

Analysis of VOCs according to EPA Method 8260

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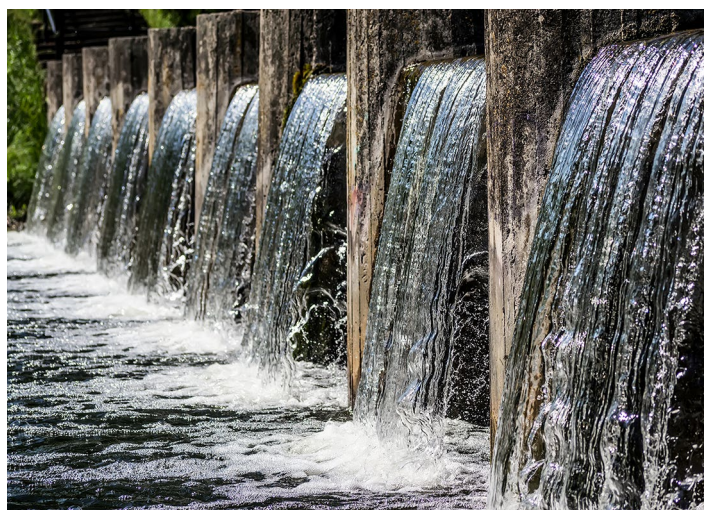
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Goal

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



Introduction

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

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

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

Experimental

Sample preparation

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

The water calibration curve was prepared from 0.2 to 200 parts per billion (ppb) (µg/L) for most compounds, while the soil calibration curve was prepared from 1 ppb to 200 ppb. The relative response factor (RF) was calculated for each compound using one of the four internal standards: pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d₅, and 1,4-dichlorobenzene-d₄. Surrogate standards consisted of dibromofluoromethane, 1,2-dichloroethane-d₄, toluene-d₈, and 4-bromofluorobenzene. Internal and surrogate standards were prepared together in methanol from Restek standards at a concentration of 25 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 25 ppb.

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

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

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

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

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

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

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

Instrument control and data processing

Data were acquired, processed, and reported using Chromeleon CDS software, version 7.2. This software can control both the GC-MS system and the Tekmar Atomx XYZ P&T. This allows a single software to be utilized for the full workflow simplifying the instrument operation. Figure 1

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

Purge	Variable
Pre-purge time	0.00 min
Pre-purge flow	0 mL/min
Pre-heat mix speed	Slow
Sample pre-heat time	0.00 min
Pre-sweep time	0.25 min
Water volume	10.00 mL
Sweep water time	0.25 min
Sweep water flow	100 mL/min
Sparge vessel heater	Off
Purge mix speed	Medium
Purge time	11.00 min
Purge flow	40 mL/min
Purge temp.	20 °C
Condensate purge temp.	20 °C
Dry purge time	2.00 min
Dry purge flow	100 mL/min
Dry purge temp.	20 °C
Desorb	Variable
Methanol needle rinse	Off
Methanol needle rinse volume	0.00 mL
Water needle rinse volume	7.00 mL
Sweep needle time	0.25 min
Desorb preheat temp.	245 °C
GC start signal	Begin Desorb
Desorb time	2.00 min
Drain flow	300 mL/min
Desorb temp.	250 °C
Bake	Variable
Bake time	2.00 min
Bake flow	400 mL/min
Bake temp.	280 °C
Condensate bake temp.	200 °C
Trap	#9
Purge gas	Nitrogen

shows the Chromeleon control of the Atomx XYZ P&T. The fully optimized method used within this application note is available for download as a Chromeleon eWorkflow™ via Thermo Scientific™ AppsLab. AppsLab contains all the parameters needed to acquire, process, and report the analytical data for EPA Method 8260.²

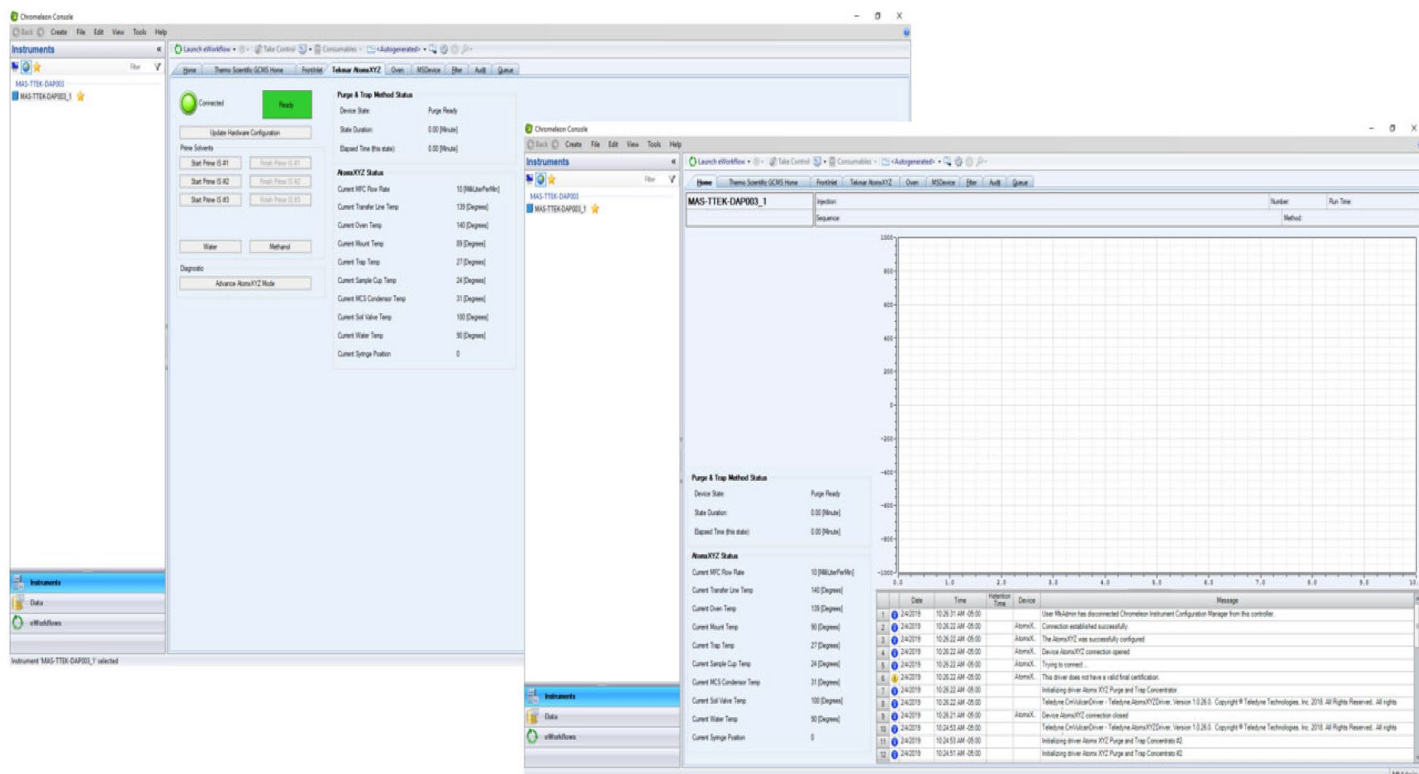


Figure 1. Chromeleon control of the Atomx XYZ P&T

GC-MS parameters

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

Table 3. GC-MS conditions

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

Results and discussion

Chromatography

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

Linearity and sensitivity

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

Peaks:

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

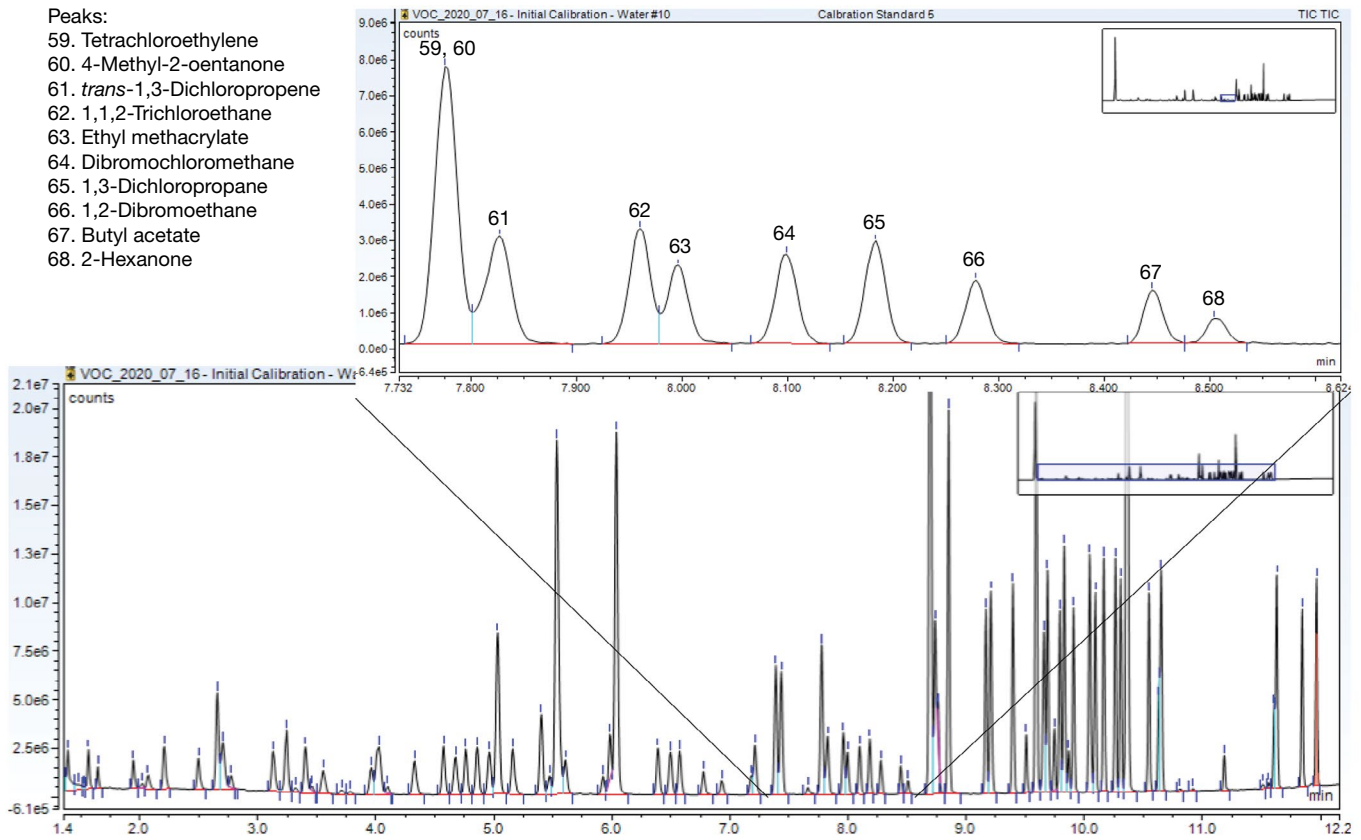


Figure 2. Total ion chromatogram (TIC) of a water method 5 ppb ($\mu\text{g/L}$) VOC standard with an inset indicating peak shapes and separation

Peaks:

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

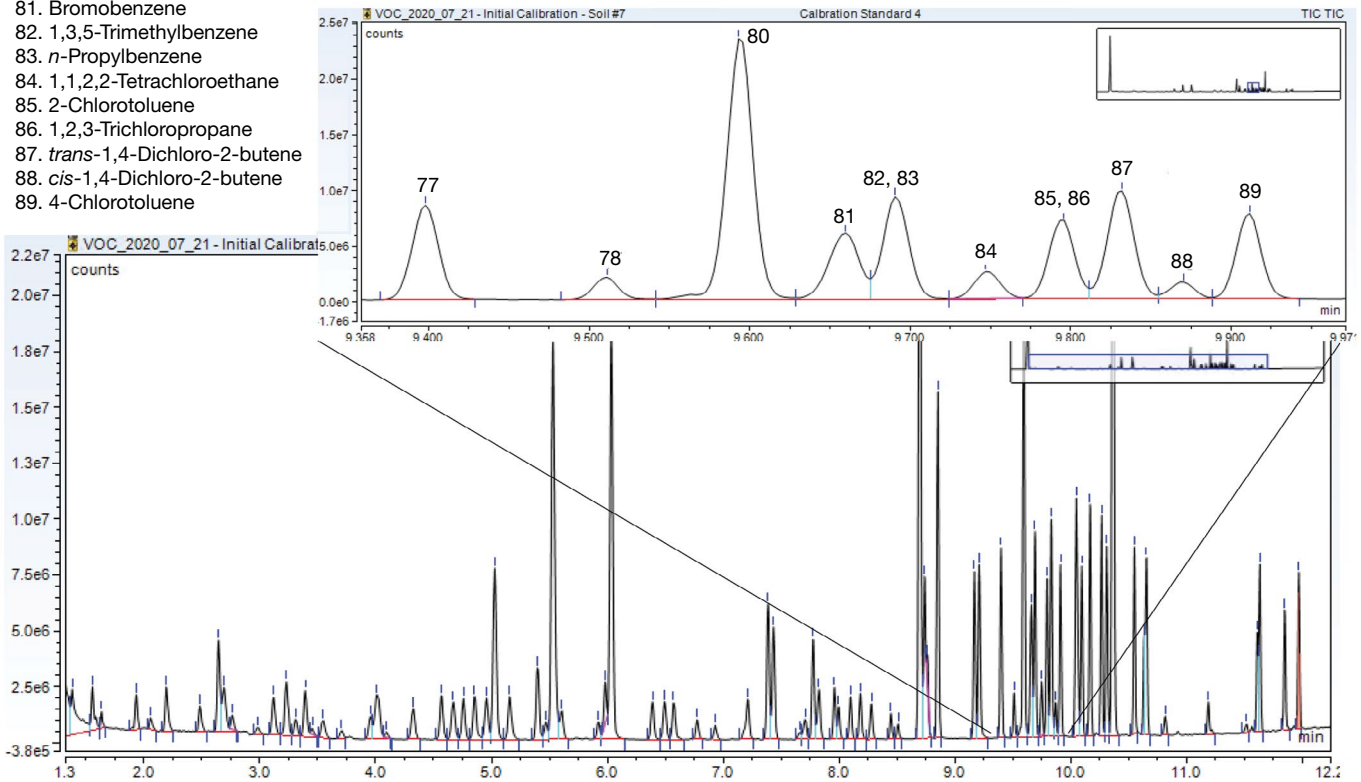


Figure 3. Total ion chromatogram (TIC) of a soil method 5 ppb ($\mu\text{g/kg}$) VOC standard with an inset indicating peak shapes and separation

Examples of the linearity for the water calibration curve for chloromethane and 1,2-dichlorobenzene are shown in Figures 4 and 5. These figures show the lowest point of the water calibration curve at 0.2 ppb, producing an excellent response, and the linearity of the curve giving R^2

value above 0.99 and average response factor RSD <20%. Figures 5 and 6 show similar data for the soil calibration for dibromomethane and styrene. The lowest point of the curve was 1 ppb, and even in soil, the peak response meets the regulatory requirements.

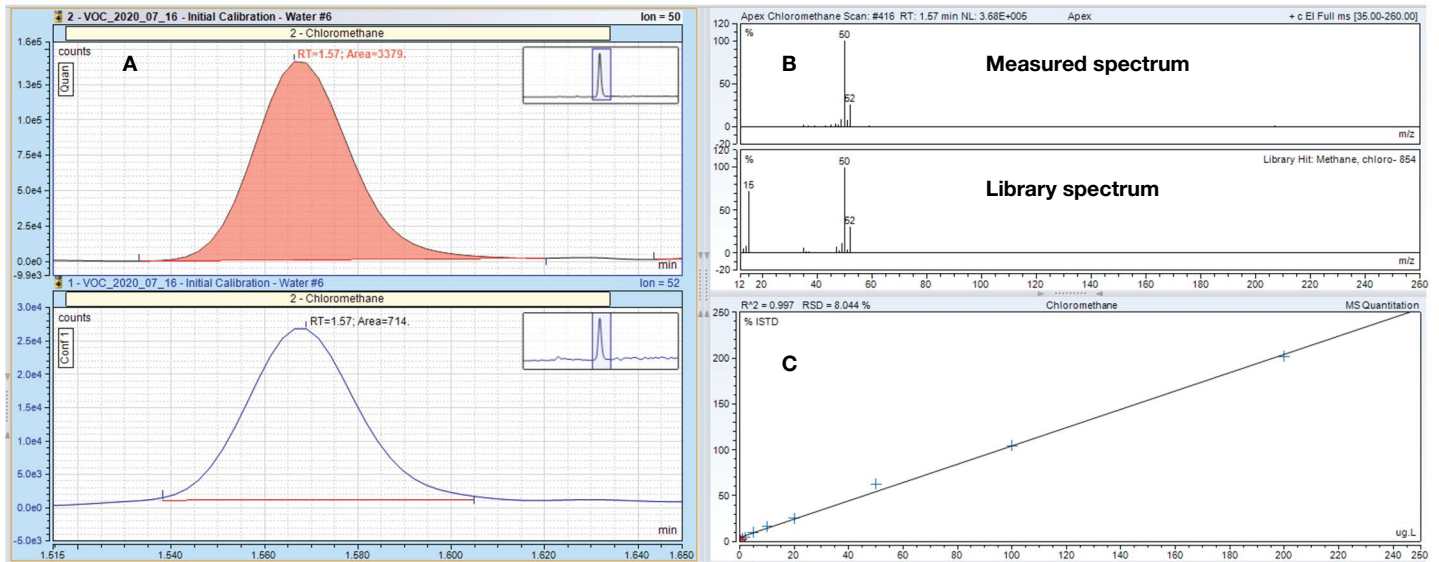


Figure 4. Chromeleon results browser showing extracted ion chromatograms for chloromethane in the 0.2 ppb water standard, quantitation ion and two confirming ions (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 0.2 ppb to 200 ppb ($\mu\text{g/L}$)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

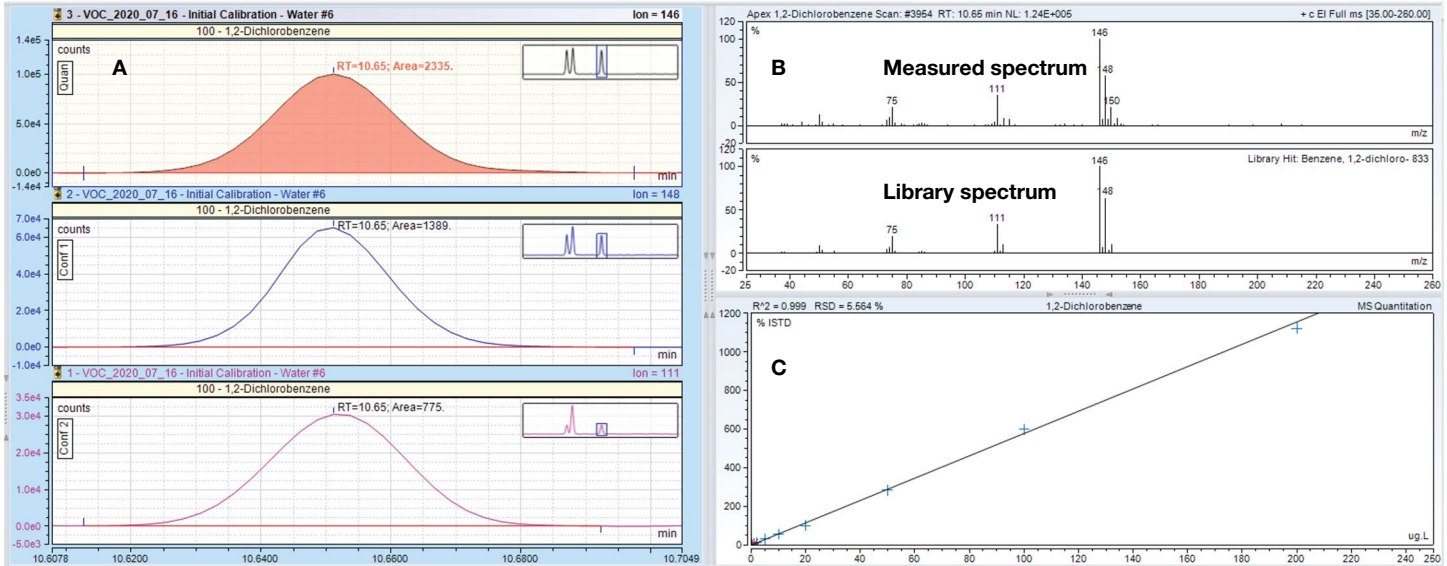


Figure 5. Chromeleon results browser showing extracted ion chromatograms for 1,2-dichlorobenzene in the 0.2 ppb water standard, quantitation ion and two confirming ions (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 0.2 ppb to 200 ppb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

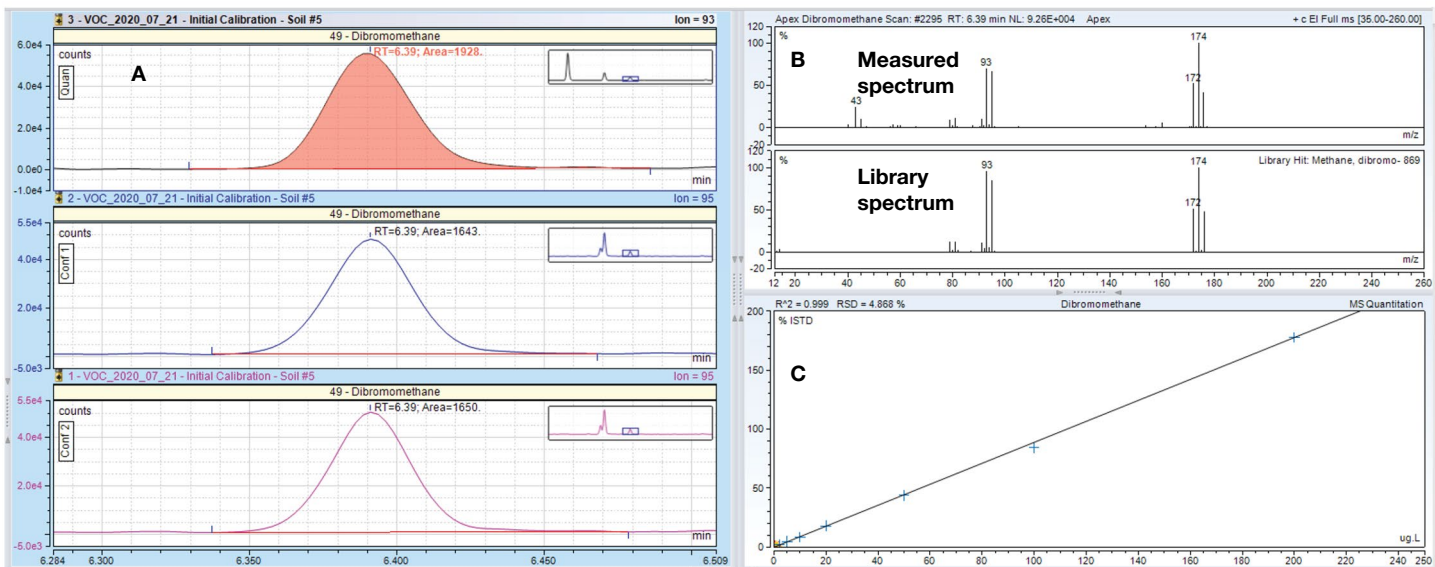


Figure 6. Chromleon results browser showing extracted ion chromatograms for dibromomethane in the 1 ppb soil standard, quantitation ion and two confirming ions (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 1 ppb to 200 ppb (C)

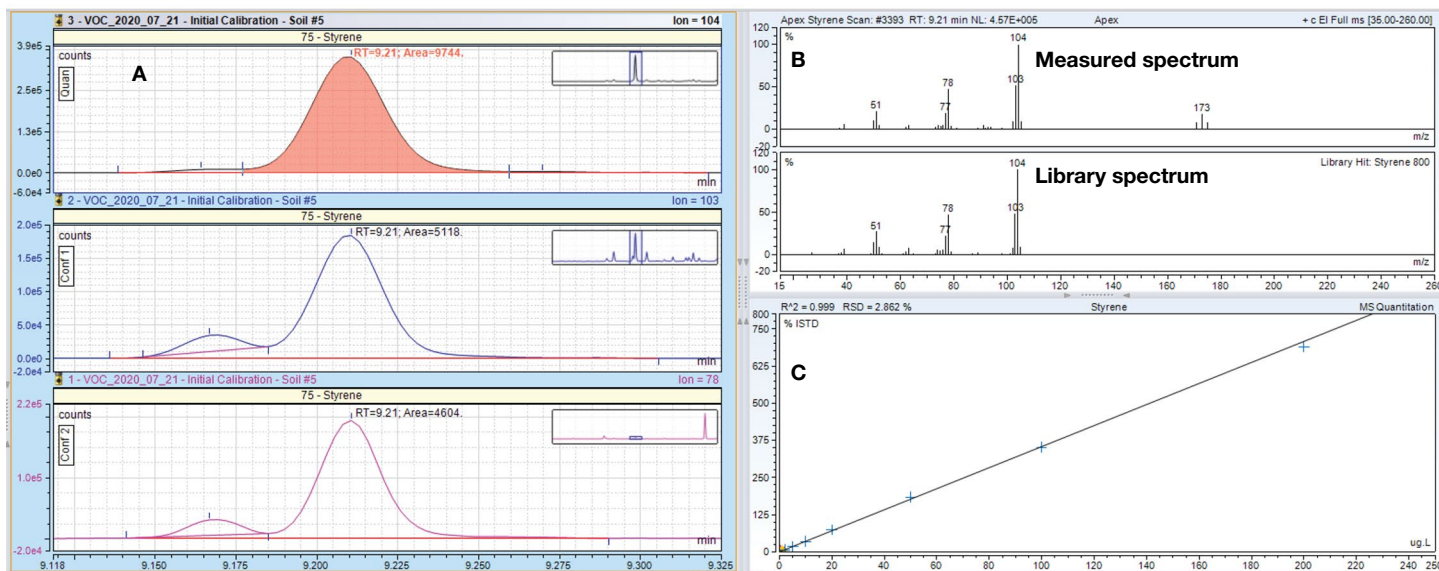


Figure 7. Chromleon results browser showing extracted ion chromatograms for styrene in the 1 ppb soil standard, quantitation ion (m/z 104) and two confirming ions (m/z 103 and m/z 74) (A), a matching measured spectrum to the NIST library (B), and a linear response over a concentration range of 1 to 200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

Precision and accuracy

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

Method robustness

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

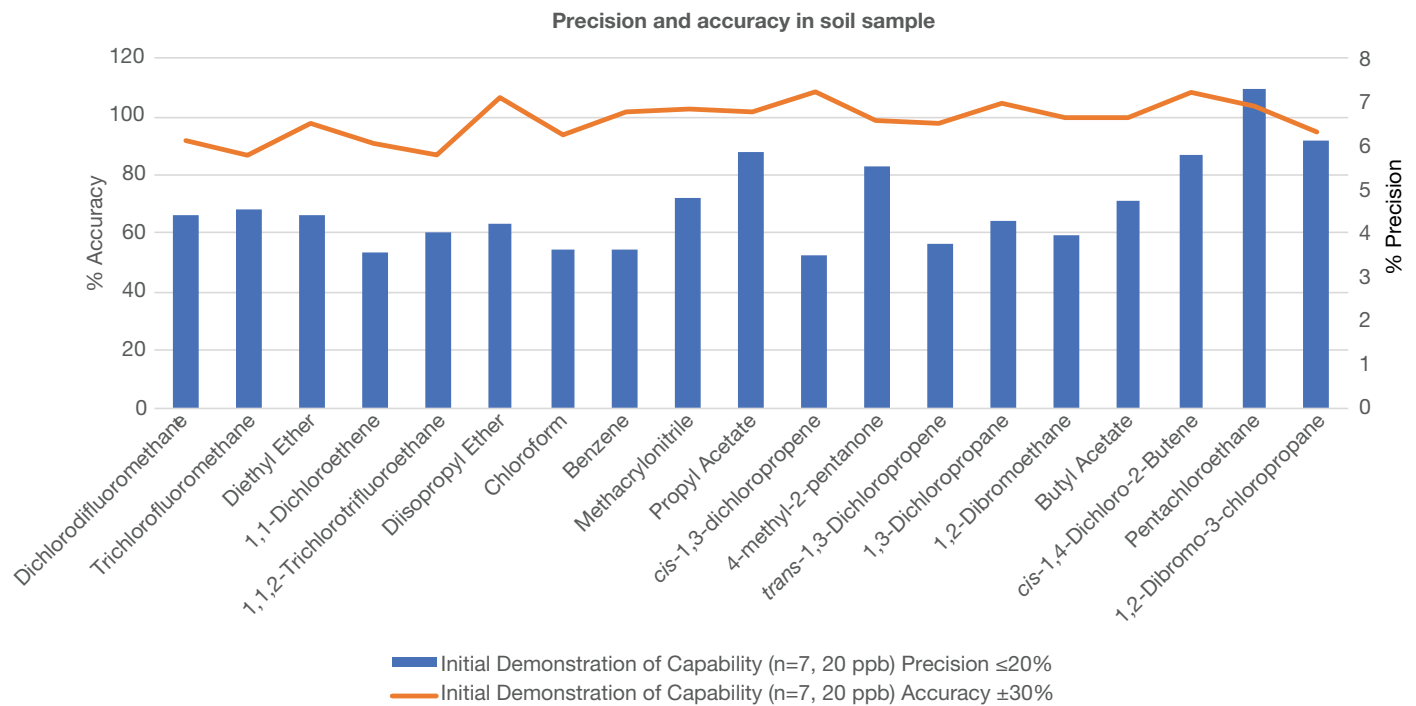


Figure 8. Demonstration of accuracy (% recovery) and precision (calculated concentration) by analyzing $n=7$ replicates of a 20 ppb soil standard

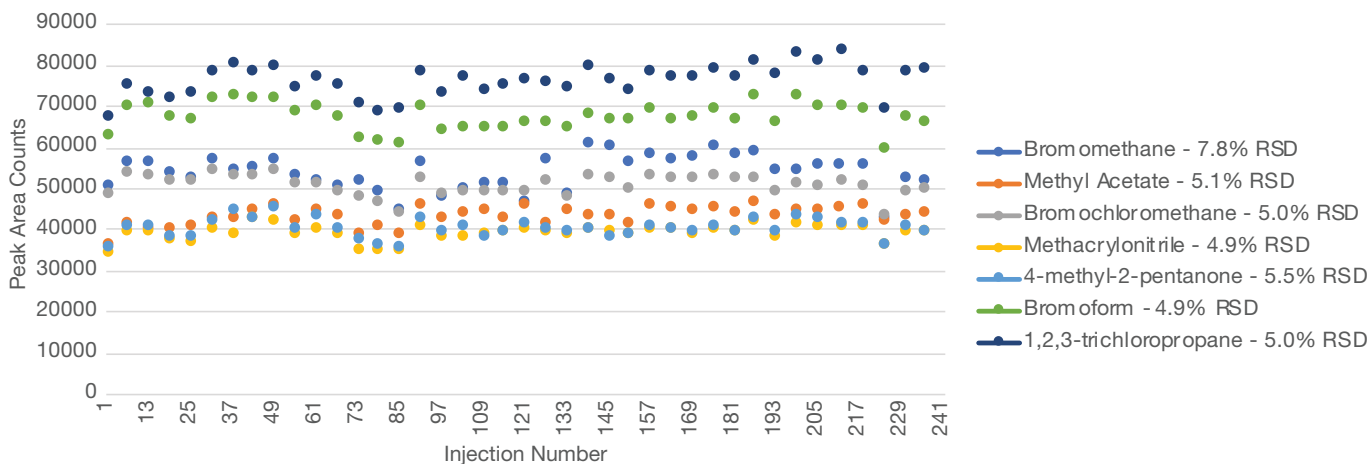


Figure 9. Repeatability (absolute peak area) of a 20 ppb water standard assessed over n=240 consecutive injections over three days of analysis

Conclusion

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

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

- The modularity of the TRACE 1310 GC and the ISQ 7000 VPI and ExtractaBrite ion source allows users to easily service the injection ports and to exchange ionization sources and analytical columns without venting the mass spectrometer. This significantly reduces instrument downtime and minimizes sample analysis interruptions. The Atomx XYZ concentrator's efficient trap cooling design reduces sample cycle time and allows for increased sample throughput. The moisture control system improves water vapor removal, thereby reducing peak interference and increasing the GC column life span.
- The ISQ 7000 VPI coupled with the Tekmar Atomx XYZ P&T exceeds all the requirements outlined in EPA Method 8260 for analysis of VOCs in wastewater and solid waste.
- MDLs calculated from n=7 repeat injections of 0.5 ppb water standards and n=7 analyzed of 1 ppb soil standards showed no interference from unwanted water entering the system and resulted in values <0.25 ppb for most compounds.

- Precision and accuracy for n=7 20 ppb water standards showed excellent results with %RSD <20% with 100 of 103 compounds having <10% RSD and a mean recovery of 88% for the compounds.
- Precision and accuracy (assessed from n=7 repeat injections of a 20 ppb soil standard) showed excellent values with all compounds having %RSD <11% for the calculated concentration and recovery values between 76% and 117%, with an average recovery of 98%.
- System robustness was tested by continuously acquiring 240 injections of environmental samples over three days with no user intervention at all. The average %RSD of the calculated concentration was 8.30% with an average compound recovery of 90%.
- Combined, these technologies effectively address the challenges of routine VOC analysis in environmental samples and provide a robust, sensitive solution needed for ensuring maximized instrument output and regulatory method compliance.
- Further information on VOC analysis using the ISQ 7000 system and the Atomx XYZ P&T can be found in the Thermo Scientific AppsLab library.²

References

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Appendix

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

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

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

Compounds	Calibration (0.5–200 ppb)			Method detection limit (n=7, 0.5 ppb)		Initial Demonstration of Capability (n=7, 20 ppb)	
	Ret. Time (min)	Linearity (%RSD)	Avg. RF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Methacrylonitrile	5.48	6.31	0.139	0.10	8.9	5.4	66
Pentafluorobenzene (ISTD)	5.53						84
1,2-Dichloroethane-d ₄ (surr)	5.54	10.4	0.088		3.0	1.8	79
tert-Amyl methyl ether	5.56	9.82	0.396	0.08	6.2	4.6	78
1,2-Dichloroethane	5.61	7.29	0.482	0.12	8.2	5.3	75
Isobutanol ^{4,7}	5.68	13.3	0.008	2.1	14.3	7.2	82
Isopropyl acetate	5.93	17.9	0.354	0.06	4.1	5.8	83
Trichloroethene	5.99	10.6	0.438	0.11	8.8	7.4	80
1,4-Difluorobenzene (ISTD)	6.04						82
Dibromomethane	6.39	5.00	0.289	0.09	6.4	5.5	92
1,2-Dichloropropane	6.49	8.26	0.312	0.07	5.2	5.9	80
Bromodichloromethane	6.58	4.05	0.557	0.11	7.9	5.6	81
Methyl methacrylate	6.78	17.6	0.217	0.14	11.1	6.5	79
Propyl acetate	6.94	15.9	0.284	0.15	13.1	6.1	86
2-Chloroethyl vinyl ether	7.18	18.2	0.112	0.08	5.3	5.7	81
cis-1,3-Dichloropropene	7.21	9.53	0.434	0.04	3.8	4.8	85
Toluene-d ₈ (surr)	7.39	2.69	0.345		1.9	1.1	73
Toluene	7.43	5.30	1.77	0.07	4.9	6.9	94
2-Nitropropane	7.66	11.6	0.085	0.10	6.1	5.7	83
Tetrachloroethylene	7.78	19.5	0.822	0.15	11.1	15.5	90
4-Methyl-2-pentanone	7.82	13.6	0.082	0.30	9.2	5.4	90
trans-1,3-Dichloropropene	7.83	17.0	0.494	0.09	7.2	6.0	97
1,1,2-Trichloroethane	7.96	11.7	0.277	0.08	6.4	6.1	86
Ethyl methacrylate	8.00	12.2	0.355	0.07	6.3	5.9	102
Dibromochloromethane	8.10	13.0	0.449	0.09	7.6	5.6	90
1,3-Dichloropropane	8.18	10.9	0.553	0.04	3.3	5.1	92
1,2-Dibromoethane	8.28	11.7	0.386	0.05	4.0	6.0	84
Butyl acetate	8.45	12.8	0.324	0.09	6.9	6.5	75
2-Hexanone	8.51	12.0	0.052	0.35	10.7	5.6	74
Chlorobenzene-d ₅ (ISTD)	8.69						87
Chlorobenzene	8.70	4.14	1.25	0.09	6.0	6.2	83
Ethylbenzene	8.74	5.39	1.83	0.07	4.8	6.5	80
1,1,1,2-Tetrachloroethane	8.76	5.23	0.312	0.09	7.0	5.1	96
m,p-Xylene	8.85	7.21	0.634	0.18	6.9	7.4	90
o-Xylene	9.17	6.84	0.613	0.06	4.4	7.0	77
Styrene	9.21	6.48	0.996	0.09	7.7	6.3	87
Bromoform	9.22	9.40	0.290	0.08	7.3	7.1	81
Isopropylbenzene	9.40	9.90	1.48	0.07	5.8	7.4	86
Amyl acetate	9.51	7.03	0.329	0.06	5.4	7.8	80
4-Bromofluorobenzene (surr)	9.59	4.64	0.525		2.0	1.9	100

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

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

¹Linear calibration

²Calibration range 0.5–200 ppb

³Calibration range 1.25–500 ppb

⁴Calibration range 2–200 ppb

⁵Calibration range 5–200 ppb

⁶Calibration range 10–200 ppb

⁷5 ppb MDL

⁸20 ppb MDL

⁹Compound displayed interference with the CO₂ peak during desorb

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

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

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

Compounds	Calibration (0.5–200 ppb)			Method detection limit (n=7, 0.5 ppb)		Initial Demonstration of Capability (n=7, 20 ppb)	
	Ret. Time (min)	Linearity (%RSD)	Avg. RF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Methacrylonitrile	5.48	3.25	0.119	0.14	4.5	4.8	102
Pentafluorobenzene (ISTD)	5.53						
1,2-Dichloroethane-d ₄ (surr)	5.54	10.4	0.076		1.5	2.3	108
<i>tert</i> -Amyl methyl ether	5.57	3.89	0.307	0.13	4.6	4.1	96
1,2-Dichloroethane	5.61	5.19	0.370	0.15	4.5	2.9	97
Isobutanol ²	5.75	9.98	0.012	1.26	6.8	7.9	97
Isopropyl acetate	5.93	13.2	0.368	0.14	5.1	5.0	101
Trichloroethene	5.98	8.32	0.413	0.13	4.5	3.4	106
1,4-Difluorobenzene (ISTD)	6.03						
Dibromomethane	6.39	4.87	0.222	0.16	4.8	3.6	99
1,2-Dichloropropane	6.50	6.98	0.272	0.16	4.9	3.3	111
Bromodichloromethane	6.58	5.23	0.459	0.13	4.2	3.5	101
Methyl methacrylate	6.78	16.9	0.199	0.30	9.9	5.6	108
Propyl acetate	6.94	6.94	0.293	0.17	5.7	5.8	102
2-Chloroethyl vinyl ether	7.18	14.6	0.064	0.17	8.9	5.1	76
<i>cis</i> -1,3-Dichloropropene	7.21	3.76	0.358	0.16	5.8	3.5	108
Toluene-d ₈ (surr)	7.39	3.72	0.346		1.2	1.5	97
Toluene	7.44	3.80	1.59	0.14	4.5	3.3	101
2-Nitropropane	7.66	13.5	0.094	0.24	7.1	5.4	94
Tetrachloroethylene	7.78	9.44	0.614	0.09	3.2	10.8	95
4-Methyl-2-pentanone	7.82	7.08	0.084	0.78	10.6	5.5	99
<i>trans</i> -1,3-Dichloropropene	7.83	15.0	0.424	0.07	2.8	3.7	98
1,1,2-Trichloroethane	7.96	3.07	0.226	0.16	5.2	4.2	105
Ethyl methacrylate	8.00	16.1	0.287	0.21	8.9	5.3	94
Dibromochloromethane	8.10	3.39	0.371	0.12	4.0	3.7	99
1,3-Dichloropropane	8.19	2.20	0.446	0.12	4.1	4.3	104
1,2-Dibromoethane	8.28	2.15	0.317	0.11	3.8	4.0	99
Butyl acetate	8.45	7.13	0.294	0.17	6.4	4.8	99
2-Hexanone	8.51	10.5	0.060	0.53	7.2	5.5	98
Chlorobenzene-d ₅ (ISTD)	8.69						
Chlorobenzene	8.71	3.53	1.08	0.10	3.4	3.3	96
Ethylbenzene	8.74	5.06	1.64	0.08	2.8	2.8	98
1,1,1,2-Tetrachloroethane	8.76	5.11	0.250	0.15	5.4	3.3	95
<i>m,p</i> -Xylene	8.85	6.01	0.584	0.19	3.5	3.4	102
<i>o</i> -Xylene	9.17	4.85	0.549	0.12	4.5	4.1	95
Styrene	9.21	2.86	0.884	0.10	3.9	3.6	97
Bromoform	9.22	2.67	0.239	0.15	5.4	3.8	98
Isopropylbenzene	9.40	7.12	1.41	0.11	4.5	4.3	97
Amyl acetate	9.51	3.44	0.263	0.20	7.8	5.3	105
4-Bromofluorobenzene (surr)	9.60	3.38	0.543		1.8	2.2	99

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

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

¹Linear calibration

²Calibration range 2–200 ppb

³Calibration range 5–200 ppb

⁴Calibration range 10–200 ppb

⁵20 ppb MDL

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

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

Compounds	Analyte recovery n=40	
	Precision (%)	Accuracy (%)
Methacrylonitrile	8.2	103
Pentafluorobenzene (ISTD)		
1,2-Dichloroethane-d ₄ (surr)	4.9	127
<i>tert</i> -Amyl methyl ether	4.5	81
1,2-Dichloroethane	8.1	113
Isobutanol	16.2	115
Isopropyl acetate	7.7	105
Trichloroethene	12.6	87
1,4-Difluorobenzene (ISTD)		
Dibromomethane	6.9	101
1,2-Dichloropropane	8.0	110
Bromodichloromethane	7.5	102
Methyl methacrylate	4.6	92
Propyl acetate	5.9	96
2-Chloroethyl vinyl ether	4.1	81
<i>cis</i> -1,3-Dichloropropene	4.5	91
Toluene-d ₈ (surr)	1.4	103
Toluene	8.2	87
2-Nitropropane	6.0	101
Tetrachloroethylene	26.2	81
4-Methyl-2-pentanone	7.2	97
<i>trans</i> -1,3-Dichloropropene	4.5	96
1,1,2-Trichloroethane	8.3	106
Ethyl methacrylate	4.1	86
Dibromochloromethane	6.8	93
1,3-Dichloropropane	7.1	102
1,2-Dibromoethane	6.8	96
Butyl acetate	5.3	93
2-Hexanone	7.4	100
Chlorobenzene-d ₅ (ISTD)		
Chlorobenzene	6.7	90
Ethylbenzene	8.6	89
1,1,1,2-Tetrachloroethane	7.9	87
<i>m,p</i> -Xylene	8.5	82
<i>o</i> -Xylene	7.4	71
Styrene	6.4	81
Bromoform	6.1	81
Isopropylbenzene	10.1	75

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

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

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

¹Compound displayed interference with the CO₂ peak during desorb

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