane (ISTD)		
1,1,2-Trichloroethane	3.95	94
Dibromochloromethane	4.43	94
Chlorobenzene	5.99	90
trans-1,3-Dichloropropene	5.82	91
Ethylbenzene	7.86	91
Bromoform	4.52	92
4-Bromofluorobenzene (surr)	3.13	106
1,4-Dichlorobutane (ISTD)		
1,1,2,2-Tetrachloroethane	7.05	77
1,3-Dichlorobenzene	6.36	97
1,4-Dichlorobenzene	6.65	98
1,2-Dichlorobenzene	5.96	99

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Improvements for the analysis of volatile (VOC) and very volatile (VVOC) organic compounds using In-Tube Extraction-Dynamic Headspace (ITEX-DHS) and cryogen-free refocusing

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Keywords
VOC, VVOC, water, dynamic headspace, ITEX-DHS, refocusing, PTV, TRACE 1610 GC, TriPlus RSH SMART autosampler

Goal

To demonstrate how the technological development of dynamic headspace extraction/enrichment techniques, such as ITEX-DHS (In-Tube Extraction-Dynamic Headspace) coupled to a cryogen-free refocusing in the PTV injector, enables the achievement of lower detection limits for volatile and very volatile organic compounds.

Introduction

Volatile organic compounds (VOCs) are a group of organic chemicals with low vapor pressure that can easily evaporate into the air, even at room temperature. These compounds can originate from various sources, including industrial processes, vehicle emissions, and natural sources. While VOCs are often associated with air pollution, they can also contaminate water, thus posing potential risks to human health and the environment.[1] VOCs can enter water through direct discharges, atmospheric deposition, or runoff from contaminated areas. Common VOCs found in water include benzene, toluene, ethylbenzene, and xylene (BTEX), as well as chlorinated compounds such as trichloroethylene (TCE) and tetrachloroethylene (PCE). These compounds can cause adverse health effects, ranging from short-term irritation to long-term chronic conditions, depending on the concentration and duration of exposure.

Regulatory authorities all over the world have established limits to control the maximum amount of VOCs in drinking water, groundwater, or surface water (e.g., Safe Drinking Water Act (SDWA) in the USA or the European Directive 2008/105/EC).[2,3] Therefore, monitoring and analyzing VOCs in water play crucial roles in identifying and addressing potential contamination issues, guiding remediation efforts, and ensuring compliance with water quality regulations.[4]

Common methods to analyze VOCs in water include headspace, purge and trap, solid-phase microextraction, and liquid-liquid extraction as possible sample preparation techniques employed to extract and concentrate VOCs before GC-MS analysis. As technology advances, continuous improvements in analytical methods and instrumentation contribute to more accurate and efficient VOC analysis, enhancing the ability to safeguard water resources and public health.

When dealing with drinking water testing, the limits of detection are particularly challenging, requiring an efficient enrichment before GC-MS analysis.

In-Tube Extraction-Dynamic Headspace (ITEX-DHS) is a sample preparation technique for the extraction and preconcentration of volatile compounds from different matrices, such as water, soil, or biological samples. One of the key advantages of ITEX-DHS is its high sensitivity and selectivity for volatile compounds. It allows for the extraction of low concentrated analytes from complex matrices while minimizing interference from non-volatile matrix components. Additionally, the technique offers an automated and efficient sampling process through a robotic autosampler, making it suitable for unattended and time-sensitive analyses.

ITEX-DHS has found applications in various fields, including environmental monitoring, food analysis, and forensic science. Its versatility makes it particularly valuable in situations where trace-level analysis of volatile compounds is crucial. An example of the use of ITEX-DHS for the detection of odorants in water at ng/L level is reported in a previous application note.[5]

In this study, the performance of the ITEX-DHS sampling technique has been evaluated for trace level detection of volatile and very volatile compounds (VVOCs) in water, in combination with peak refocusing into a Programmed Temperature Vaporizer (PTV) injector, to enhance peak shape and signal-to-noise ratio.

Experimental

The Thermo Scientific™ TriPlus™ RSH SMART autosampler equipped with the ITEX-DHS tool has been coupled to the Thermo Scientific™ TRACE™ 1610 gas chromatograph connected to a Thermo Scientific™ ISQ™ 7610 single quadrupole mass spectrometer, which features the Thermo Scientific™ ExtractaBrite™ EI ion source with NeverVent™ technology. The AEI ion source, offering even higher sensitivity, is optional in case lower detection limits are required.

The ITEX-DHS technique involves the use of a small trap embedded into a gas-tight syringe (Figure 1), which selectively adsorbs and enriches the target compounds from the sample headspace during the withdrawing step. The adsorbent material used in this study was the standard Tenax™ TA 80/100 mesh, suitable for volatile compounds. The collection of the headspace through repeated strokes of the syringe allows for a scalable sensitivity level according to the number of strokes, making this approach versatile towards low and high concentration samples.

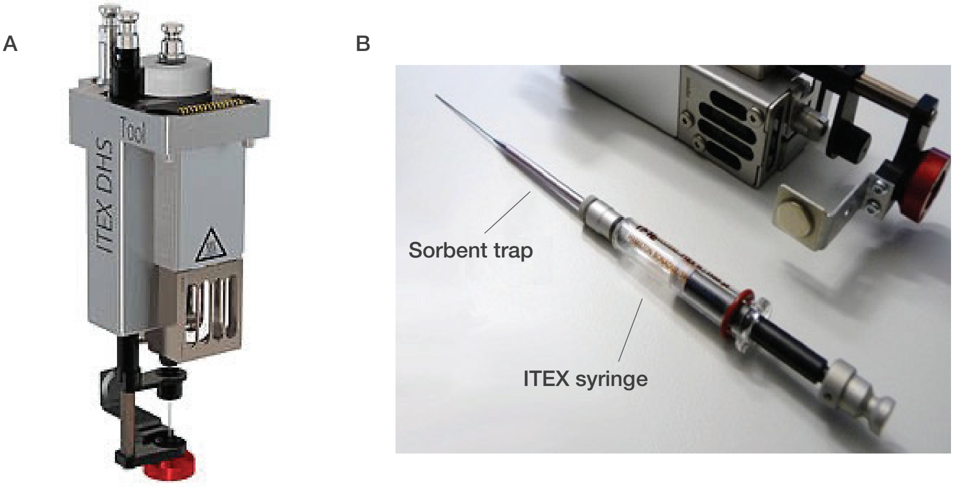


Figure 1. ITEX-DHS tool for the TriPlus RSH SMART autosampler (A) and ITEX gas-tight syringe (B)

This enrichment provides a clear benefit in terms of sensitivity compared to the static headspace sampling approach where only a limited headspace volume (typically 1 mL) is sampled and analyzed. As more strokes of the gas-tight syringe typically result in higher enrichment of the volatile compounds in the trap, this setup is suitable to deliver sensitivity levels comparable to those obtained using a purge and trap system, however, with a less complex setup and more flexible operations.

Following the adsorption step, the trap is thermally desorbed by rapid heating while the syringe delivers the desorbed analytes into the GC inlet for the analysis (Figure 2).

A refocusing step after the trap desorption can be achieved into the Thermo Scientific™ iConnect™ PTV injector by using a packed liner dedicated to VOCs analysis (Figure 3), improving peak shape and sensitivity especially for very volatile compounds such as vinyl chloride.

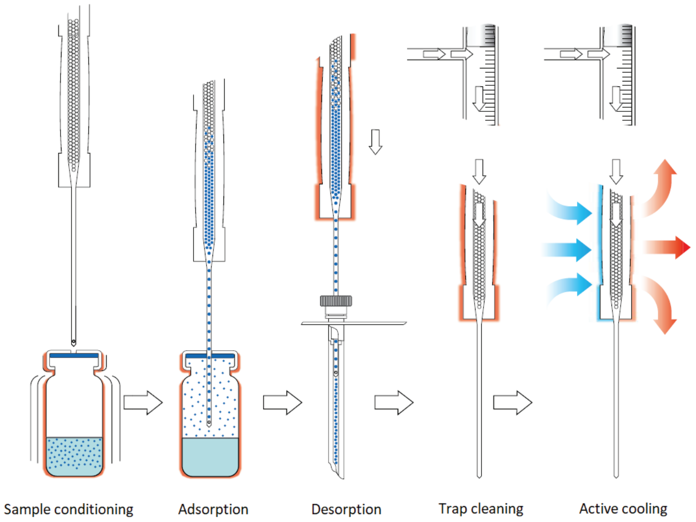


Figure 2. Schematic of the ITEX-DHS sample extraction and desorption process

Figure 3. 2 mm ID packed deactivated glass liner for the iConnect PTV injector module

The method parameters are summarized in Tables 1 and 2, while the list of target compounds along with SIM Quan/Qual ions are reported in Appendix Table A1.

Table 1. ITEX-DHS parameters

Parameter	Setting
Vial size	20 mL
ITEX-DHS trap	Tenax TA 80/100 mesh (P/N 1R77010-1126)
Incubation time	15 min
Incubation temperature	70 °C
Agitator speed	500 rpm
Trap pre-cleaning temperature	280 °C
Trap pre-cleaning time	240 s
Extraction strokes	40
Trap extraction temperature	35 °C
Syringe temperature	50 °C
Extraction volume	1,000 µL
Extraction aspirate flow rate	100 µL/s
Extraction dispense flow rate	100 µL/s
Sample volume in vial	10 mL
Sample prefill ratio	40%
Water removal	Disabled
Desorb temperature	280 °C
Injector aspirate flow rate	10 µL/s
Desorb flow rate	80 µL/s
Sample volume	1,300 µL
Injector penetration speed	50 mm/s
Trap post cleaning time	240 s

Table 2. GC-MS parameters

Parameter	Setting
Inlet	PTV
PTV program	35 °C (0.3 min), 14 °C/s to 280 °C (30 min)
Inlet mode	Split
Split flow	2 mL/min
Carrier gas	Helium (99.999% purity)
Carrier gas flow rate	1.2 mL/min
Oven temperature program	35 °C (5 min), 7 °C/min to 250 °C (3 min)
GC run time	38.7 min
MS transfer line temperature	250 °C
Ionization mode	EI, 70 eV
MS acquisition mode	Timed SIM see table Appendix Table A1
Ion source temperature	250 °C

Data acquisition, processing, and reporting

Data was acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3. The integrated instrument control ensures full automation of the entire analytical workflow from sample incubation and extraction to data analysis, processing, customizable reporting, and storage in compliance with the United States Food and Drug Administration Title 21 Code of Federal Regulations Part 11 (Title 21 CFR Part 11).

Standard and sample preparation

A 50 µg/L dilution in water was prepared from a stock solution containing 1,000 µg/mL of the VOCs analyzed in this study, dissolved in methanol. 50 µg/L 1-bromo-2-chloroethane and 30 µg/L fluorobenzene were also added to this solution as internal standards.

Of this solution, 1,000 µL were diluted with 9,000 µL deionized water containing NaCl at a concentration of 55 g/L. This operation was done directly into a 20 mL headspace vial, which was immediately sealed with magnetic crimp caps.

Results and discussion

PTV refocusing

VVOCs are characterized by low boiling points, and their chromatographic separation can be challenging. Due to their low retention (primarily influenced by the low boiling point), they may initially overload the GC column, causing band broadening with reduced peak intensity. The refocusing effect is particularly beneficial when analyzing these highly volatile compounds to improve the precision and sensitivity of the analysis.

In this work, the refocusing effect has been achieved inside of the PTV injector by using a dedicated liner packed with Tenax TA and has had an impactful effect without the use of any cryogenic device. This means a simplification of the hardware setup and method parameters and the avoidance of issues related to moisture potentially frozen out in a cryogenic trap. By concentrating the analytes before they enter the GC column, better peak shapes and improved signal-to-noise ratios can be achieved, leading to more accurate and reliable results. Figure 4 shows the effect of using the packed liner on some very volatile compounds.

Chromatography

The separation was achieved on a Thermo Scientific™ TraceGOLD™ TG-624SilMS GC column, 60 m x 0.25 mm x 1.4 µm (P/N 26059-3330), which offers a medium polarity and a suitable phase ratio for a good separation over a wide range of volatile compounds from vinyl chloride to trichlorobenzene.

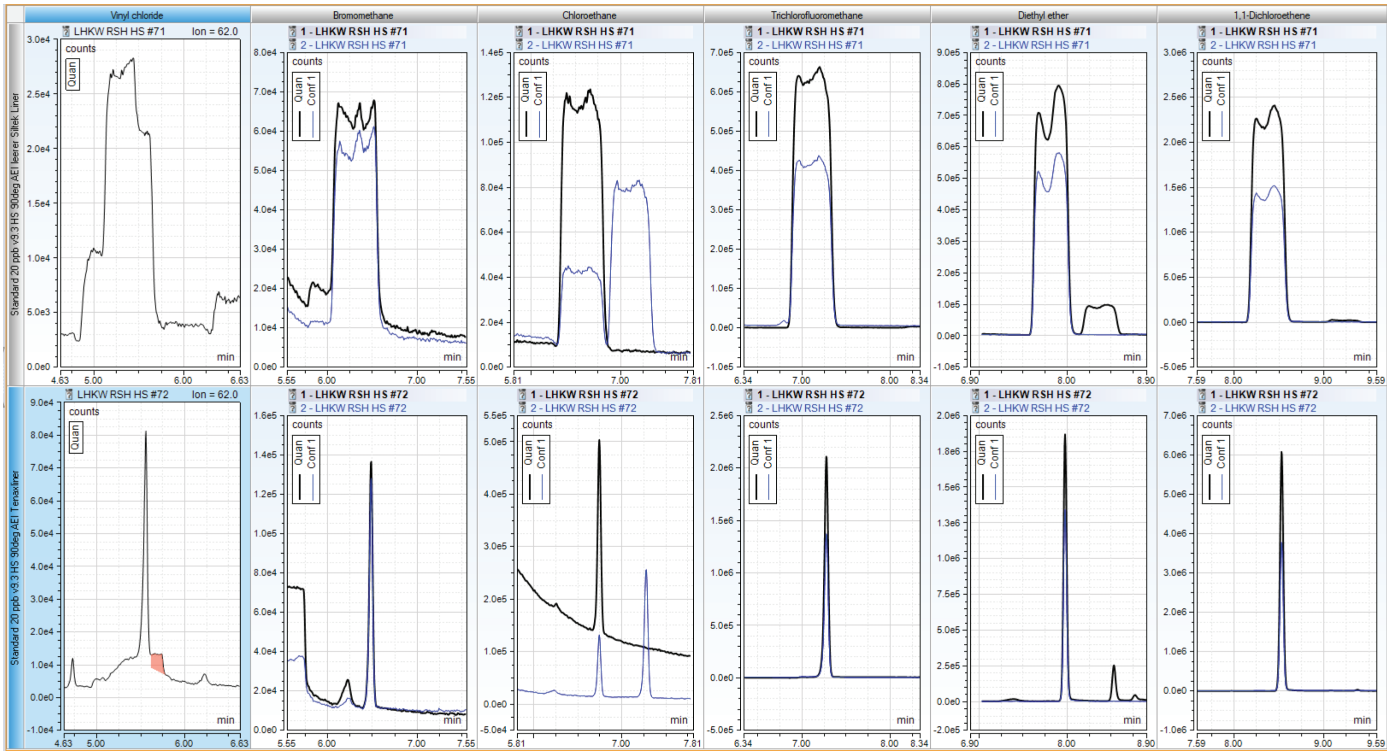


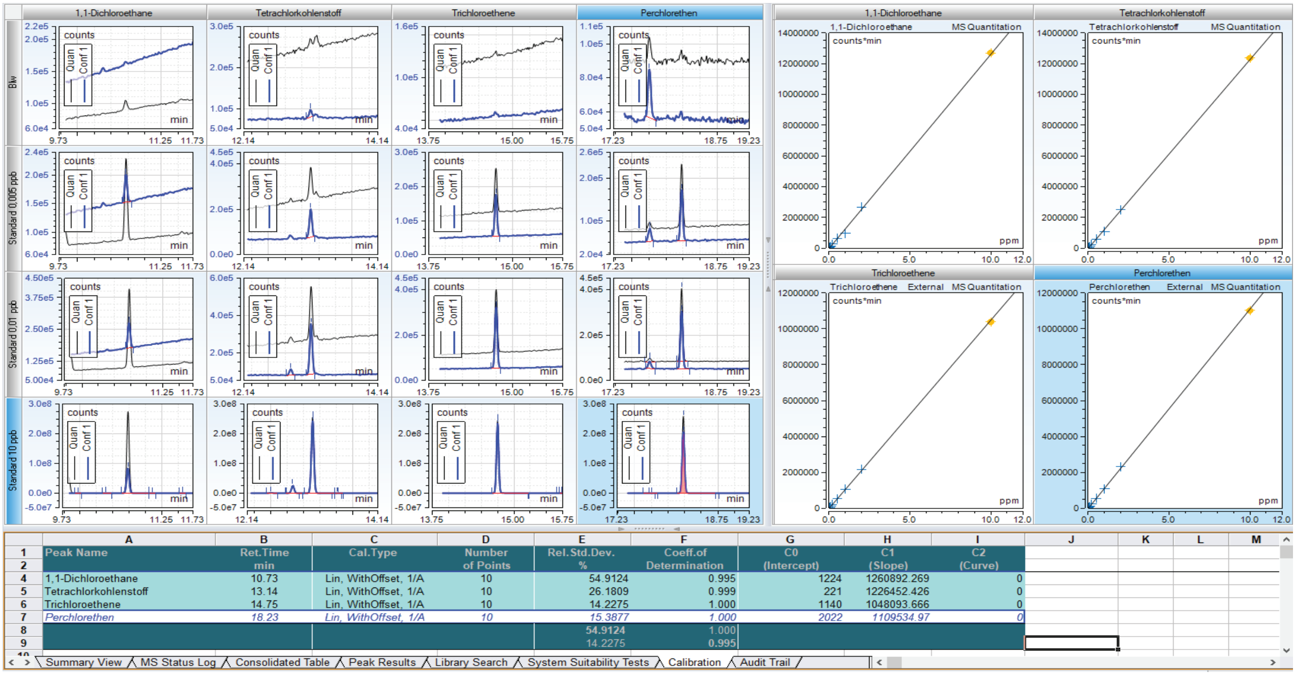
Figure 4. Comparison of VVOC peak shape with a standard PTV liner (upper) and the PTV with the packed VOC-liner (bottom)

The use of the ITEX-DHS technique to perform a dynamic headspace sampling effectively removed the matrix so that a clean sample was injected onto the GC, which helped in turn to reduce baseline noise and simplify operations by using a t-SIM acquisition mode.

Linearity and limit of detection

Linearity of the recovery has been assessed across the concentration range from 0.005 µg/L to 10 µg/L with a coefficient of determination $R^2 > 0.995$ and an average calibration factor %RSD < 3.17%, as reported in Appendix Table A2. Figures 5 and 6 show examples of linearity for chlorinated hydrocarbons and aromatics compounds, respectively.

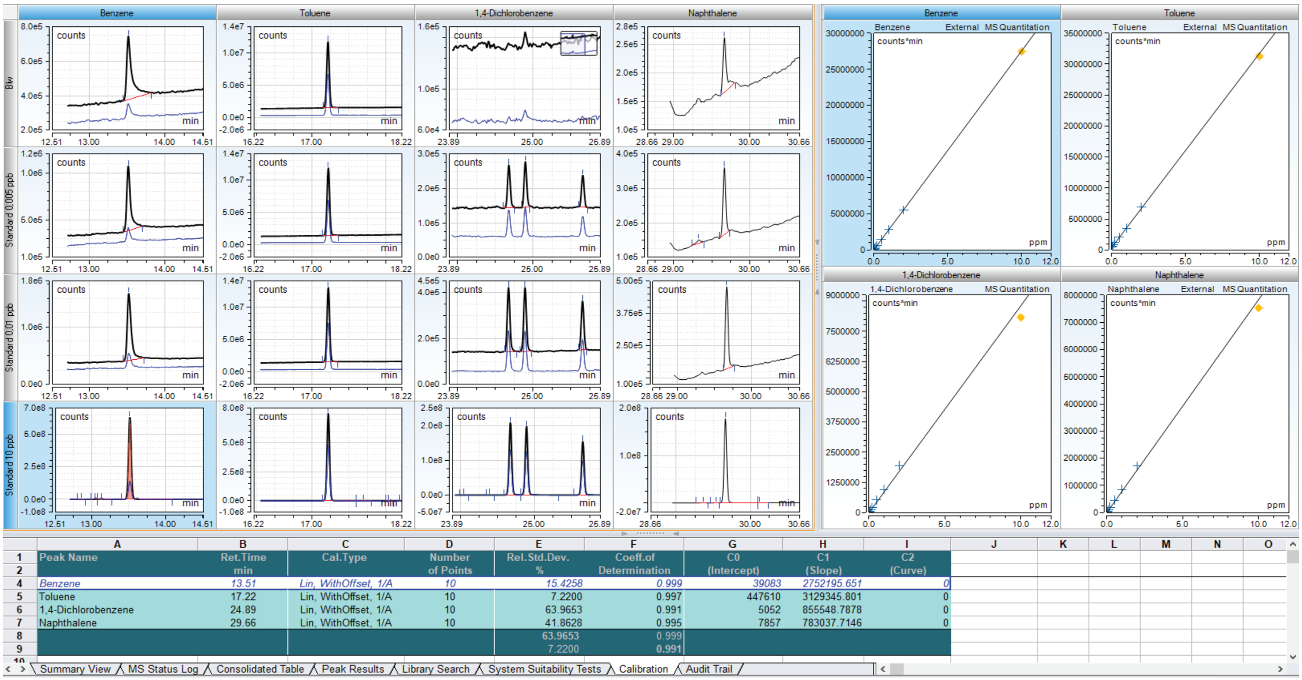
Considering the targeted low detection limits, the blank contamination from the environment was found to be an issue for some aromatic compounds used as solvents in the lab, as evident in Figure 6. For those compounds, it was not possible to evaluate a limit of quantification below the contamination level.



	A	B	C	D	E	F	G	H	I
1	Peak Name	Ret.Time	Cal.Type	Number	Rel.Std.Dev.	Coeff.of	C0	C1	C2
2		min		of Points	%	Determination	(Intercept)	(Slope)	(Curve)
4	1,1-Dichloroethane	10.73	Lin, WithOffset, 1/A	10	54.9124	0.995	1224	1260892.269	0
5	Tetrachlorkohlenstoff	13.14	Lin, WithOffset, 1/A	10	26.1809	0.999	221	1226452.426	0
6	Trichloroethene	14.75	Lin, WithOffset, 1/A	10	14.2275	1.000	1140	1048093.666	0
7	*Perchlorethen*	*18.23*	*Lin, WithOffset, 1/A*	*10*	*15.3877*	*1.000*	*2022*	*1109534.97*	*0*
8					54.9124	1.000			
9					14.2275	0.995			

Summary View / MS Status Log / Consolidated Table / Peak Results / Library Search / System Suitability Tests / Calibration / Audit Trail

Figure 5. Examples of linearity response for some chlorinated hydrocarbons. Top to bottom: blank, 0.005 µg/L, 0.01 µg/L, 10 µg/L



	A	B	C	D	E	F	G	H	I
1	Peak Name	Ret.Time	Cal.Type	Number	Rel.Std.Dev.	Coeff.of	C0	C1	C2
2		min		of Points	%	Determination	(Intercept)	(Slope)	(Curve)
4	*Benzene*	*13.51*	*Lin, WithOffset, 1/A*	*10*	*15.4258*	*0.999*	*39083*	*2752195.651*	*0*
5	Toluene	17.22	Lin, WithOffset, 1/A	10	7.2200	0.997	447610	3129345.801	0
6	1,4-Dichlorobenzene	24.89	Lin, WithOffset, 1/A	10	63.9653	0.991	5052	855548.7878	0
7	Naphthalene	29.66	Lin, WithOffset, 1/A	10	41.8628	0.995	7857	783037.7146	0
8					63.9653	0.999			
9					7.2200	0.991			

Summary View / MS Status Log / Consolidated Table / Peak Results / Library Search / System Suitability Tests / Calibration / Audit Trail

Figure 6. Examples of linearity response for some aromatic hydrocarbons. Top to bottom: blank, 0.005 µg/L, 0.01 µg/L, 10 µg/L

The headspace enrichment capacity of the ITEX-DHS technique, combined with a SIM mode MS acquisition, allows the achievement of low ppt level sensitivity (Appendix Table A2), suitable to meet stringent regulatory requirements for drinking water testing. The limits of detection reported in Table A2 were extrapolated to S/N=3 after blank subtraction.

Repeatability

The entire process of extraction, enrichment, injection, and re-focusing is very repeatable as demonstrated over a sequence of 12 subsequent injections of fresh aliquots of the same sample with and without internal standard.

As shown in Table 3, the analysis demonstrates the excellent precision of the process, with an average of 4.4% RSD on quantitative recovery from a standard solution at 2.5 µg/L with the use of an external standard. The precision is further improved to an average of 2.7% RSD with the use of the internal standard.

Even if the average RSD has improved with the use of the IS, such improvement is not visible for all the compounds. In fact, the IS should be individually selected. Some recommendations on the IS selection are reported in the new EN ISO 20595:2023.

Carryover

When dealing with trace analysis, possible carryover from more concentrated samples can pose a critical challenge. In this study, carryover has been checked by running clean DI-water after the analysis of a standard mixture at 10 µg/L, obtaining for all analytes a carryover less than 0.027%, without blank subtraction, as shown in Figure 7.

Table 3. Recovery precision over n=12 repetitions with and without internal standard

Compound	ESTD	ISTD
Dichlorodifluoromethane	5.0%	4.4%
Trichlorofluoromethane	3.1%	2.0%
1,1-Dichloroethene	3.0%	1.7%
Dichloro-methane	4.4%	1.8%
trans-1,2-Dichloroethene	3.6%	0.9%
cis-1,2-Dichloroethene	4.4%	0.9%
Chloroform	4.1%	0.8%
1,1,1-Trichloroethane	3.3%	1.3%
Carbon tetrachloride	4.1%	1.9%
Benzene	5.6%	2.3%
1,2-Dichloroethane	6.0%	3.1%
Fluorobenzene (ISTD)	4.1%	--
Trichloroethene	3.9%	4.3%
Bromodichloromethane	5.0%	1.5%
1-Bromo-2-chlorethane (ISTD)	6.4%	--
Toluene	3.4%	3.6%
Perchloroethylene	3.1%	4.8%
Dibromochloromethane	6.4%	2.2%
Ethylbenzene	3.5%	4.3%
m/*p*-Xylene	3.6%	4.2%
o-Xylene	3.9%	4.1%
Bromoform	7.9%	4.2%
Average value	**4.4%**	**2.7%**

	A	B	C	D	E	F	G
1	Inj.	Injection Name	Type	Area			
2	No.	Selected Peak:		counts*min			
4				Chloroform	Bromodichloromethane	Dibromchlormethan	Bromoform
5	*20*	*Blw DI Wasser*	*Unknown*	*2783*	*2085*	*2189*	*1834*
6	21	Standard 10ppb	Unknown	21624751	13704484	9000149	5182601
7	22	Blw DI Wasser	Unknown	3276	1681	1472	1401
8	Maximum						
9	**Average**						
10	Minimum						

Figure 7. Carryover for all analytes is <0.027%. Top traces: clean DI-water before standard mix analysis. Middle traces: standard mixture at 10 µg/L. Bottom traces: clean DI-water after standard mix analysis.

Conclusion

The use of the ITEX-DHS technique for headspace enrichment coupled to cryogen-free refocusing into the PTV injector is a suitable approach for trace level analysis of VOC and VVOC in water samples, offering a clean method to comply with more stringent regulatory limits of quantitation.

- Combined with refocusing prior to transfer into the column and SIM acquisition mode, the ITEX-DHS technique achieves limits of quantification at low ppt levels and extrapolated limits of detection in the sub-ppt range, even for VVOC such as vinyl chloride, with high recovery precision (<5% RSD) and a linear response over four orders of magnitude.
- ITEX-DHS offers a flexible enrichment technique capable of handling low and high concentrated samples to comply with different sensitivity requirements.
- The complete workflow, from method set up to data processing and reporting, can be fully controlled through Chromeleon CDS, which greatly facilitates operations on a day-to-day basis.

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5. Thermo Scientific AN73471 In-Tube Extraction Dynamic Headspace (ITEX-DHS) sampling technique coupled to GC-MS for sensitive determination of odorants in water

Appendix

Table A1. List of target VOC compounds with RT and Quan/Qual ions

Component	Retention time (min)	Quantifier ion	Qualifier ion
Dichlorodifluoromethane	4.863	85	87
Trichlorofluoromethane	7.843	101	103
1,1-Dichloroethene	9.236	61	96
Dichloromethane	10.482	84	49
trans-1,2-Dichloroethene	10.917	96	61
cis-1,2-Dichloroethene	13.092	96	61
Chloroform	13.677	83	85
1,1,1-Trichloroethane	13.978	97	99
Carbon tetrachloride	14.217	117	119
Benzene	14.686	78	51
1,2-Dichloroethane	14.863	62	64
Fluorobenzene (ISTD)	15.227	96	70
Trichloroethene	15.878	130	132
Bromodichloromethane	16.892	83	85
1-Bromo-2-chloroethane (ISTD)	17.577	63	144
Toluene	18.313	91	92
Perchloroethylene	19.321	166	164
Dibromochloromethane	19.956	129	127
Ethylbenzene	21.269	91	106
m/p-Xylene	21.506	91	106
o-Xylene	22.338	91	106
Bromoform	22.86	173	79
1,4-Dichlorobenzene	24.89	146	148
Naphthalene	29.66	128	-

Table A2. List of compounds with coefficient of variation (%), extrapolated limit of detection, and coefficient of correlation R^2 (in the conc. range 0.005 µg/L to 10 µg/L)

Peak name	Var. coeff. (%)	Detection limit* (µg/L)	R^2
Dichlorodifluoromethane	2.39	0.0043	0.9994
Trichlorofluoromethane	2.42	0.0001	0.9994
1,1-Dichloroethene	2.3	0.0001	0.9995
Dichloromethane	2.06	0.0001	0.9995
trans-1,2-Dichloroethene	2.82	0.0001	0.9992
cis-1,2-Dichloroethene	2.81	0.0001	0.9989
Chloroform	1.63	0.0001	0.9997
1,1,1-Trichloroethane	2.03	0.0006	0.9996
Carbon tetrachloride	3.68	0.0047	0.9986
Benzene**	5.41	0.132	0.9953
1,2-Dichloroethane	2.03	0.0003	0.9996
Fluorobenzene (ISTD)	n.a.	n.a.	n.a.
Trichloroethene	3.43	0.0002	0.9949
Bromodichloromethane	2.56	0.0002	0.9993
1-Bromo-2-chloroethane (ISTD)	n.a.	n.a.	n.a.
Toluene**	2.53	0.102	0.9972
Perchloroethylene	4.24	0.0003	0.9976
Dibromochloromethane	3.2	0.0001	0.9989
Ethylbenzene	2.78	0.0001	0.9992
m/p-Xylene	3.35	0.0001	0.9988
o-Xylene	3.23	0.0001	0.9989
Bromoform	5.04	0.0004	0.9974
1,4-Dichlorobenzene	14.6	0.0005	0.9780
Naphthalene	13.2	0.0082	0.9724

*Extrapolated to S/N = 3 after blank subtraction

**Detection limits are influenced by laboratory blanks from ambient air in the lab or DI-water used for sample preparation.

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Environmental analysis

Determination of BTEX and volatile organic compounds (VOCs) in drinking water by GC-MS/MS coupled to static headspace and solid-phase microextraction sampling

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Keywords

Volatile organic compounds (VOCs), BTEX, drinking water, gas chromatography-mass spectrometry, GC-MS, triple quadrupole, TSQ 9000 mass spectrometer, ExtractaBrite ion source, static headspace, HS, solid-phase microextraction, SPME Arrow

Goal

The aim of this application note is to report the analytical performance of static headspace (SHS) and solid-phase microextraction using Arrow technology (SPME Arrow) for the determination of benzene, toluene, ethylbenzene, and xylenes (BTEX) and chlorinated and brominated volatile organic compounds (VOCs) in drinking water using a Thermo Scientific™ TSQ™ 9000 triple quadrupole GC-MS/MS system.

Introduction

Volatile organic compounds (VOCs) are characterized by a high vapor pressure and low water solubility and are typically used in industrial applications, petroleum fuels, hydraulic fluids, paint thinners, and dry-cleaning agents. Their presence in the environment is thus strongly dependent on human activities. VOCs easily evaporate into air at ambient temperature and dissolve in water leading to contamination of water resources.[1] This poses serious concerns for human health as many VOCs are known, or suspected, to be human carcinogens.[1] Regulatory authorities all over the world have established limits to control the amount of VOCs in drinking water, groundwater, or surface water (e.g., Safe Drinking Water Act (SDWA) in the USA or the European Directive 2008/105/EC),[2,3] therefore, public water service providers must ensure that distributed drinking water is in compliance with the maximum contaminant levels established for VOCs.[4]

Due to the high volatility of the compounds, analysis of VOCs is usually performed using gas chromatography coupled to static headspace sampling (SHS),[5,6] which offers the advantage of quick and minimal sample preparation combined with lower consumption of reagents and solvents. However, one of the main limitations of this sampling technique is the relatively low sensitivity, especially regarding the regulatory limits that have been established for certain VOCs, such as vinyl chloride.

Solid-phase microextraction (SPME)[7] has proven to be an effective alternative to SHS, combining extraction of VOCs and enrichment in a single step and consequently allowing lower detection limits to be achieved. It consists of a fiber coated with an organic solid phase that, when exposed to the sample, extracts and concentrates the analytes using selective absorptive/adsorptive processes, providing improved extraction efficiency and superior sensitivity. The fiber can be exposed in the vapor phase above the liquid or solid matrix (headspace-SPME) or directly immersed in the liquid sample (direct immersion-SPME) offering the flexibility to analyze several matrices with one single solution.

The advantages offered by SPME led to the adoption of this sampling technique in many official methods.[8-10] For example, the method specified by ISO 17943:2016[11] applies SPME for the determination of VOCs, including halogenated hydrocarbons, gasoline additives, volatile aromatic compounds, and highly odorous substances in drinking water, groundwater, surface water, and treated wastewater.

In this study, the performance of SHS and SPME sampling techniques were evaluated for the determination of chlorinated and brominated VOCs and BTEX in drinking water. The TSQ 9000 GC-MS/MS provided ease-of-use and operational flexibility in both single ion monitoring (SIM) acquisition mode for fast screening of samples and selected reaction monitoring (SRM) acquisition mode when higher selectivity was required to reduce interferences. Hydrogen was used as carrier gas for these experiments, providing good separation efficiency in shorter run times.

Experimental

A TSQ 9000 triple quadrupole mass spectrometer featuring Thermo Scientific™ NeverVent™ technology was coupled to a Thermo Scientific™ TRACE™ 1310 gas chromatograph equipped with a Thermo Scientific™ iConnect Split/Splitless (SSL) injector. The Thermo Scientific™ ExtractaBrite™ ion source and the NeverVent option offered proven robustness and sensitivity to meet regulatory requirements, even allowing switching between EI and CI modes without breaking the MS vacuum. To confidently stay ahead to the toughest regulatory methods and business demands, the new Thermo Scientific™ TSQ 9610 GC-MS/MS coupled to the Thermo Scientific™ TRACE™ 1600 Series GC offers the benefits of the ExtractaBrite ion source combined with the new Thermo Scientific™ XLXR™ detector for extended lifetime and dynamic range for similar and even better results.[12] A Thermo Scientific™ TriPlus™ RSH autosampler configured for SHS and SPME Arrow sampling was used to automate analyte extraction and transfer into the analytical system. To ensure the extraction of a wider number of analytes, a dual phase carbon WR/PDMS coated fiber (Thermo Scientific™ SPME Arrow fiber, Carbon Wide Range, P/N 36SA12B1) was selected and used for trace-level volatiles determination. Chromatographic separation was achieved on a Thermo Scientific™ TraceGOLD™ TG-624SilMS capillary column, 20 m × 0.18 mm × 1.0 µm (P/N 26059-4950). The TriPlus RSH autosampler allows overlap of independent chromatographic injections. Combined with a fast GC oven ramp, it ensures a short cycle time, enabling high sample throughput without compromising the chromatographic performance. For advanced automation, the new Thermo Scientific™ TriPlus™ RSH SMART autosampler provides an additional layer of reliability and confidence in the analytical results thanks to the automatic SMART syringes, fiber identification, and usage tracking capabilities for a smarter management of the consumables.[13]

Additional SHS and HS-SPME Arrow and GC-MS/MS parameters as well as a complete list of the target compounds are detailed in Appendixes 1 and 2, respectively.

Data acquisition, processing, and reporting

Data was acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3. Integrated instrument control ensures full automation of the entire analytical workflow from sample incubation and extraction to data analysis, processing, customizable reporting, and storage in compliance with the United States Food and Drug Administration Title 21 Code of Federal Regulations Part 11 (Title 21 CFR Part 11).

Standard and sample preparation

Standard preparation

Volatile organic compounds standard mix (P/N 126253-01) and BTEX standard mix (P/N 120340-01) were purchased from o2si smart solutions. Tap water, previously tested negative for the presence of VOCs, was used as diluent.

The VOCs standard mix was diluted to obtain two sets of calibration solutions ranging from 0.5 to 20 µg/L (ppb) for VOCs assessments using SHS sampling and 0.1 to 2 µg/L for vinyl chloride determination using SPME Arrow extraction. BTEX were assessed using SHS sampling over a concentration range of 0.3 to 3.0 µg/L. Each calibration solution (10 mL) was transferred into 20 mL screw top headspace vials (P/N 6ASV20-1, with caps, P/N 6PMSC18-ST2) for analysis.

Drinking water samples, previously tested negative for VOCs, were spiked at the regulatory limits (VOCs and BTEX: 0.3 µg/L, vinyl chloride: 0.1 µg/L), and 10 mL aliquots were transferred into 20 mL screw top headspace vials before analysis.

Calibration solutions and spiked water samples were used to assess method linearity, sensitivity, recovery, and repeatability by using both SHS and SPME Arrow sampling techniques.

Sample preparation for drinking water samples

Real water samples were provided by CAP Holding, a company that manages the Integrated Water Service in about 200 municipalities belonging to the Metropolitan City of Milan. Sample aliquots (10 mL) were transferred into 20 mL screw top headspace vials before analysis and used for method validation purposes by running typical sequences including calibration curves and QC spiked at the regulatory limits.

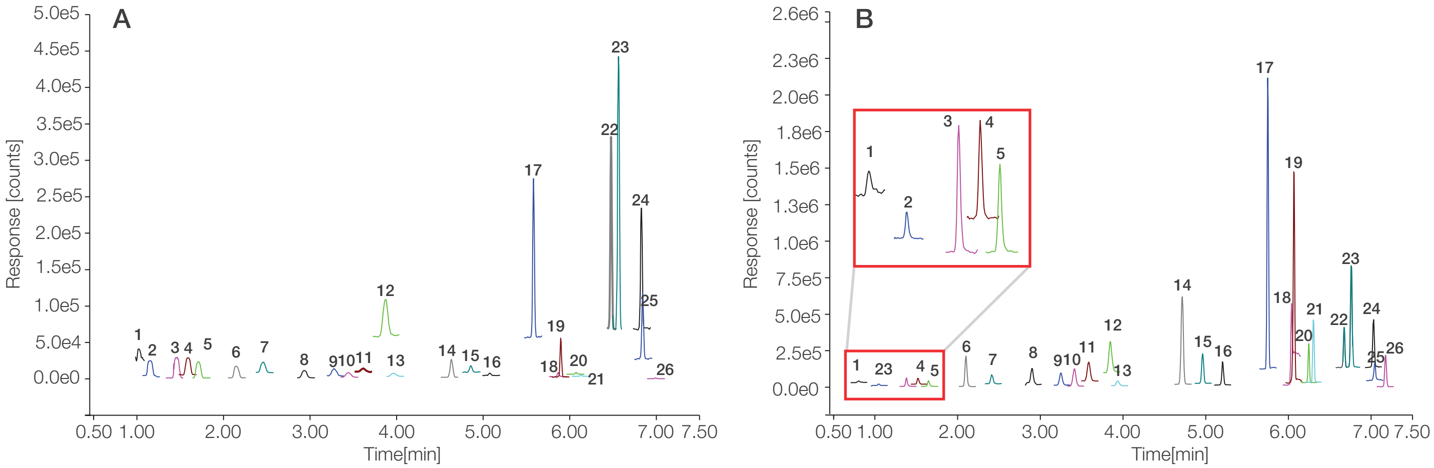
Results and discussion

Chromatography

The high thermal stability, low-bleed, and mid-polarity of the TraceGOLD TG-624SilMS capillary column offered ideal chromatographic performance and helped to simplify method development. The use of the headspace sampling effectively removed the matrix, so that a clean sample was injected onto the GC, which helped in turn to reduce baseline noise. This allowed for faster sample analysis, and operations were simplified by using a *t*-SIM acquisition mode. The SHS sampling technique provided adequate sensitivity to meet the regulatory limits set at 0.3 µg/L for the investigated VOCs and BTEX with the exception of vinyl chloride, for which the enrichment through the SPME Arrow technique was required to achieve the regulatory threshold set at 0.1 µg/L. As an example, the *t*-SIM acquisitions of VOCs and BTEX standards spiked at 0.3 µg/L (SHS extraction) and 0.1 µg/L (SPME Arrow) are shown in Figure 1.

Linearity and method detection limit (MDL)

Calibration curves ranging from 0.50 to 20 µg/L for VOCs and from 0.3 to 3.0 for BTEX were used to assess method linearity and detection limits using SHS extraction. Linearity for HS-SPME extraction was evaluated by injecting four VOC calibration standards ranging from 0.10 to 2.0 µg/L. External calibration curves were plotted using a linear fit and acceptance criteria for linearity were: (i) coefficient of determination (R^2) > 0.990, (ii) average calibration factor %RSD (AvCF %RSD) < 20%, and (iii) concentration tolerance of 25% at the lowest calibration point. All three acceptance criteria were met for both SHS and HS-SPME sampling techniques, with average R^2 of 0.999 and 0.996, respectively, AvCF %RSD < 9%, and concentration deviations within 25% of the expected values at the lowest calibration point, as reported in Appendix 3. Examples of calibration curves for benzene (SHS sampling) and vinyl chloride (HS-SPME sampling) are reported in Figure 2.



1=Difluorochloromethane (Freon 22), **2**=Vinyl chloride, **3**=Trichloromonofluoromethane (Freon 11), **4**=1,1-Dichloro-1-fluoroethane (Freon 141), **5**=1,1,2-Trichloro-1,2,2-trifluoro-ethane (Freon 113), **6**=*trans*-1,2-Dichloroethylene, **7**=1,1-Dichloroethane, **8**=*cis*-1,2-Dichoroethylene, **9**=Chloroform, **10**=Methyl-Chloroform, **11**=Carbon tetrachloride, **12**=Benzene, **13**=1,2-Dichloroethane, **14**=Trichloroethylene, **15**=1,2-Dichloropropane, **16**=Bromodichloromethane, **17**=Toluene, **18**=1,1,2-Trichloroethane, **19**=Tetrachloroethylene, **20**=Dibromochloromethane, **21**=1,2-Dobromoethane, **22**=Ethylbenzene, **23**=*m,p*-Xylene, **24**=*o*-Xylene, **25**=Styrene, **26**=Bromoform

Figure 1. *t*-SIM acquisition for tap water samples spiked with VOCs and BTEX. (A) at 0.3 µg/L, SHS sampling; (B) at 0.1 µg/L, SPME Arrow sampling.

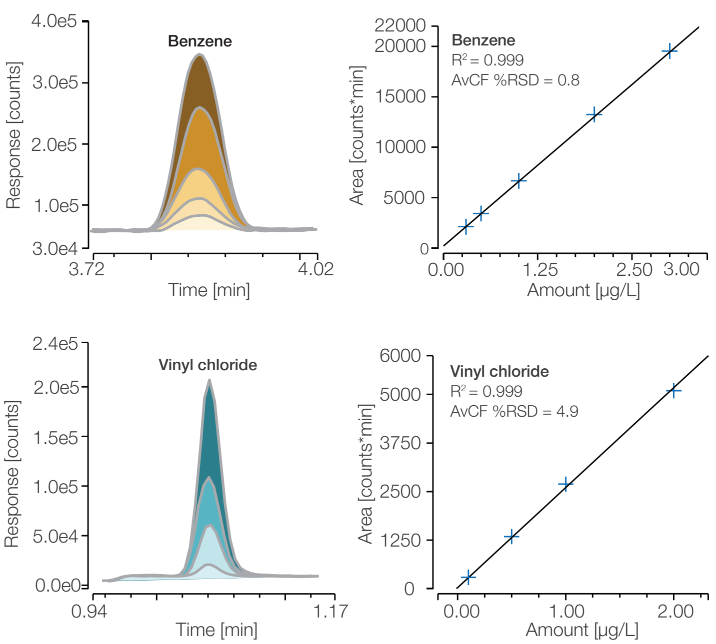


Figure 2. Examples of calibration curves for benzene (SHS sampling, 0.3–3.0 µg/L) and vinyl chloride (HS-SPME sampling, 0.1–2.0 µg/L). R^2 and AvCF %RSD are annotated.

To evaluate the method detection limits, tap water samples (n=10) were spiked with BTEX at 0.3 µg/L and VOCs at 0.5 µg/L for SHS sampling, and BTEX at 0.1 µg/L and VOCs at 1.0 µg/L for HS-SPME sampling. MDLs were then calculated considering the one-tailed Students *t*-test values for the corresponding n-1 degrees of freedom at 99% confidence and multiplying them for the standard deviation of the replicated analysis. Calculated MDLs resulted in the range of 0.01–0.13 µg/L as reported in Figure 3 and Appendix 3, with recoveries between 60 and 130%. HS-SPME Arrow sampling was confirmed to be the required solution when lower limits of detection need to be achieved. Remarkably lower extraction efficiency was observed for difluorochloromethane as a result of the low affinity for the coating phase, thus resulting in poor linearity $R^2 < 0.95$ and MDL > 20 µg/L. In a similar way, the lower affinity of toluene and xylenes for the carbon WR/PDMS coating phase compared to the DVB/Carbon WR/PDMS (divinylbenzene/carbon WR/PDMS) can explain the higher MDLs for the high boiling BTEX compared to the SHS sampling.[14]

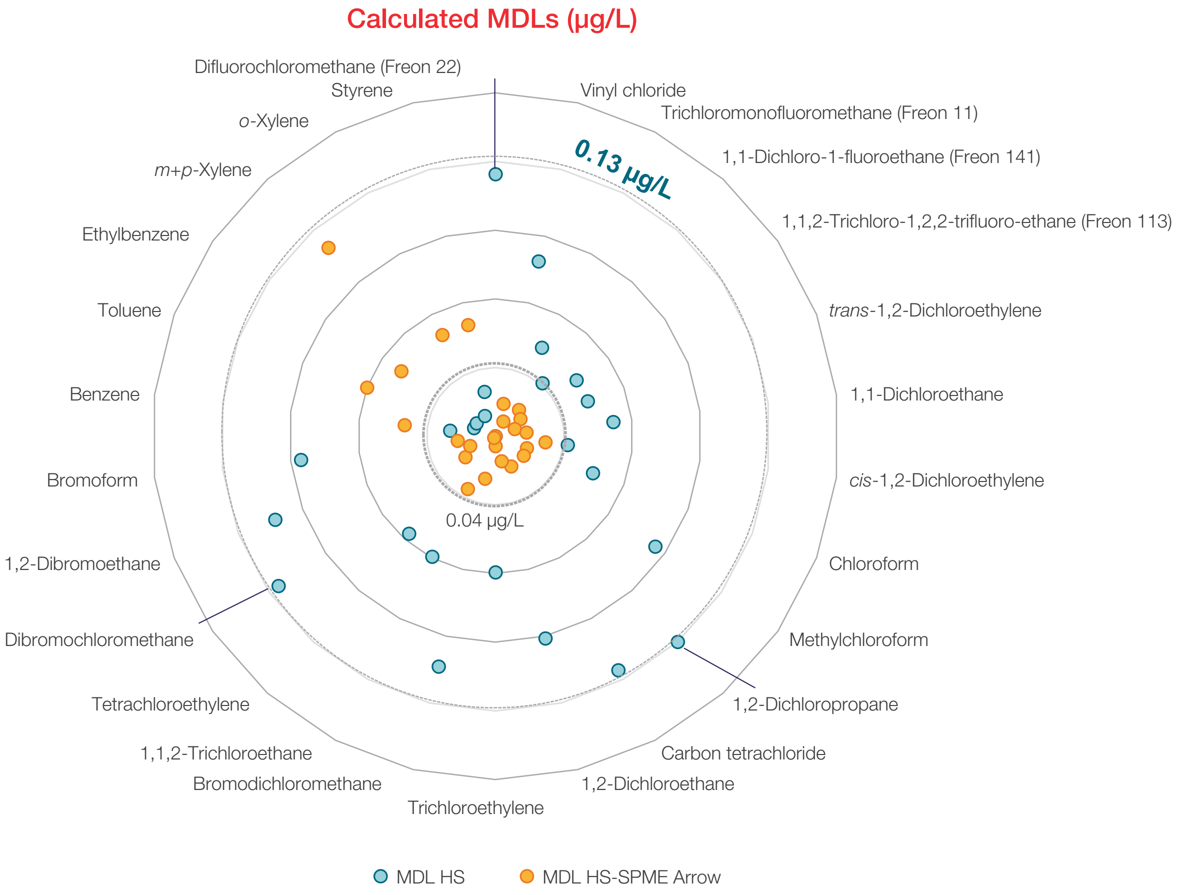
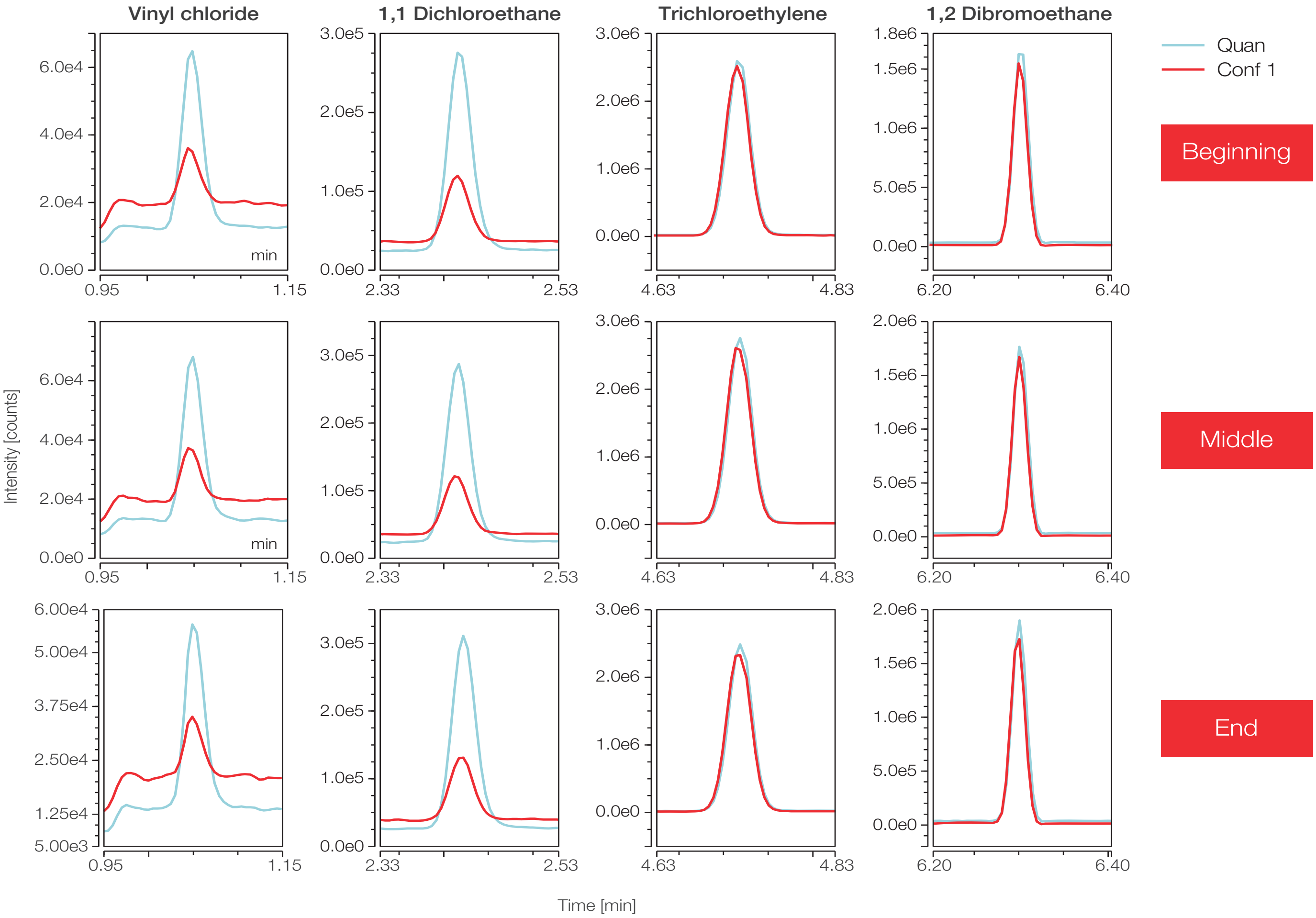


Figure 3. Calculated MDLs for VOCs using both SHS and HS-SPME Arrow sampling. Overall HS-SPME Arrow sampling was confirmed to be the required solution to achieve lower limits of detection.

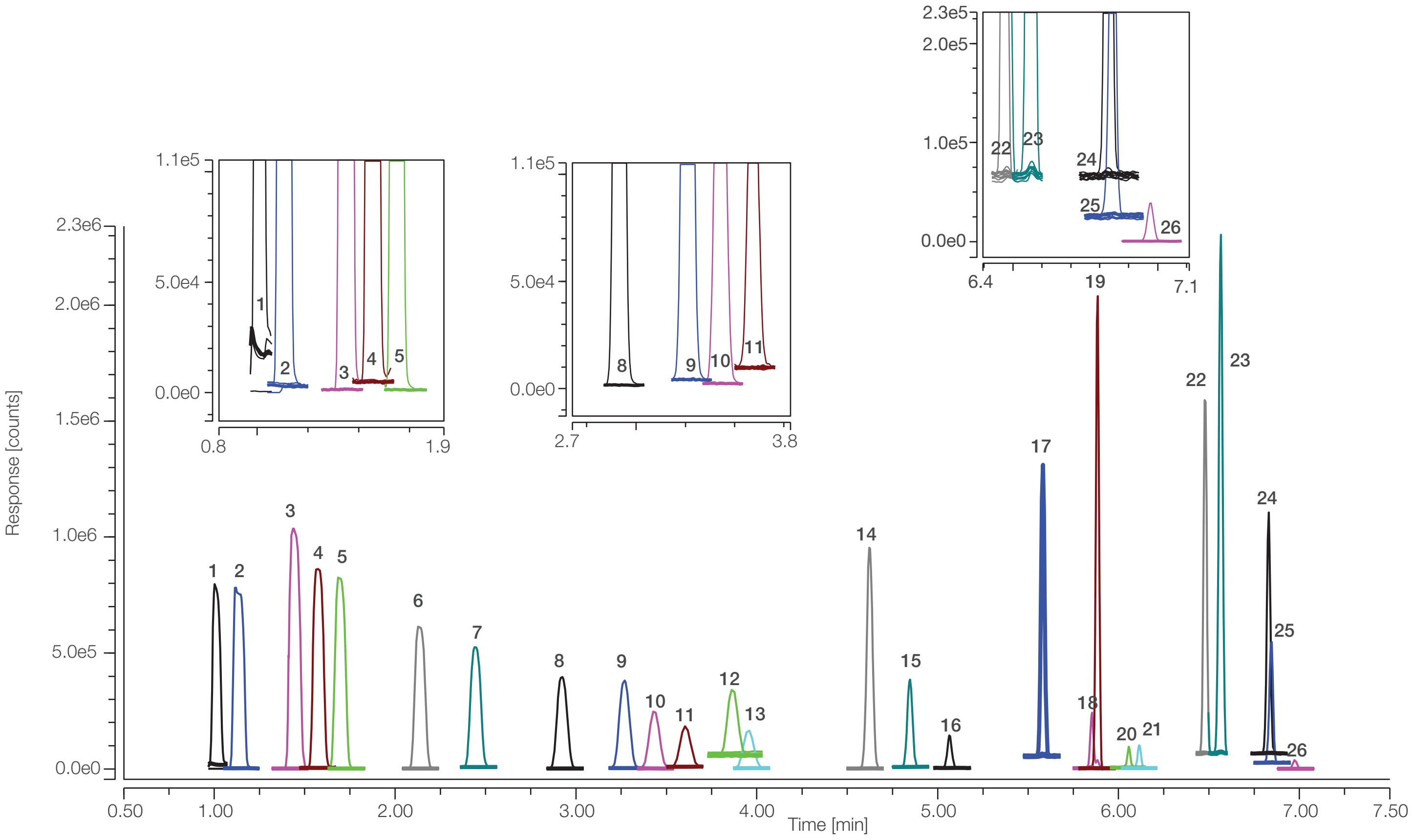
Method validation for everyday analysis

Method performance for everyday analysis was evaluated for both sampling techniques by running two sequences including calibration curves, spiked tap water samples, QCs, and real water samples for a period of approximately 48 hours (n=129 samples in total). An empty vial was run every 10 samples to monitor the carryover. To evaluate system stability over time, a calibration curve and a QC spiked at 0.5 µg/L were run at the beginning, middle, and end of the sequence. Overall retention time was stable with a standard deviation of less than 0.04 minutes. Absolute peak area %RSDs, calculated concentrations, and ion ratios were well within ±15% of the expected values, and examples are reported in Figure 4 for HS-SPME Arrow sampling. Carryover could not be detected (less than 0.01%) for both sampling techniques when running an injection from an empty vial. As an example, the XICs for empty vials run every n=10 samples over an 80-sample sequence with SHS sampling are shown in Figure 5.



Peak name	RT (min)			Absolute peak area (counts * min)			Amount (µg/L)			Ion ratio (%)			
	Beginning	Middle	End	Beginning	Middle	End	Beginning	Middle	End	Expected	Beginning	Middle	End
Vinyl chloride	1.05	1.05	1.05	1339	1536	1127	0.50	0.58	0.42	34.04	29.44	28.48	28.86
1,1 Dichloroethane	2.42	2.42	2.42	8196	8445	8646	0.55	0.57	0.59	32.26	32.93	33.68	34.96
Trichloroethylene	4.72	4.72	4.72	83032	87967	78875	0.52	0.55	0.49	99.47	99.32	98.95	98.90
1,2 Dibromoethane	6.30	6.30	6.30	33127	34863	36912	0.51	0.54	0.58	93.22	92.07	93.91	93.08

Figure 4. Examples of XICs for qualifier and quantifier ions for calibration standard and QC samples spiked at 0.5 µg/L run at the beginning, middle, and end of a typical sequence (HS-SPME Arrow sampling). Retention times were stable across the entire sequence with absolute peak area %RSDs, calculated concentrations, and ion ratios (expected and measured) within 15% of the expected values.



1=Difluorochloromethane (Freon 22), **2**=Vinyl chloride, **3**=Trichloromonofluoromethane (Freon 11), **4**=1,1-Dichloro-1-fluoroethane (Freon 141), **5**=1,1,2-Trichloro-1,2,2-trifluoro-ethane (Freon 113), **6**=*trans*-1,2-Dichloroethylene, **7**=1,1-Dichloroethane, **8**=*cis*-1,2-Dichoroethylene, **9**=Chloroform, **10**=Methyl-Chloroform, **11**=Carbon tetrachloride, **12**=Benzene, **13**=1,2-Dichloroethane, **14**=Trichloroethylene, **15**=1,2-Dichloropropane, **16**=Bromodichloromethane, **17**=Toluene, **18**=1,1,2-Trichloroethane, **19**=Tetrachloroethylene, **20**=Dibromochloromethane, **21**=1,2-Dobromoethane, **22**=Ethylbenzene, **23**=*m,p*-Xylene, **24**=*o*-Xylene, **25**=Styrene, **26**=Bromoform

Figure 5. Overlaid XICs for empty vials (n=8) run every n=10 samples and a VOCs/BTEX standard at 0.3 µg/L. Carryover was assessed by running an 80-sample sequence (SHS sampling) including calibration curves, spiked tap water samples, and real water samples. Empty vials were run every n=10 samples to monitor the carryover. The insets show zoomed details of the overlaid XICs for empty vials and standard solutions.

Conclusions

The TSQ 9000 triple quadrupole GC-MS/MS system in combination with the TriPlus RSH autosampler configured for SHS and HS-SPME Arrow sampling allows for robust and reliable routine analysis of BTEX and VOCs in drinking water in compliance with the regulatory limits of quantitation, making this configuration ideal for analytical testing laboratories requiring fast and high-throughput testing.

- SHS and HS-SPME sampling significantly reduce the efforts required for sample preparation step and ensure fully automated sample extraction and pre-concentration in a single step.

- SHS sampling provided adequate sensitivity to meet the regulatory limits set at 0.3 µg/L for the investigated VOCs and BTEX, with the exception of vinyl chloride. For this compound, the SPME Arrow technique was used to reach the regulatory limits set at 0.1 µg/L.

- Acceptance criteria for linearity of the method were met for both SHS and HS-SPME sampling techniques with average R^2 values of 0.999 and 0.996, respectively. AvCF %RSD was found to be <9% and concentration deviations were found within 25% of the expected values at the lowest calibration point.

- Calculated MDLs resulted in the range of 0.01–0.13 µg/L with recovery between 60 and 130%. HS-SPME Arrow sampling is required to reach lower limits of detection compared to the SHS sampling technique, especially for critical VOCs such as vinyl chloride.

- System stability evaluation over time demonstrated stable retention times, as well as absolute peak area (RSD <11 %), calculated concentrations, and ion ratios within 15% the expected values.

- Less than 0.01% carryover could be detected for both sampling technique when bracketing samples with empty vials across 48-hour sequences.

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Appendix 1

Table A1. HS, HS-SPME Arrow, and GC-MS/MS experimental conditions for the analysis of VOCs

TriPus RSH - HS Autosampler parameters	
Injection type	HS
Syringe volume (mL) and type	2.5, HT gas-tight syringe (P/N 365Q2131)
Sample draw (mL)	1
Sampling depth mode	Standard
Agitator temperature (°C)	80
Incubation time (min)	25
Agitation speed (rpm)	250
Syringe temperature (°C)	90
Fill strokes volume (mL)	1.5
Fill strokes counts	3
Filling delay (s)	1
Pre-injection syringe flush	Enabled
Post-injection syringe flush (s)	120
Filling speed (mL/min)	30
Injection speed (mL/min)	30
Injection depth (mm)	45
Penetration speed (mm/s)	25
Pre-injection delay (s)	1
Post-injection delay (s)	3

iC-SSL parameters	
Injection temperature (°C)	230
Liner	SPME Arrow Liner Straight, 1.7 mm i.d. (P/N 453A0415)
Inlet module and mode	SSL, split
Split flow (mL/min)	10
Split ratio	20:1
Septum purge flow (mL/min)	5, constant
Carrier gas, flow (mL/min)	H_2, 0.5

TRACE 1310 GC parameters	
Oven temperature program	
Temperature (°C)	50
Hold time (min)	4
Rate (°C/min)	40
Temperature 2 (°C)	130
Hold time (min)	2
GC run time (min)	8
Column	
TraceGOLD TG-624 SilMS	20 m, 0.18 mm, 1.0 µm (P/N 26059-4950)

Appendix 1 *(continued)*

Table A1. HS, HS-SPME, and GC-MS/MS experimental conditions for the analysis of VOCs

TSQ 9610 Mass Spectrometer parameters	
Transfer line temperature (°C)	280
Ion source type and temperature (°C)	ExtractaBrite, 300
Ionization type	EI
Emission current (µA)	50
Electron energy (eV)	70
Aquisition mode	timed-SIM (*t*-SIM)
Tuning parameters	EI SmartTune

TriPus RSH - SPME Arrow Autosampler parameters	
Injection type	SPME Arrow
Fiber type	Carbon WR/PDMS (P/N 36SA12B1)
Incubation / extraction temperature (°C)	40
Incubation time (min)	20
Agitation speed (rpm)	500
Extraction speed (rpm)	1000
Needle speed in vial (mm/s)	20
Needle depth in vial mode and depth (mm)	Custom, 20
Injection depth (mm)	70
Penetration speed (mm/s)	60
Desorption time (min)	1
Conditioning temperature (°C)	270
Pre-desorption conditioning time (min)	1
Post-desorption conditioning time (min)	3

iC-SSL parameters	
Injection temperature (°C)	270
Liner	SPME Arrow Liner Straight, 1.7 mm i.d. (P/N 453A0415)
Inlet module and mode	SSL, split
Split flow (mL/min)	5
Split ratio	10:1
Septum purge flow (mL/min)	Off
Carrier gas, flow (mL/min)	H_2, 0.5

TRACE 1310 GC parameters	
Oven temperature program	
Temperature (°C)	35
Hold time (min)	0.1
Rate (°C/min)	50
Temperature 2 (°C)	125
Hold time (min)	4
Rate (°C/min)	40
Temperature 2 (°C)	130
Hold time (min)	2
GC run time (min)	9

Appendix 2

Table A2. List of target VOCs, retention times (RT, min), and SIM ions (*m/z*)

Compound	RT (min) - HS	RT (min) - SPME	Quantifier ion (*m/z*)	Qualifier ion (*m/z*)
Difluorochloromethane (Freon 22)	1.00	0.81	51	67
Vinyl chloride	1.14	1.05	62	64
Trichloromonofluoromethane (Freon 11)	1.45	1.39	101	103
1,1-Dichloro-1-fluoroethane (Freon 141)	1.57	1.53	81	83
1,1,2-Trichloro-1,2,2-trifluoro-ethane (Freon 113)	1.70	1.66	101	151
trans-1,2-Dichloroethylene	2.13	2.11	61	96
1,1-Dichloroethane	2.45	2.42	63	65
cis-1,2-Dichloroethylene	2.92	2.91	61	96
Chloroform	3.26	3.26	83	85
Methylchloroform	3.43	3.42	97	99
Carbon tetrachloride	3.60	3.60	117	119
Benzene	3.88	3.85	78	77
1,2-Dichloroethane	3.94	3.95	62	64
Trichloroethylene	4.62	4.72	130	132
1,2-Dichloropropane	4.84	4.97	63	62
Bromodichloromethane	5.06	5.21	83	85
Toluene	5.58	5.75	91	92
1,1,2-Trichloroethane	5.85	6.04	97	83
Tetrachloroethylene	5.88	6.07	166	164
Dibromochloromethane	6.06	6.24	129	127
1,2-Dibromoethane	6.11	6.31	107	109
Ethylbenzene	6.48	6.67	91	106
m+p-Xylene	6.57	6.76	91	106
o-Xylene	6.84	7.03	91	106
Styrene	6.83	7.04	104	103
Bromoform	6.98	7.18	173	171

Appendix 3

Table A3. Calibration ranges, as well as R^2, AvCF %RSD, calculated MDL (µg/L), recovery (%), and absolute peak area %RSD for VOCs and BTEX by using SHS sampling

Peak name	SHS sampling						
	Retention time (min)	Calibration range (µg/L)	Coefficient of determination (R^2)	AvCF %RSD	Calculated MDL (µg/L)	Recovery (%)	Absolute peak area %RSD
Difluorochloromethane (Freon 22)	1.00	0.5–20	0.9989	3.4	0.12	88	10.8
Vinyl chloride	1.14	0.5–20	0.9998	3.5	0.09	110	5.3
Trichloromonofluoromethane (Freon 11)	1.45	0.5–20	0.9999	1.1	0.05	88	3.6
1,1-Dichloro-1-fluoroethane (Freon 141)	1.57	0.5–20	0.9999	1.1	0.04	90	2.8
1,1,2-Trichloro-1,2,2-trifluoro-ethane (Freon 113)	1.70	0.5–20	0.9998	1.3	0.05	95	3.6
trans-1,2-Dichloroethylene	2.13	0.5–20	0.9995	2.2	0.05	106	3.4
1,1-dichloroethane	2.45	0.5–20	1.0000	0.6	0.06	95	4.0
cis-1,2-dichloroethylene	2.92	0.5–20	0.9999	1.2	0.04	120	2.7
Chloroform	3.26	0.5–20	0.9999	1.1	0.06	118	3.6
Methylchloroform	3.43	0.5–20	0.9997	1.8	0.09	111	6.3
Carbon tetrachloride	3.60	0.5–20	0.9990	3.3	0.13	105	9.1
1,2-Dichloroethane	3.94	0.5–20	1.0000	0.6	0.10	108	6.7
Trichloroethylene	4.62	0.5–20	0.9995	5.2	0.07	108	4.6
1,2-Dichloropropane	4.84	0.5–20	0.9998	1.3	0.13	114	8.2
Bromodichloromethane	5.06	0.5–20	0.9999	1.0	0.11	123	8.2
1,1,2-Trichloroethane	5.85	0.5–20	0.9996	2.1	0.07	130	3.9
Tetrachloroethylene	5.88	0.5–20	0.9994	2.6	0.07	119	4.6
Dibromochloromethane	6.06	0.5–20	0.9994	2.4	0.13	107	9.7
1,2-dibromoethane	6.11	0.5–20	0.9997	1.9	0.11	117	8.6
Bromoform	6.98	0.5–20	0.9995	5.4	0.10	112	6.3
Benzene	3.88	0.3–3.0	0.9999	0.8	0.03	96	3.5
Toluene	5.58	0.3–3.0	0.9999	1.1	0.02	96	2.2
Ethylbenzene	6.48	0.3–3.0	1.0000	0.7	0.02	95	2.1
m+*p*-Xylene	6.57	0.3–3.0	0.9999	1.0	0.01	98	1.7
o-Xylene	6.84	0.3–3.0	0.9998	1.2	0.02	99	2.9
Styrene	6.83	0.3–3.0	0.9999	0.9	0.03	96	3.5

Appendix 3 *(continued)*

Table A3. Calibration ranges, as well as R^2, AvCF %RSD, calculated MDL (µg/L), recovery (%), and absolute peak area %RSD for VOCs and BTEX by using HS-SPME Arrow sampling

Peak name	HS-SPME sampling						
	Retention time (min)	Calibration range (µg/L)	Coefficient of determination (R^2)	AvCF %RSD	Calculated MDL (µg/L)	Recovery (%)	Absolute peak area %RSD
Difluorochloromethane (Freon 22)	0.81	0.1–2.0	< 0.950	n.a.	> 20	n.a.	n.a.
Vinyl chloride	1.05	0.1–2.0	0.9994	4.9	0.02	93	8
Trichloromonofluoromethane (Freon 11)	1.39	0.1–2.0	0.9931	8.4	0.02	97	4.3
1,1-Dichloro-1-fluoroethane (Freon 141)	1.53	0.1–2.0	0.9948	7.3	0.03	97	6.2
1,1,2-Trichloro-1,2,2-trifluoro-ethane (Freon 113)	1.66	0.1–2.0	0.9943	7.8	0.02	106	6.1
trans-1,2-Dichloroethylene	2.11	0.1–2.0	0.9930	8.5	0.02	95	5.2
1,1-dichloroethane	2.42	0.1–2.0	0.9902	9.7	0.02	95	5.3
cis-1,2-dichloroethylene	2.91	0.1–2.0	0.9970	5.0	0.03	97	4.3
Chloroform	3.26	0.1–2.0	0.9950	11.6	0.02	93	5
Methylchloroform	3.42	0.1–2.0	0.9980	8.1	0.02	97	5.5
Carbon tetrachloride	3.60	0.1–2.0	0.9940	13.1	0.02	100	5.7
1,2-Dichloroethane	3.95	0.1–2.0	0.9930	13.3	0.02	85	4.7
Trichloroethylene	4.72	0.1–2.0	0.9958	6.7	0.02	87	4.1
1,2-Dichloropropane	4.97	0.1–2.0	0.9920	14.0	0.01	86	5.5
Bromodichloromethane	5.21	0.1–2.0	0.9930	13.0	0.03	84	6.2
1,1,2-Trichloroethane	6.04	0.1–2.0	0.9928	6.6	0.04	89	4.5
Tetrachloroethylene	6.07	0.1–2.0	0.9992	3.0	0.01	89	3.3
Dibromochloromethane	6.24	0.1–2.0	0.9911	9.1	0.03	72	5.9
1,2-dibromoethane	6.31	0.1–2.0	0.9955	6.8	0.02	76	5.8
Bromoform	7.17	0.1–2.0	0.9974	8.2	0.03	60	7.0
Benzene	3.87	0.1–2.0	0.9998	1.2	0.05	98	2.6
Toluene	5.75	0.1–2.0	0.9997	1.8	0.07	98	2.4
Ethylbenzene	6.67	0.1–2.0	0.9996	2.0	0.06	98	2.7
m+p-Xylene	6.76	0.1–2.0	0.9997	1.7	0.12	98	2.9
o-Xylene	7.03	0.1–2.0	0.9995	2.0	0.06	99	2.9
Styrene	7.04	0.1–2.0	0.9995	2.1	0.06	99	3.1

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Keywords

Automated sample preparation, TriPlus RSH SMART Sample Prep Station, volatile organic compounds, VOCs, drinking water, surface water, gas chromatography, TRACE 1610 GC, single quadrupole mass spectrometry, ISQ 7610 GC-MS

Goal

The aim of this study is to demonstrate the suitability of the Thermo Scientific™ TriPlus™ RSH SMART VOC Sample Prep Station for the analysis of volatile organic compounds (VOCs) in drinking and surface water by using a fully automated sample preparation workflow.

Introduction

Organic chemicals are widely used as ingredients in household products as well as fuels, industrial uses, and manufacturing. Through inappropriate use or disposal, they are released into the air as gases and can leach into ground water and wastewater. Consequently, they need to be considered as ubiquitous pollutants in the environment. In environmental analysis, classification is usually accomplished using a compound's volatility, either classifying them as volatile or semi-volatile organic compounds (VOCs and SVOCs, respectively). VOCs have a higher vapor pressure and lower water solubility than SVOCs. This compound class includes a variety of chemicals, some of which may have short- and long-term adverse health effects.[1] Environmental agencies worldwide strictly regulate the presence of VOCs in drinking[2] and surface water[3] by establishing the allowed limits and providing analytical methods[1] that may be considered when determining VOCs in water samples. The recent update to the Drinking Water Directive,[2] entered into force in January 2021, is the EU's main law in regulating the contaminant thresholds in drinking water, whereas the Environmental Quality Standard Directive establishes the allowed limits for contaminants in surface water.[3]

One of the main challenges in VOCs analysis is the sample preparation. These compounds are usually present at trace concentrations in a variety of complex matrices; therefore, they need to be extracted and pre-concentrated prior the analysis. Because of their chemical properties, they are also prone to evaporate or degrade, thus having limited stability for analysis. When dealing with VOCs analysis in water, multiple sample preparation techniques can be considered for extracting these compounds, such as solid-phase microextraction (SPME), purge-and-trap (P&T), liquid-liquid extraction (LLE), and headspace analysis (HS). Among these, P&T and HS sampling are the most common techniques for the analysis of aqueous samples. Headspace is a straightforward approach that allows for the extraction of volatile and very volatile compounds from non-volatile matrix in a fast and simple way, without the need for time-consuming sample preparation. Water samples are simply heated and maintained at a constant temperature in closed vials to promote the migration of volatile compounds from the matrix to the vapor phase (headspace). After equilibration, an aliquot of headspace is injected for analysis. Compared to other dynamic techniques like P&T where the volatile compounds are stripped continuously with an inert gas through the sample, the static headspace technique is not affected by foam formation and minimal maintenance of the system is required.

Internal standards are usually added to the sample vials prior to the sample preparation and used to monitor extraction efficiency. To achieve a reliable quantitative analysis, they are used in the data processing to compensate for sample loss, matrix effects, and variability of the detector. When dealing with HS sampling, the sample preparation is minimal, typically consisting of transferring the water sample into a HS vial and adding the ISTDs to a batch of samples before starting the analytical sequence (sample incubation followed by GC analysis). However, with this approach, sample vials may remain on the autosampler tray for hours, especially in case of long sequences, with possible impact on sample integrity and overall data repeatability, affecting quantitative analysis.

With the TriPlus RSH SMART VOC Sample Prep Station, reagents can be added immediately before the sample incubation by using a dedicated dual head configuration (Figure 1). One head is equipped with a liquid tool to dispense the reagents (e.g., ISTD or calibration standard) into the sample vial, whereas the second head moves the vial into the incubator for headspace analysis. The possibility of adding fresh reagents just before the incubation increases the stability of samples, therefore increasing the accuracy of the quantitation of target analytes during data reprocessing. Table 1 shows the absolute peak area %RSD comparison for two batches of samples bracketed by QCs spiked with a VOC mix at 10 ng/mL and ISTD/surrogate solutions. In batch 1 the reagents were automatically spiked before starting the sequence using a dedicated script, whereas in batch 2, the reagents were added to each sample just before incubation, with an improvement of the average RSD from 8.4% to 3.2%.

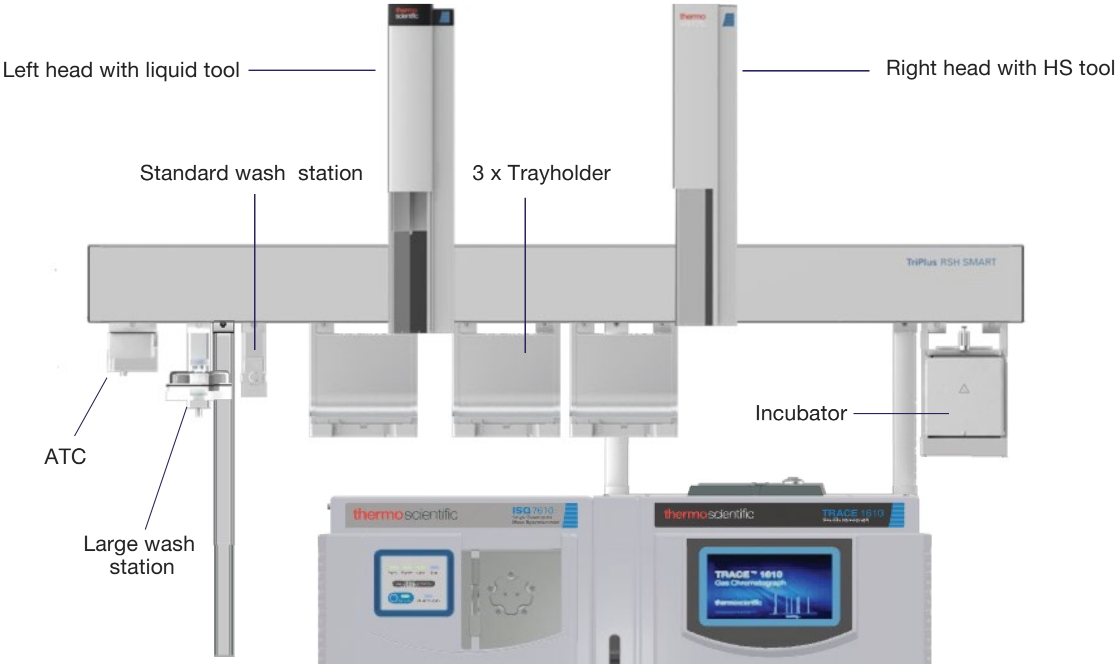


Figure 1. TriPlus RSH SMART VOC Sample Prep Station configuration for automated analysis of VOCs

Table 1. Absolute peak area %RSD comparison between two batches of samples bracketed by QCs spiked with a VOC mix at 10 ng/mL and ISTD/surrogate solutions. In batch 1 the reagents were automatically spiked before starting the sequence, whereas in batch 2 the reagents were added to each sample just before incubation.

	QC absolute peak area %RSD (n=6)	
Peak name	**Batch 1**	**Batch 2**
Dichlorodifluoromethane	5.9	5.7
Vinyl chloride	5.8	8.1
Chloroethane	7.2	2.6
Trichlorofluoromethane	4.8	2.8
1,1-Dichloroethene	5.9	3.6
Methylene chloride	5.1	1.2
1,2-Dichloroethene (Z cis)	5.9	2.9
1,1-Dichloroethane	5.6	1.9
1,2-Dichloroethene (E)	5.9	3.2
Bromochloromethane	8.1	1.5
Chloroform (Trichloromethane)	4.8	1.6
1,1,1-Trichloroethane	5	2
2,2-Dichloropropene	4.9	2.1
Surr Dibromofluoromethane	5	1.5
ISTD Pentafluorobenzene	6.5	3.8
Carbon tetrachloride	5.1	2.5
Benzene	6.1	2.7
1,2-Dichloroethane	5.3	4
ISTD 1,4-Difluorobenzene	6.5	4
Trichloroethene	5.9	3.2
1,2-Dichloropropane	5.7	2
Dibromomethane	7	1.8
Bromodichloromethane	5.3	1.5
Surr Toluene D8	7.2	4.1
1.3-Dichloropropene (Z)	8.5	3.7
Toluene	7.6	4.2
1,1,2-Trichloroethane	5.3	2.9
Tetrachloroethene	7	2.5
1,3-Dichloropropane	7.5	1.7
Dibromochloromethane	6.2	1.4
1,2-Dibromoethane	18.6	2.1
ISTD Chlorobenzene D5	7.6	3.2
Chlorobenzene	7	3.6
1,1,1,2-Tetrachloroethane	6.2	1.4
Ethylbenzene	8.9	4.6
m,p-Xylene	9.7	4.6
o-Xylene	9	4.1
Styrene	9.7	4.5
Bromoform	6.1	2.1
Isopropylbenzene (Cumene)	10.2	4.7
BFB 1-Bromo-4-fluorobenzene	8.6	3.4
1,1,2,2-Tetrachloroethane	4.4	2.1
Bromobenzene	7.1	3.5
1,2,3-Trichloropropane	14.7	3
n-Propylbenzene	12.3	4.4
1,3,5-Trimethylbenzene	12.9	4.7
2-Chlorotoluene	9.8	4.5
4-Chlorotoluene	11.2	3.7
tert-Butylbenzene	13.4	4.5
1,2,4-Trimethylbenzene	12.3	4.6
sec-Butylbenzene	14.4	4.3
4-Isopropyltoluene (*p*-Cymene)	15.3	4.9
1,3-Dicholorobenzene	9.9	2.2
ISTD 1,4-Dichlorobenzene D4	11	2.6
1,4-Dicholorobenzene	9.9	2.7
n-Butylbenzene	17.6	4.2
1,2-Dichlorobenzene	9	2.7
1,2-Dibromo-3-chloropropane	6.7	2.7
1,2,4-Trichlorobenzene	9.4	4.5
Hexachlorobutadiene	17.6	2.7
Naphtalene	8.8	4.3
1,2,3-Trichlorobenzene	8.3	4.3
Average RSD%	**8.4**	**3.2**

By using an automated approach, the analyst is only required to transfer the samples into the headspace vials, place them on the autosampler tray, and place the stock solutions containing the reagents to be dispensed, thus saving valuable analyst time, reducing the risk of human errors, and ensuring a safer laboratory environment with less exposure to harmful chemicals.

The TriPlus RSH SMART VOC Sample Prep Station is capable of processing up to 150 samples unattended. Sample capacity can be further extended up to 210 samples.

In this study, the reliability of an automated workflow including the generation of calibration curves, as well as internal standard addition for analysis of VOCs in drinking and surface water, was evaluated.

Experimental

Instrumentation

In these experiments, a TriPlus RSH SMART VOC Sample Prep Station was used to automate the calibration curve dilution and the internal standard addition by using a pre-compiled sequence of operations that is fully embedded in the Thermo Scientific™ Chromeleon™ 7.3 Chromatography Data System (CDS) for seamless and straightforward method set-up and instrument control (Figure 2). A detailed description of the autosampler configuration, including a complete list of suggested consumables, is reported in Appendix 1.

The TriPlus RSH SMART VOC Sample Prep Station was installed on top of a Thermo Scientific™ TRACE 1610 GC, equipped with a Thermo Scientific™ iConnect™ split/splitless injector working in HeSaver-H_2Safer mode, and coupled to a Thermo Scientific™ ISQ™ 7610 single quadrupole mass spectrometer.

Chromatographic separation was achieved using a Thermo Scientific™ TraceGOLD™ TG-624 SilMS, 20 m × 0.18 mm × 1.0 µm column (P/N 26059-4950). This column provided high inertness and thermal stability with maximum temperatures up to 320 °C. The phase thickness makes this column ideal for volatile organics analysis. Helium was used as carrier gas providing high chromatographic efficiency and inertness. The Thermo Scientific™ Helium Saver technology[4] ensured reduced helium consumption by using a cheaper gas (e.g., nitrogen) for inlet pressurization, analyte vaporization, and transfer to the analytical column and using helium only to feed the chromatographic column for the separation process.

Instrument parameters as well as a complete list of the target compounds, including quantifier and qualifier ions, are reported in Appendix 2.

Data acquisition, processing, and reporting

The TriPlus RSH SMART VOC Sample Prep Station instrument control is fully integrated in Chromeleon 7.3 CDS, ensuring a streamlined automated workflow covering on-line sample preparation, sequence setup, data acquisition, and reporting. The Chromeleon Environmental Analysis Extension Pack for U.S. EPA-based environmental applications provides a comprehensive set of GC-MS eWorkflow™ procedures for quick sequence set-up and reporting templates to make data review and reporting easier. Moreover, with the ever-evolving compliance requirements for data integrity and data security, Chromeleon CDS provides a secure platform for analytical laboratories to comply with modern regulatory guidelines including FDA 21 CFR Part 11 and European Commission (EU) Annex 11.

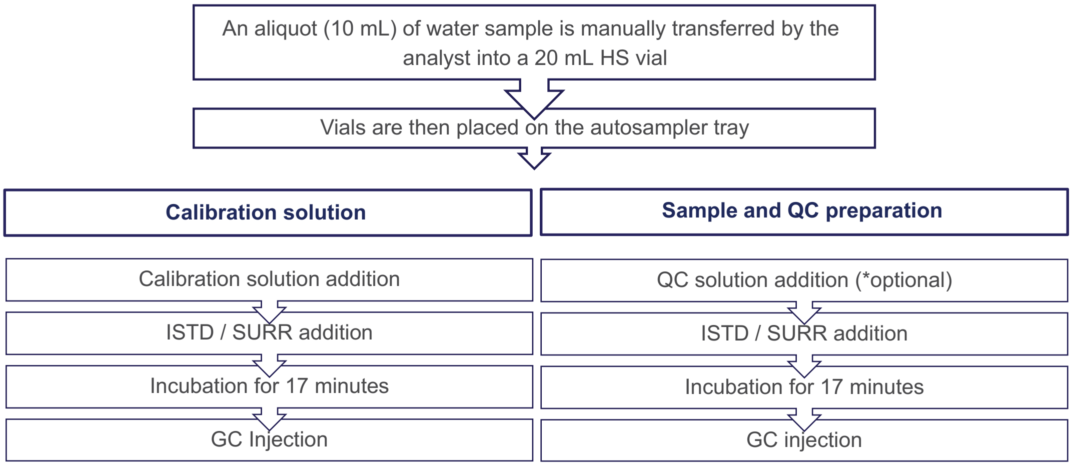


Figure 2. Schematic showing the workflow for automated preparation of calibration solution and addition of ISTD/surrogate mix to sample vials for analysis of VOCs

Standard and sample preparation

Calibration curve preparation

Multi-component standard solutions were purchased from Restek (8260 Volatile Organics Kit, 2000 µg/mL in methanol, P/N 30076) and diluted in methanol (Optima™ LC/MS grade, Fisher Scientific™, P/N A456-1) to obtain:

- Four calibration solutions (20 µg/mL, 2 µg/mL, 0.2 µg/mL, and 0.02 µg/mL)
- Internal standard and surrogate solution (20 µg/mL and 25 µg/mL, respectively).

These stock solutions were placed in the autosampler tray and different aliquots were automatically dispensed by the autosampler into 20 mL screw top headspace vials (P/N 6ASV20-1, caps P/N 6PMSC18-ST2), previously filled with tap water (10 mL) and containing solid sodium thiosulphate (>99,99%, Sigma-Aldrich, P/N 563188) to neutralize any residual chlorine, to produce a 10-point calibration curve and QC samples. The calibration curve ranged from 0.1 to 100 ng/mL according to the scheme reported in Appendix 3.

Sample preparation

Tap water samples and surface water samples were collected from different locations around the Milan metropolitan area. Solid sodium thiosulphate was added immediately after sample collection in the field. Samples were prepared for analysis by transferring 10 mL of the collected water into 20 mL screw top headspace vials.

An aliquot (10 µL) of the internal standard and surrogate solution (20 µg/mL and 25 µg/mL, respectively) was then automatically added by the autosampler to each sample immediately before vial incubation.

Results and discussion

Chromatography

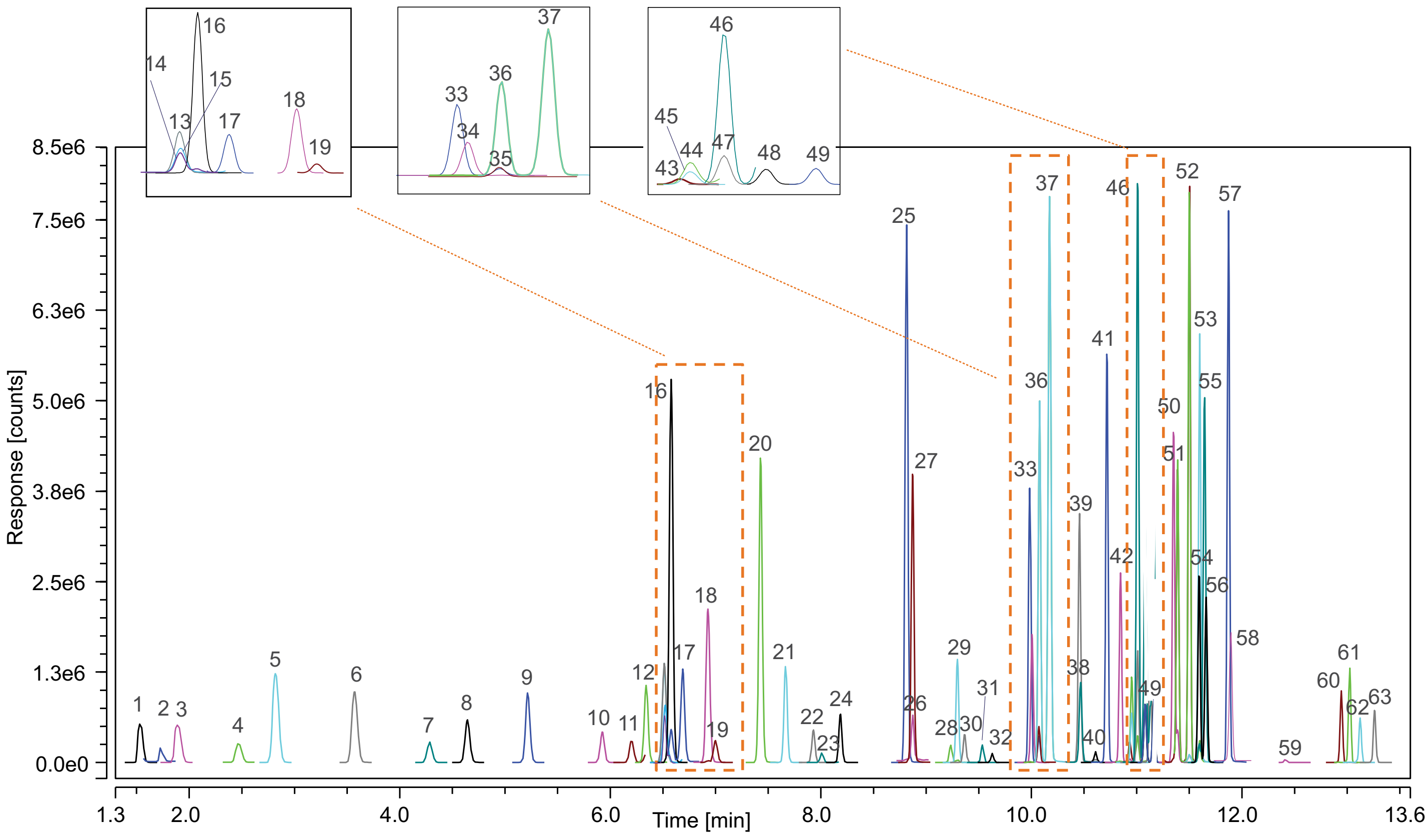
Headspace sampling allowed for the extraction of the target volatile analytes in a fast and simple way without the need for time-consuming sample preparation. A single ion monitoring (SIM) acquisition method allowed for simultaneous acquisition of multiple characteristic ions for each compound of interest, combining sensitivity with high selectivity, and thus ensuring a confident identification and subsequent quantification of analytes.

As an example, the SIM trace of a tap water sample spiked at 10 ng/mL with VOC mix, ISTD (20 ng/mL) and surrogate (25 ng/mL) is shown in Figure 3. The high thermal stability and superior inertness of the TraceGOLD TG-624 SilMS column ensured baseline chromatographic separation in a short analysis time (<14 minutes) for most of the target compounds. Very few exceptions could be identified based on their characteristic *m/z*.

Linearity and method detection limits (MDLs)

Two matrix-matched calibration curves in tap water ranging from 0.1 to 100 ng/mL were automatically diluted by the TriPlus RSH SMART VOC Sample Prep Station and used to evaluate the system repeatability for calibration curve preparation. All target analytes showed a linear trend with coefficient of determination (R^2) > 0.990, relative response factor (RRF) %RSD < 20% and calculated amount within 20% the expected values as reported in Appendix 4. Full range calibration curves (0.1–100 ng/mL) for benzene, dibromomethane, and 1,2,4-trimethylbenzene as well as an extracted ion chromatogram (XIC) showing the quantifier and qualifier ions for a tap water sample spiked at 0.1 ng/mL are reported as an example in Figure 4. The SIM trace showing all the target compounds in a tap water sample spiked with VOC mix at 0.1 ng/mL is also presented in Figure 4.

MDLs and precision were assessed using n=10 replicates of matrix-matched water samples spiked with VOC solution at 0.5 ng/mL, ISTD (20 ng/mL) and surrogate mix (25 ng/mL). Calculated MDLs were ≤ 0.17 ng/mL, with calculated absolute peak area %RSD < 20% for all compounds (Appendix 4).



Peak name	Peak no.
Dichlorodifluoromethane	1
Chloromethane	2
Vinyl chloride	3
Chloroethane	4
Trichlorofluoromethane	5
1,1-Dichloroethene	6
Methylene chloride	7
1,2-Dichloroethene (Z)	8
1,1-Dichloroethane	9
1,2-Dichloroethene (E)	10
Bromochloromethane	11
Chloroform (Trichloromethane)	12
1,1,1-Trichloroethane	13
2,2-Dichloropropene	14
Surr Dibromofluoromethane	15
ISTD Pentafluorobenzene	16
Carbon tetrachloride	17
Benzene	18
1,2-Dichloroethane	19
ISTD 1,4-Difluorobenzene	20
Trichloroethene	21
1,2-Dichloropropane	22
Dibromomethane	23
Bromodichloromethane	24
Surr Toluene D8	25
1.3-Dichloropropene (Z)	26
Toluene	27
1,1,2-Trichloroethane	28
Tetrachloroethene	29
1,3-Dichloropropane	30
Dibromochloromethane	31
1,2-Dibromoethane	32

Peak name	Peak no.
ISTD Chlorobenzene D5	33
Chlorobenzene	34
1,1,1,2-Tetrachloroethane	35
Ethylbenzene	36
m,p-Xylene	37
o-Xylene	38
Styrene	39
Bromoform	40
Isopropylbenzene (Cumene)	41
BFB 1-Bromo-4-fluorobenzene	42
1,1,2,2-tetrachloroethane	43
Bromobenzene	44
1,2,3-Trichloropropane	45
n-Propylbenzene	46
1,3,5-Trimethylbenzene	47
2-Chlorotoluene	48
4-Chlorotoluene	49
tert-Butylbenzene	50
1,2,4-Trimethylbenzene	51
sec-Butylbenzene	52
4-Isopropyltoluene (*p*-Cymene)	53
1,3-Dicholorobenzene	54
ISTD 1,4-Dichlorobenzene D4	55
1,4-Dicholorobenzene	56
n-Butylbenzene	57
1,2-Dichlorobenzene	58
1,2-Dibromo-3-chloropropane	59
1,2,4-Trichlorobenzene	60
Hexachlorobutadiene	61
Naphtalene	62
1,2,3-Trichlorobenzene	63

Figure 3. SIM trace showing an example of the chromatographic separation obtained for a tap water sample spiked at 10 ng/mL with VOC mix, ISTD (20 ng/mL), and surrogate (25 ng/mL)

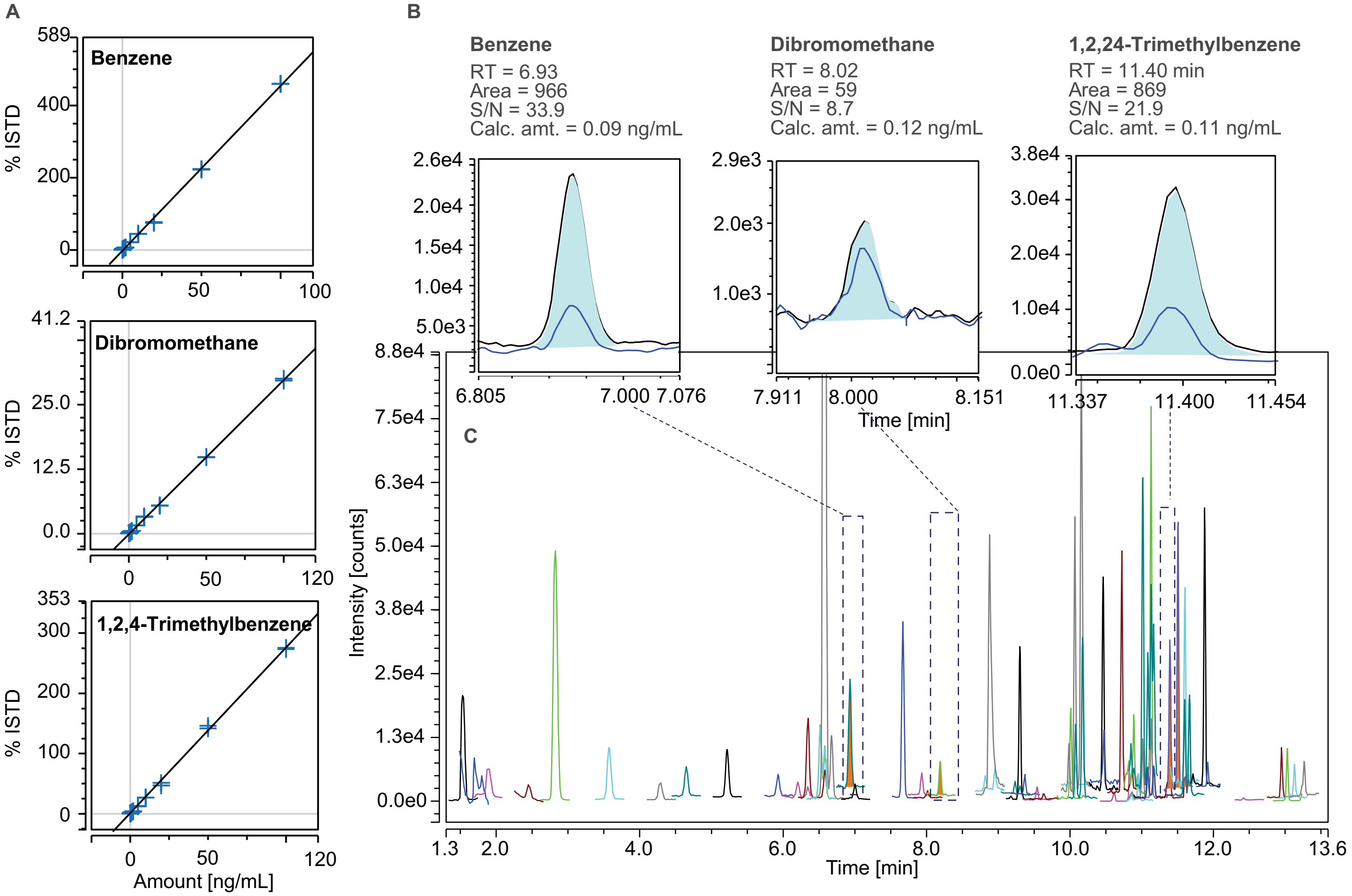


Figure 4. Full range calibration curves (0.1–100 ng/mL) for benzene, dibromomethane, and 1,2,4-trimethylbenzene (A), XIC showing the quantifier and qualifier ions for a tap water sample spiked at 0.1 ng/mL (B), and SIM trace showing the target compounds in a tap water sample spiked with a VOC mix at the lowest calibration point (0.1 ng/mL), ISTD (20 ng/mL) and surrogates (25 ng/mL) (C)

Inter-day repeatability

Analytical testing laboratories need to process a high number of samples every day. Therefore, it is critical that the instrument performs consistently every day.

The repeatability of the TriPlus RSH SMART VOC Sample Prep Station and system performance for everyday analysis were evaluated over six days of continuous operation by preparing three batches of samples (n=44 samples each) consisting of blank matrix, a calibration set ranging from 0.1 to 100 ng/mL, matrix-matched QCs spiked with VOC standard solution at 10 ng/mL bracketing series of n=5 samples of tap and surface water samples collected in different locations in the Milan area. Samples were spiked with internal standard solution and surrogate at 20 ng/mL and 25 ng/mL, respectively.

The precise mechanical control of the TriPlus RSH SMART VOC Sample Prep Station ensured reproducible addition of both the ISTD/surrogate solution as well as the VOC mix with average absolute peak area %RSD across the entire evaluation period <20%, QC calculated amount with respect to the batch ran on day 1 within 20%, and calculated recovery within 70–130%, with the only exception of 1,2-dibromo-3-chloropropane for which the % recovery was 132% (Appendix 5). As an example, the ISTD/surrogate peak area %RSD for the analyzed samples across the batches across the evaluation period is reported in Figure 5.

The analyzed samples results were compliant with the allowed threshold limits established by the current EU directives on the quality of water intended for human consumption and for the surface waters. Quantitative results are detailed in Appendix 6.

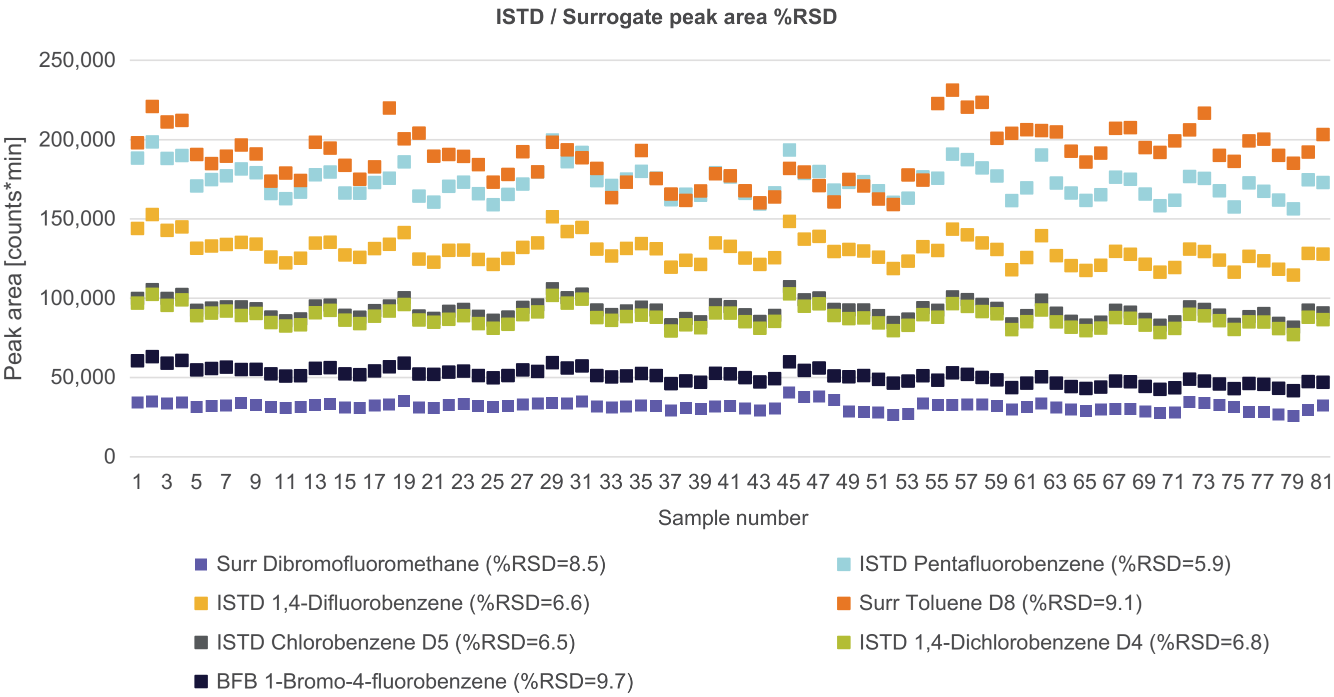


Figure 5. ISTD/surrogate peak area %RSD across the samples in the evaluation period of six working days

Conclusions

The results of these experiments demonstrate that the automated sample preparation capability of the TriPlus RSH SMART VOC Sample Prep Station coupled to the ISQ 7610 GC-MS system provides an ideal solution for water testing laboratories looking to improve productivity and deliver confident results.

- Static headspace is a convenient solventless extraction technique for volatiles in water with almost no sample preparation required.
- Unattended operations of up to 210 samples can be achieved with the automated calibration dilution and ISTD addition workflows.
- The automated addition of fresh reagent just before the incubation increases the stability of ISTD/surrogates mix, therefore improving the accuracy of the quantitation of target analytes during data reprocessing.
- The TriPlus RSH SMART VOC Sample Prep Station ensures increased sample integrity for highly reliable quantitative analysis, and reduced errors or possible cross-contaminations, maximizing the productivity of the laboratory. Additionally, it allows saving valuable analyst time and improving safety by limiting the user's exposure to toxic chemicals.
- The integrated control for both autosampler and GC-MS in a single CDS ensures a streamlined automated workflow from on-line sample preparation to sequence setup, data acquisition, and reporting.
- Suitability of headspace sampling for analysis of VOCs was demonstrated with $R^2 > 0.990$, RRF %RSD < 20%, and calculated amount within 20% of the spiked concentration.
- Inter-day reproducibility was demonstrated by running three batches of samples bracketed with QCs. Average absolute peak area %RSD across the entire evaluation period was <20%, the QC calculated amount was within 20% of the expected value, and the calculated recovery was within 70–130%, with the only exception of 1,2-dibromo-3-chloropropane for which the % recovery was 132.
- Reliable quantitative analysis was achieved for drinking water samples and surface water samples analyzed in three different batches across six working days. All the sample results were compliant with the thresholds set by the current EU regulation.

References

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2. Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption, EUR-Lex - 32020L2184 - EN - EUR-Lex (europa.eu)
3. Directive 2008/105/ec of the european parliament and of the council of 16 December 2008 on environmental quality standards in the field of water policy, https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008L0105
4. Thermo Fisher Scientific, Technical Note 001218: Addressing gas conservation challenges when using helium or hydrogen as GC carrier gas, https://assets.thermofisher.com/TFS-Assets/CMD/Technical-Notes/tn-001218-gc-hesaver-h2safer-trace1600-tn001218-na-en.pdf

Appendix 1. TriPlus RSH SMART VOC Sample Prep Station configuration and list of suggested consumables

TriPlus RSH SMART VOC Sample Prep Station configuration*	Part number
TriPlus RSH SMART VOC Sample Prep Station including:	1R77010-2010
• mounting brackets for TRACE 1600/1610 GC (P/N 1R77010-1005)	
• one extra single leg for TRACE 1600/1610 GC, 667 mm (P/N 1R77010-1141)	
• one Automatic Tool Change Station (ATC) Station (P/N 1R77010-1019)	
• one universal liquid syringe tool, for syringes of 0.5, 1.0, 5, 10, 25, 50 or 100 µL with a 57 mm needle length (P/N 1R77010-1007)	
• two 100 µL SMART syringes, 57 mm needle length, 26S gauge, cone needle type (P/N 365H2141-SM)	
• three tray holders (P/N 1R77010-1021)	
• one VT54 tray, for 54 vials of 2 mL (P/N 1R77010-1023)	
• one standard washing station with 5 x 10 mL vials (P/N 1R77010-1029)	
• one large wash station for 2 × 100 mL solvent bottles and one waste position (P/N 1R77010-1030)	
• one headspace tool for 2.5 mL syringe (P/N 1R77010-1013)	
• two vial tray R60 aluminum tray for 60 vials of 10/20 mL (P/N 1R77010-1025)	
• two VT 15 trays, for 15 vials of 10/20 mL (P/N 1R77010-1022)	
• one Incubator/Agitator (P/N 1R77010-103)	
• two HT 2.5 mL GT SMART syringes (P/N 365L2321-SM)	
Suggested consumables	**Part number**
Thermo Scientific™ GC SMART Gas tight syringe, 100 µL, Fixed needle, 57 mm length, 26s gauge, Cone	365H2161-SM
Thermo Scientific™ GC SMART Gas tight syringe, 2.5 mL, Fixed needle, 65 mm length, 23 gauge, Side hole	365L2321-SM
Thermo Scientific™ SureSTART™ 20 mL Glass screw top headspace vials, Level 2 High-Throughput Applications	6ASV20-1
Thermo Scientific™ SureSTART™ 18 mm Precision screw caps, Level 3 High Performance Applications	6PMSC18-ST2
TraceGOLD TG-624SilMS column, 20 m × 0.18 mm × 1.0 µm	26059-4950
Thermo Scientific™ Deactivated direct straight liner, 1.2 mm ID, 78.5 mm, 5/P	453A1335

*This configuration provides a 150-vial capacity.

For more details about orders and quotations, please refer to your Thermo Fisher Scientific sales representatives.

Appendix 2. Instrument parameters and list of the target compounds, including quantifier and qualifier ion

TriPlus RSH SMART VOC Sample Prep Station parameters

ISTD addition	
ISTD volume (µL)	10
ISTD fill speed (µL/s)	2
ISTD dispense speed (µL/s)	5
ISTD rinsing cycles	1
ISTD rinsing volume (µL)	20
ISTD filling stokes cycles	4
ISTD filling stokes volume (µL)	20
Sample vial penetration depth (mm)	20
Syringe pre-cleaning cycles	1
Syringe pre-cleaning volume (methanol)	70%
Syringe post-cleaning cycles	1
Syringe post-cleaning volume (isopropanol)	70%
Calibration reagent	
Reagent volume (µL)	According to table in Appendix 3
Reagent fill speed (µL/s)	10
Reagent dispense speed (µL/s)	25
Reagent rinsing cycles	1
Reagent rinsing volume (µL)	Reagent volume
Reagent filling stokes cycles	4
Regaent filling stokes volume (µL)	Reagent volume
Sample vial penetration depth (mm)	20
Syringe pre-cleaning cycles	1
Syringe pre-cleaning volume (methanol)	70%
Syringe post-cleaning cycles	1
Syringe post-cleaning volume (isopropanol)	70%
Syringe	Thermo Scientific™ GC SMART Gas tight syringe, 100 µL (P/N 365H2161-SM)

Injection volume (µL)	1,000
Syringe temperature (°C)	80
Incubation temperature (°C)	60
Incubation time (min)	17
Agitation speed (rpm)	750
Sample vial penetration depth (mm)	25
Pre-filling sample vial	TRUE
Pre-filling volume (%)	90
Sample fill speed (incubation temperature) (µL/s)	100
Sample filling stokes counts	1
Sample filling stokes volume (mL)	1,000
Delay after filling strokes (s)	10
Sample post-aspirate delay (s)	0
Injector penetration depth (mm)	45
Injection speed (µL/s)	500
Pre-injection delay (s)	0
Post-injection delay (s)	0
Pre-injection syringe purge time (s)	5
Post-injection syringe purge time (s)	150
Analysis time (min)	25
Syringe	Thermo Scientific™ GC SMART Gas tight syringe, 2.5 mL (P/N 365L2321-SM)

TRACE 1610 GC parameters

iC-SSL HeSaver - H_2Safer	
Temperature (°C)	80
Liner	SSL direct straight liner (P/N 453A1335)
Inlet module and mode	SSL upgraded to HeSaver - H_2Safer, split
Split flow (mL/min)	10
Septum purge flow (mL/min)	5, constant
Hydrogen delay (min)	0.15
Carrier gas, flow (mL/min)	He, 0.3

Oven temperature program	
Temperature (°C)	35
Hold time (min)	3
Rate (°C/min)	12
Temperature 2 (°C)	85
Rate (°C/min)	25
Temperature 3 (°C)	260
Hold time (min)	3
GC run time (min)	17.167
Oven equilibration time (min)	0.2
Ready delay (min)	1.2
Analytical column	
TraceGOLD TG-624SilMS	20 m × 0.18 mm × 1.0 µm (P/N 26059-4950)

ISQ 7610 mass spectrometer parameters	
Transfer line temperature (°C)	270
Ion source type and temperature (°C)	Thermo Scientific™ ExtractaBrite™, 280
Ionization type	EI
Emission current (µA)	50
Aquisition mode	SIM
Tuning parameters	BFB Tune

Compound name	RT (min)	Quantitation ion (*m/z*)	Confirming ion 2 (*m/z*)	Confirming ion 3 (*m/z*)
Dichlorodifluoromethane	1.54	85	87	
Chloromethane	1.72	50	52	
Vinyl chloride	1.88	62	64	
Chloroethane	2.47	64	66	
Trichlorofluoromethane	2.82	101	103	
1,1-dichloroethene	3.58	61	96	63
Methylene chloride	4.3	84	86	49
1,2-Dichloroethene (Z cis)	4.65	96	61	98
1,1 Dichloroethane	5.22	63	65	
1,2-Dichloroethene (E)	5.94	96	91	98
Bromochloromethane	6.18	49	130	128
Chloroform (Trichloromethane)	6.39	83	85	
2,2-Dichloropropene	6.51	61	99	
1,1,1,-Trichloroethane	6.53	97	61	
Surr Dibromofluoromethane	6.53	111	113	192
ISTD Pentafluorobenzene	6.58	168	99	137
Carbon tetrachloride	6.69	117	119	
Benzene	6.94	78	77	
1,2-dichlroethane	7.01	62	64	98
ISTD 1,4-Difluorobenzene	7.44	114	63	
Trichloroethene	7.67	95	130	97
1,2-Dichloropropane	7.94	63	112	
Dibromomethane	8.02	93	95	174
Bromodichloromethane	8.2	83	85	
Surr Toluene D8	8.82	98	100	
1,3-Dichloropropene (Z)	8.87	39	75	77
Toluene	8.89	91	92	
1,1,2-Trichloroethane	9.24	83	97	85
Tetrachloroethene	9.31	164	129	131
1,3-Dichloropropane	9.38	76	78	
Dibromochloromethane	9.54	129	127	
1,2-Dibromoethane	9.64	107	109	
ISTD Chlorobenzene D5	9.99	117	119	
Chlorobenzene	10.02	112	77	114
1,1,1,2-Tetrachloroethane	10.08	131	133	119
Ethylbenzene	10.08	91	106	
m,p-Xylene	10.18	91	106	
o-Xylene	10.47	91	106	
Styrene	10.48	78	103	104
Bromoform	10.62	173	175	254
Isopropylbenzene (Cumene)	10.72	105	120	
BFB 1-Bromo-4-fluorobenzene	10.85	95	174	176
1,1,2,2-tetrachloroethane	10.95	83	131	85
1,2,3-Trichloropropane	10.95	77	75	
Bromobenzene	10.96	156	77	158
1,3,5-Trimethylbenzene	11	120	105	
n-Propylbenzene	11.02	91	120	92
2-Chlorotoluene	11.09	126	91	
4-Chlorotoluene	11.16	126	91	
tert-Butylbenzene	11.36	119	91	134
1,2,4-Trimethylbenzene	11.4	105	120	
sec-Butylbenzene	11.51	105	134	
4-Isopropyltoluene (*p*-Cymene)	11.6	119	134	
1,3-Dicholorobenzene	11.6	146	111	148
ISTD 1,4-Dichlorobenzene D4	11.64	150	152	
1,4-Dicholorobenzene	11.67	146	111	148
n-Butylbenzene	11.89	91	92	134
1,2-Dibromo-3-chloropropane	12.5	157	155	
1,2,4-Trichlorobenzene	12.95	180	182	145
Hexachlorobutadiene	13.03	225	223	227
Naphtalene	13.11	128		
1,2,3-Trichlorobenzene	13.27	180	182	145

Appendix 3. Schematics for automated calibration curve preparation

Calibration level	Concentration in vial (ng/mL)	Bulk calibration solution (µg/mL)	Spiking amount (µL)	ISTD / Surrogate concentration in vial (ng/mL)	Bulk ISTD / Surrogate solution (µg/mL)	ISTD/ Surrogate spiking amount (µL)
Blank	--					
1	0.1	0.02	50	20 / 25	20 / 25	10
2	0.2	0.02	100	20 / 25	20 / 25	10
3	0.5	0.2	25	20 / 25	20 / 25	10
4	1	0.2	20	20 / 25	20 / 25	10
5	2	0.2	100	20 / 25	20 / 25	10
6	5	2	25	20 / 25	20 / 25	10
7	10	2	50	20 / 25	20 / 25	10
8	20	2	100	20 / 25	20 / 25	10
9	50	20	25	20 / 25	20 / 25	10
10	100	20	50	20 / 25	20 / 25	10

Appendix 4. Coefficient of determination (R^2), relative response factor (RRF) %RSD, calculated amount (ng/mL) and absolute peak area %RSD at MDL (0.5 ng/mL, n=10)

Peak name	RT (min)	Linear range (ng/mL)	R^2	AvCF %RSD	RRF% RSD	Calculated MDL (ng/mL)	Absolute peak area %RSD at MDL (n=10)
Dichlorodifluoromethane	1.53	2-100	0.999	5	15.2	0.11	5.6
Chloromethane	1.73	2-100	0.998	6	14.4	0.17	6.8
Vinyl chloride	1.89	0.1-100	0.999	4.3	16.6	0.04	5
Chloroethane	2.47	0.1-100	1	3.6	9.3	0.04	4.5
Trichlorofluoromethane	2.82	1-100	0.999	4.2	13.9	0.1	4.9
1,1-Dichloroethene	3.57	0.1-100	0.999	6.4	9.5	0.02	4.1
Methylene chloride	4.28	0.1-100	0.999	4	15.4	0.03	2.9
1,2-Dichloroethene (Z)	4.65	0.1-100	0.998	7	10.4	0.02	3.5
1,1-Dichloroethane	5.22	0.1-100	0.999	5	9.8	0.02	3.2
1,2-Dichloroethene (E)	5.93	0.1-100	0.998	7.2	10.8	0.02	4
Bromochloromethane	6.2	0.1-100	1	3.3	9.2	0.04	3.1
Chloroform (Trichloromethane)	6.35	0.1-100	1	3.5	19	0.03	3
1,1,1-Trichloroethane	6.51	0.1-100	0.999	4.9	10.8	0.01	2.5
2,2-Dichloropropene	6.52	0.1-100	0.999	3.8	12.2	0.04	4.2
Surr Dibromofluoromethane	6.53	--	--	--	--	--	3.3
ISTD Pentafluorobenzene	6.58	--	--	--	--	--	3.6
Carbon tetrachloride	6.69	0.1-100	0.999	4.7	10.6	0.02	3.1
Benzene	6.93	0.1-100	0.999	6.5	10.8	0.01	3.3
1,2-Dichloroethane	7	0.1-100	0.999	4.1	10.6	0.03	3.7
ISTD 1,4-Difluorobenzene	7.43	--	--	--	--	--	4
Trichloroethene	7.67	0.5-100	0.999	4.8	12.6	0.02	3.7
1,2-Dichloropropane	7.93	0.1-100	0.999	5.2	9.7	0.02	3.5
Dibromomethane	8.01	0.1-100	0.999	3.6	11.5	0.05	4.1
Bromodichloromethane	8.19	0.1-100	0.999	3.7	10	0.04	3
Surr Toluene D8	8.82	--	--	--	--	--	4.1
1,3-Dichloropropene (Z)	8.87	0.5-100	0.999	5.1	14.5	0.08	5
Toluene	8.87	0.2-100	0.997	7.7	13.4	0.12	6.2

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Appendix 4. Continued from previous page

Peak name	RT (min)	Linear range (ng/mL)	R^2	AvCF %RSD	RRF% RSD	Calculated MDL (ng/mL)	Absolute peak area %RSD at MDL (n=10)
1,1,2-Trichloroethane	9.24	0.1-100	0.999	3.7	10.6	0.05	4.7
Tetrachloroethene	9.3	0.2-100	0.999	5.2	15.6	0.03	4.5
1,3-Dichloropropane	9.37	0.1-100	0.999	4.1	10.3	0.02	4.5
Dibromochloromethane	9.54	0.1-100	0.999	4.4	12.3	0.03	5.2
1,2-Dibromoethane	9.63	0.1-100	0.999	3.9	12.9	0.04	4.2
ISTD Chlorobenzene D5	9.99	--	--	--	--	--	4.1
Chlorobenzene	10.01	0.1-100	0.998	7.1	10.8	0.01	4.7
1,1,1,2-Tetrachloroethane	10.08	0.1-100	0.999	4.9	11.3	0.06	3.3
Ethylbenzene	10.08	0.1-100	0.994	13.7	15	0.01	4.1
m,p-Xylene	10.18	0.2-50	0.99	17.3	12	0.01	4.9
o-Xylene	10.46	0.1-100	0.995	12.3	17.9	0.01	4.9
Styrene	10.47	0.2-100	0.995	12.6	18.2	0.01	4.5
Bromoform	10.61	0.1-100	0.999	6.1	13	0.07	6.7
Isopropylbenzene (Cumene)	10.72	0.1-100	0.999	4.4	10.3	0.02	4.1
BFB 1-Bromo-4-fluorobenzene	10.85	--	--	--	--	--	4.6
1,1,2,2-tetrachloroethane	10.94	0.5-100	0.999	3.7	10.5	0.18	9.7
Bromobenzene	10.96	0.1-100	0.996	9.1	17.7	0.06	5.1
1,2,3-Trichloropropane	10.96	0.2-100	0.999	4.9	18.6	0.02	4.5
n-Propylbenzene	11.01	0.1-100	0.999	4.8	10.1	0.02	4.5
1,3,5-Trimethylbenzene	11.01	0.1-100	0.999	4.3	10.5	0.03	4.8
2-Chlorotoluene	11.08	0.1-100	0.998	6.6	10.3	0.05	5.1
4-Chlorotoluene	11.17	0.2-100	0.998	6.3	12.8	0.05	5.7
tert-Butylbenzene	11.35	0.1-100	0.999	4.9	10.9	0.05	5.3
1,2,4-Trimethylbenzene	11.39	0.1-100	0.999	4.9	12.5	0.03	6.7
sec-Butylbenzene	11.5	0.1-100	0.999	4.8	10.2	0.01	4.2
4-Isopropyltoluene (*p*-Cymene)	11.6	0.1-100	0.999	4.9	12.9	0.02	5.2
1,3-Dicholorobenzene	11.6	0.2-100	0.993	12.5	15.2	0.04	5.4
ISTD 1,4-Dichlorobenzene D4	11.65	--	--	--	--	--	4.2
1,4-Dicholorobenzene	11.67	0.2-100	0.993	12.2	13.7	0.05	5.4
n-Butylbenzene	11.88	0.1-100	0.999	4.7	10.7	0.02	5.1
1,2-Dichlorobenzene	11.92	0.2-100	0.994	11.1	12	0.04	4.3
1,2-Dibromo-3-chloropropane	12.42	0.2-50	0.99	13.6	14.1	0.06	3.4
1,2,4-Trichlorobenzene	12.95	1.0-100	0.997	7.9	17.6	0.15	10.1
Hexachlorobutadiene	13.03	0.1-50	0.993	11.2	13	0.04	3
Naphtalene	13.13	0.2-100	0.998	6	17.7	0.06	6.4
1,2,3-Trichlorobenzene	13.27	1.0-100	0.997	7.6	19.3	0.11	8.2

Appendix 5. QC absolute peak area %RSD as well QC calculated amount deviation with respect to batch 1 and % recovery obtained injecting three batch of samples over a period of six working days

Peak name	RT (min)	QC delta respect to batch 1	QC delta respect to batch 1	QC % Recovery	QC absolute peak area %RSD (n=18)
Dichlorodifluoromethane	1.53	1	1.8	80	9.4
Chloromethane	1.73	0.6	0.8	98	8
Vinyl chloride	1.89	0.8	1	94	8.7
Chloroethane	2.47	0.6	0.8	102	5.8
Trichlorofluoromethane	2.82	0.6	0.7	101	4.4
1,1-Dichloroethene	3.57	0.4	0.4	94	4.8
Methylene chloride	4.28	-2.8	-2.7	118	18.5
1,2-Dichloroethene (Z)	4.65	0.4	0.4	94	4.5
1,1-Dichloroethane	5.22	0.4	0.5	103	3.3
1,2-Dichloroethene (E)	5.93	0.4	0.4	95	5.6
Bromochloromethane	6.2	0.3	0.5	108	5.3
Chloroform (Trichloromethane)	6.35	0.4	0.5	109	4
1,1,1-Trichloroethane	6.51	0.4	0.4	104	4
2,2-Dichloropropene	6.52	0.4	0.4	107	3.1
Surr Dibromofluoromethane	6.53	0.4	0.2	103	1.8
ISTD Pentafluorobenzene	6.58	0	0	100	3.4
Carbon tetrachloride	6.69	0.3	0.3	100	4.6
Benzene	6.93	0.3	0.3	90	5.9
1,2-Dichloroethane	7	0.5	0.5	106	6.8
ISTD 1,4-Difluorobenzene	7.43	0	0	100	3.9
Trichloroethene	7.67	0.1	0.2	98	5.1
1,2-Dichloropropane	7.93	0.4	0.4	102	7.4
Dibromomethane	8.01	0.3	0.5	106	4.8
Bromodichloromethane	8.19	0.3	0.5	107	3.9
Surr Toluene D8	8.82	-0.1	0	100	7.2
1.3-Dichloropropene (Z)	8.87	0.1	0	97	6.3
Toluene	8.87	0.3	0.3	87	6.1
1,1,2-Trichloroethane	9.24	0.3	0.7	108	4.8
Tetrachloroethene	9.3	0.6	0.6	97	4.9
1,3-Dichloropropane	9.37	0.4	0.4	103	3.5
Dibromochloromethane	9.54	0.3	0.5	105	4.1

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Appendix 5. Continued from previous page

Peak name	RT (min)	QC delta respect to batch 1	QC delta respect to batch 1	QC % Recovery	QC absolute peak area %RSD (n=18)
1,2-Dibromoethane	9.63	0.5	0.6	106	4.7
ISTD Chlorobenzene D5	9.99	0	0	100	3.4
Chlorobenzene	10.01	0.3	0.4	92	5.3
1,1,1,2-Tetrachloroethane	10.08	0.3	0.5	99	3.8
Ethylbenzene	10.08	0.2	0.1	76	7.7
m,p-Xylene	10.18	0	0	77	7.9
o-Xylene	10.46	0.1	0	71	7.6
Styrene	10.47	-0.1	-0.2	71	10
Bromoform	10.61	0.3	0.5	99	5.3
Isopropylbenzene (Cumene)	10.72	0.2	0	98	7.8
BFB 1-Bromo-4-fluorobenzene	10.85	0.2	0.3	97	6.9
1,1,2,2-tetrachloroethane	10.94	0.7	0.7	108	3.7
Bromobenzene	10.96	0.6	0.7	121	7.7
1,2,3-Trichloropropane	10.96	-0.1	0.1	89	4.2
n-Propylbenzene	11.01	0.3	0.1	100	7.7
1,3,5-Trimethylbenzene	11.01	0.1	0	91	7.7
2-Chlorotoluene	11.08	0.2	0	101	6.9
4-Chlorotoluene	11.17	0.1	-0.1	100	6.3
Tert-butylbenzene	11.35	0	-0.2	95	8.3
1,2,4-Trimethylbenzene	11.39	0.2	-0.1	88	8.6
sec-Butylbenzene	11.5	0.4	0	94	8.1
4-Isopropyltoluene (*p*-Cymene)	11.6	0	-0.4	88	8.2
1,3-Dicholorobenzene	11.6	-0.8	0.2	121	4
ISTD 1,4-Dichlorobenzene D4	11.65	0	0	100	2.4
1,4-Dicholorobenzene	11.67	0.4	0.4	125	4.1
n-Butylbenzene	11.88	0.2	-0.2	99	8
1,2-Dichlorobenzene	11.97	0.3	0.4	127	4.1
1,2-Dibromo-3-chloropropane	12.42	0.1	0.3	132	3.6
1,2,4-Trichlorobenzene	12.95	0.2	0.3	120	6.3
Hexachlorobutadiene	13.03	0.6	0.5	125	5.5
Naphtalene	13.13	0.2	0.4	113	7.2
1,2,3-Trichlorobenzene	13.27	0	0.1	116	5.8

Appendix 6. Results obtained for analysis of tap water samples (three locations) and surface water samples (two locations)

		Drinking water samples (ng/mL)				Surface water samples (ng/mL)		
Peak name	RT (min)	1	2	3	Limits[2] (ng/mL)	1	2	Limits[3] (ng/mL)
Dichlorodifluoromethane	1.53	< MDL	< MDL	< MDL		< MDL	<MDL	
Chloromethane	1.73	--	--	--		--	--	
Vinyl chloride	1.89	--	--	--	**0.5**	< MDL	< MDL	
Chloroethane	2.47	--	--	--		--	--	
Trichlorofluoromethane	2.82	0.13	--	--		--	--	
1,1-Dichloroethane	3.57	--	0.06			--	0.07	
Methylene chloride	4.28	0.23	0.23	0.27		0.26	0.23	
1,2-Dichloroethene (Z)	4.65	--	--	--		--	--	
1,1 Dichloroethane	5.22	--	0.02	0.02		--	0.02	
1,2-Dichloroethene (E)	5.93	--	0.17	0.05		--	0.2	
Bromochloromethane	6.2	--	--	--		--	--	
Chloroform (Trichloromethane)	6.35	0.06	0.07	< MDL	**100****	0.03	0.08	**2.5**
1,1,1,-Trichloroethane	6.51	--	0.04	--		--	0.05	
2,2-Dichloropropene	6.52	--	--	--		--	--	
Carbon tetrachloride	6.69	--	--	--		--	--	**12**
Benzene	6.93	--	--	--	**1**	--	--	**50**
1,2-Dichloroethane	7	--	--	--	**3**	--	--	**10**
Trichloroethene	7.67	0.13	0.12	--	**10***	--	0.14	
1,2-Dichloropropane	7.93	--	--	--		--	--	
Dibromomethane	8.01	--	--	--		--	--	**20**
Bromodichloromethane	8.19	--	--	--	**100****	--	--	
1,3-Dichloropropene (Z)	8.87	--	--	--		--	--	
Toluene	8.87	0.13	0.14	0.12		0.17	0.12	
1,1,2-Trichloroethane	9.24	--	--	--		--	--	
Tetrachloroethene	9.3	0.09	1.28	< MDL	**10***	--	1.42	
1,3-Dichloropropane	9.37	--	--	--		--	--	
Dibromochloromethane	9.54	--	--	--	**100****	--	--	

* = Sum of tetrachloroethene and trichloroethene
** = Sum of chloroform, bromoform, dibromochloromethane, and bromodichloromethane

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Appendix 6. Continued from previous page

Peak name	RT (min)	Drinking water samples (ng/mL)			Limits[2] (ng/mL)	Surface water samples (ng/mL)		Limits[3] (ng/mL)
		1	2	3		1	2	
1,2-Dibromoethane	9.63	--	--	--		--	--	
Chlorobenzene	10.01	0.01	0.01	0.01		0.01	0.01	
1,1,1,2-Tetrachloroethane	10.08	--	--	--		--	--	
Ethylbenzene	10.08	0.01	0.01	0.01		0.01	0.01	
m,p-Xylene	10.18	0.01	0.01	0.01		0.01	0.01	
o-Xylene	10.46	0.01	0.01	0.01		0.01	0.01	
Styrene	10.47	--	--	--		0.02	--	
Bromoform	10.61	--	--	--	**100****	--	--	
Isopropylbenzene (Cumene)	10.72	--	--	--		--	--	
1,1,2,2-Tetrachloroethane	10.94	--	--	--		--	--	
Bromobenzene	10.96	--	--	--		--	--	
1,2,3-Trichloropropane	10.96	--	--	-		--	--	
n-Propylbenzene	11.01	< MDL	< MDL	< MDL		< MDL	0.02	
1,3,5-Trimethylbenzene	11.01	< MDL	< MDL	--		< MDL	< MDL	
2-Chlorotoluene	11.08	--	--	--		--	--	
4-Chlorotoluene	11.17	--	--	--		--	--	
tert-Butylbenzene	11.35	--	--	--		--	--	
1,2,4-Trimethylbenzene	11.39	< MDL	< MDL	< MDL		< MDL	< MDL	
sec-Butylbenzene	11.5	--	--	--		--	--	
4-Isopropyltoluene (*p*-Cymene)	11.6	< MDL	< MDL	< MDL		--	< MDL	
1,3-Dicholorobenzene	11.6	< MDL	< MDL	< MDL		< MDL	< MDL	
1,4-Dicholorobenzene	11.67	< MDL	< MDL	< MDL		< MDL	< MDL	
n-Butylbenzene	11.88	< MDL	< MDL	< MDL		< MDL	0.02	
1,2-Dichlorobenzene	11.92	< MDL	< MDL	<MDL		< MDL	< MDL	
1,2-Dibromo-3-chloropropane	12.42	--	--	--		--	--	
1,2,4-Trichlorobenzene	12.95	< MDL	< MDL	< MDL		< MDL	< MDL	**0.4**
Hexachlorobutadiene	13.03	< MDL	< MDL	< MDL		< MDL	0.01	**0.6**
Naphtalene	13.13	0.1	0.08	0.07		0.08	0.07	**1.2**
1,2,3-Trichlorobenzene	13.27	< MDL	< MDL	< MDL		< MDL	< MDL	**0.4**

* = Sum of tetrachloroethene and trichloroethene

** = Sum of chloroform, bromoform, dibromochloromethane, and bromodichloromethane

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> Eurofins Eaton Analytical, LLC

GC-based systems for the analyses of hundreds of water samples

To support clients’ public health protection efforts, Eurofins Eaton Analytical, LLC is focused on the analysis of water for a full range of contaminants per United States Environmental Protection Agency (U.S. EPA), US Food and Drug Administration (FDA), and other standard methods. At the Eurofins Eaton Analytical South Bend, Indiana, Organics Testing Laboratories, gas chromatography/electron capture detection (GC-ECD), GC-mass spectrometry (GC-MS), and GC-tandem MS (GC-MS/MS) techniques are essential to the identification and quantification of volatile organic compounds (VOCs), pesticides, and synthetic organic compounds (SOCs) in municipal drinking water per the U.S. EPA’s 500 series of methods. To meet client demands for water analyses, the laboratory overseen by Rhonda Day, Technical Manager, Eurofins Eaton Analytical, LLC, typically extracts and analyzes several hundreds of water samples every day using approximately 35 GC-based instrument systems configured with autosamplers. Efficiently performing these analyses requires reliable and sensitive instrument systems and world-class service and support.

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> “Downtime is much less with the new instruments, due to their enhanced robustness and great service and support when needed. When we call for service, we get very quick feedback. Compared to our older GCs, instrument downtime is 20% of what it used to be.”
>
> —Rhonda Day

To enhance their analyses of VOCs and SOCs in waters, the laboratory is updating the majority of their GC-based instruments to Thermo Scientific™ TRACE™ 1600 Series GC systems. By offering extended uptime, excellent support services, and ease of use, TRACE 1600 Series GC systems are augmenting the power and performance of the laboratory’s hyphenated systems.

TRACE 1600 Series GC systems replace obsolete instruments, increasing uptime

Whether used in hyphenated or standalone configurations, GC instruments are key in achieving the sample throughput necessary to respond to the needs of Eurofins Eaton Analytical clients. According to Day, “We need to have reliable equipment with little downtime so we can process as many samples as possible as quickly as we can.” Reliable GC systems, as well as rapid service response when problems occur, are essential to minimizing downtime that would interfere with sample analyses, creating sample backlogs.

The need for supportable GC instruments was among the reasons the laboratory decided to replace their obsolete GCs with TRACE 1600 Series GC systems. A Thermo Scientific GC system is always ready to run, and the TRACE 1600 Series GC system is designed to maximize operational efficiency and profitability. “The GCs we had were out of date and unsupported, so we could no longer purchase parts for them. We had a graveyard of old instruments that we would pirate parts off of to try and keep them running. The other concern was that the GCs did not support Microsoft® Windows® 10, which we needed for IT security,” explained Day. As a result of the new equipment, along with renowned Thermo Scientific service and support, the laboratory’s GC uptime has measurably increased.

Fast response from Thermo Scientific support staff rapidly resolves problems

Instrument downtime can impact contract testing laboratory revenues and damage reputation for fast sample turnaround. Like any other contract testing laboratory, Eurofins Eaton Analytical expects quick response to requests for service. Thermo Scientific GC and GC-MS instruments are designed for easier and faster servicing. These innovative instrument designs, along with substantial technical expertise, enable Thermo Scientific service and support staff to consistently meet and even exceed expectations for service response. Said Day, “We have great service and support. I appreciate having direct contact with the people who can answer our technical questions, without having to go through a phone tree. We have a great relationship with our service engineer who helps us with preventative maintenance, and we can get parts immediately, so our downtime is much less.”

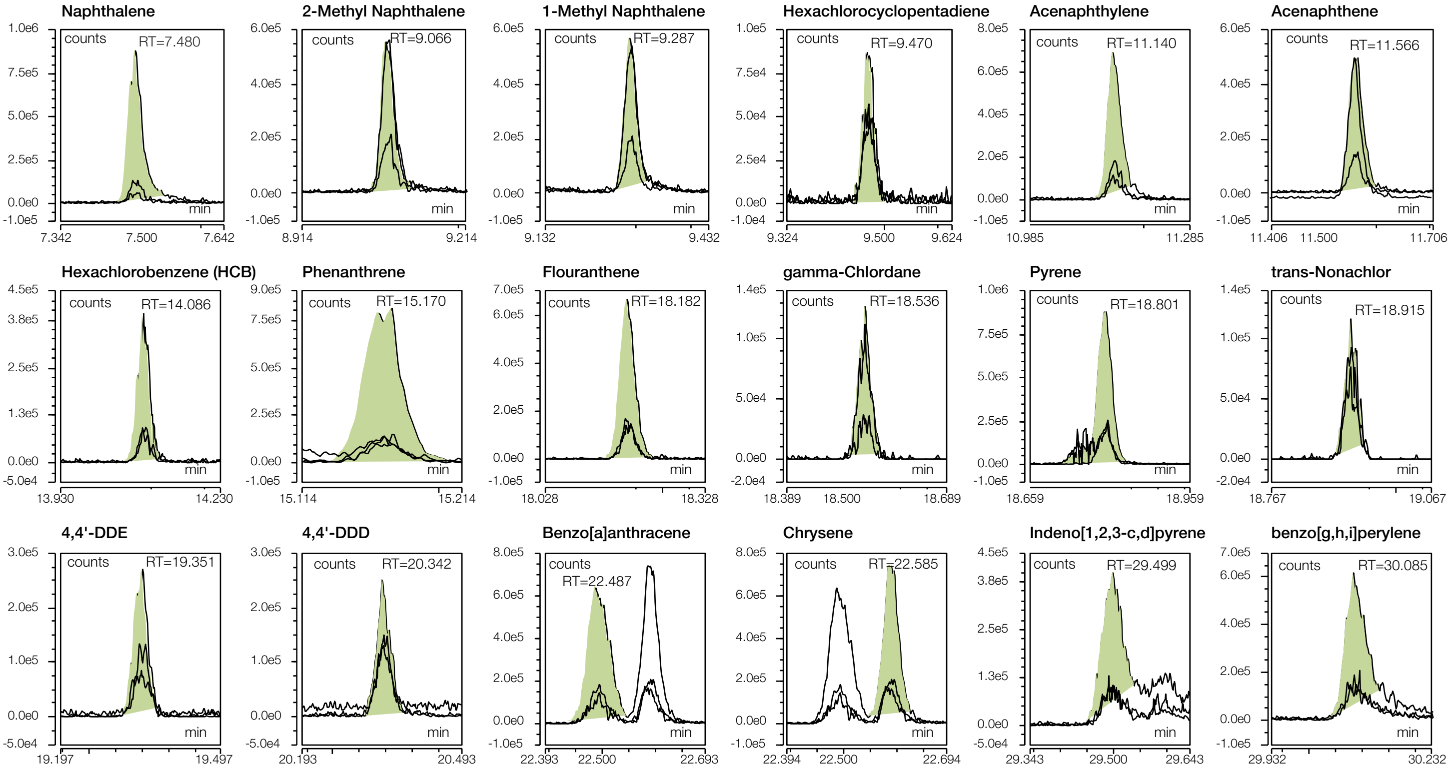
Additionally, a tailored approach to customer support offers an opportunity to further enhance productivity, enabling laboratories to keep pace with demands for increased throughput and on-time results. That’s the reason behind Thermo Scientific™ Premier Plus service, a service plan tailored to specific laboratory needs. “Because we beta tested the Premier Plus service plan, we were among the first to get this highest level of personalized treatment, and it has made a difference in our operations,” noted Day.

> “Other GC-MS systems could not meet the sensitivity requirements of U.S. EPA Method 525.2. Thermo Scientific helped us reach our desired sensitivity by developing methods for us, so we didn’t have to spend precious time doing development. After that, we decided to change all the GCs to TRACE 1600 Series GC systems in our labs.”
>
> —Rhonda Day

GC-MS performance ensures method requirements are met

Certain U.S. EPA methods, such as U.S. EPA Method 525.2, require instrument systems able to achieve low detection limits. Day explained, “the detection limits that we are required to obtain are very low and getting lower all the time. We need instruments that can meet the sensitivity requirements of our clients. We made the choice to go with Thermo Fisher Scientific after a competitive comparison that proved the Thermo Scientific instruments could do what we needed, for U.S. EPA Method 525.2 in particular, to reach our required sensitivity levels. Thermo Scientific support staff helped the laboratory to reach the sensitivity required and saved valuable time by providing pre-developed methods.”

After the demonstration, the laboratory ordered 17 instruments to replace their obsolete GCs. Describing the deployment of the TRACE 1600 Series GC systems, Day noted, “it’s very intuitive to use compared to what we had used before. We use Thermo Scientific™ Chromeleon™ [Chromatography Data System (CDS)] software which is very user friendly and super powerful.” By the end of 2022, the laboratory expects that there will be less than a handful of their systems that are not configured with TRACE 1610 Series GCs.



Quan/Qual ions for selected compounds at 0.05 µg/L analyzed according to U.S. EPA Method 525.2

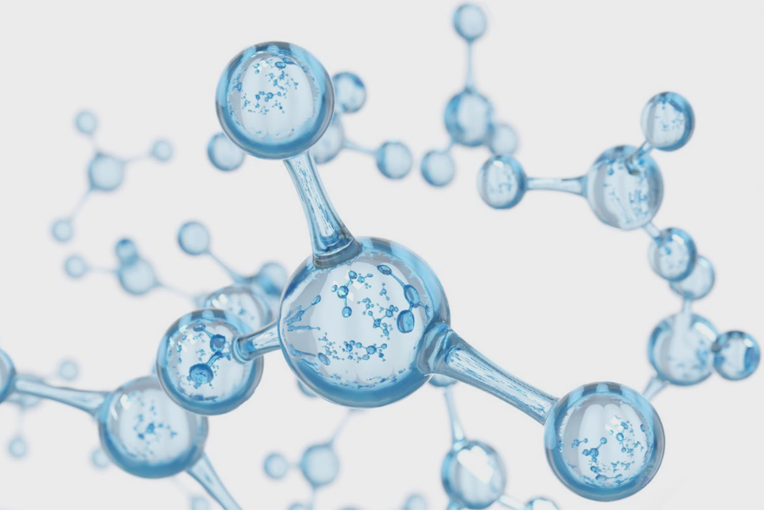
Conclusion

For laboratories needing to update their GC-based systems to a reliable, modern solution, the TRACE 1600 Series GC systems deliver increased uptime along with renowned support services, while augmenting the efficiency and performance of Thermo Scientific hyphenated systems. In particular, for environmental-testing laboratories facing considerable sample workloads and looking for enhanced robustness, uptime, and sensitivity to meet demanding regulations, Thermo Fisher Scientific is the ideal partner to help stay ahead.

About Rhonda Day

Rhonda Day, Technical Manager for the Organics Laboratories at the South Bend site of Eurofins Eaton Analytical, LLC, has a Bachelor of Science degree in chemistry. She joined the laboratory in 1990 and has spent the majority of her time in the Organics department. She has held her current position since 2014.

South Bend Indiana site of Eurofins Eaton Analytical, LLC



About Eurofins Eaton Analytical, LLC

Eurofins Eaton Analytical, LLC (EEA), founded in 1969, is an analytical laboratory focused on the analysis of water (raw, municipal, bottled, saline, or reuse) for a full range of chemical, microbial, and radiological contaminants. It is the largest potable water testing laboratory in the U.S., with over 100,000 combined square feet of laboratory space and nearly 200 qualified staff at its East and West coast laboratories and Service Centers. EEA recognizes water quality to be critical to public health protection, whether in water supplies or as a component of food and beverages.

Using methods from EPA, FDA, and in-house techniques, EEA provides clients with high quality, low-reporting-limit data for water quality assessment. EEA also assists clients with quality assurance consulting and development of internal water quality standards. EEA stays on the leading edge of both compliance and emerging contaminant analyses by partnering with U.S. EPA and instrument manufacturers on method development and validation projects. EEA is accredited under the National Environmental Accreditation Program and ISO 17025 in multiple states and holds drinking water certification in all 50 U.S. states and territories.

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