

## Environmental analysis

# 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<sub>5</sub>, or 1,4-dichlorobenzene-d<sub>4</sub>. Surrogate standards consisted of dibromofluoromethane, 1,2-dichloroethane-d<sub>4</sub>, toluene-d<sub>8</sub>, 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.<sup>2</sup>

## 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 x 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.



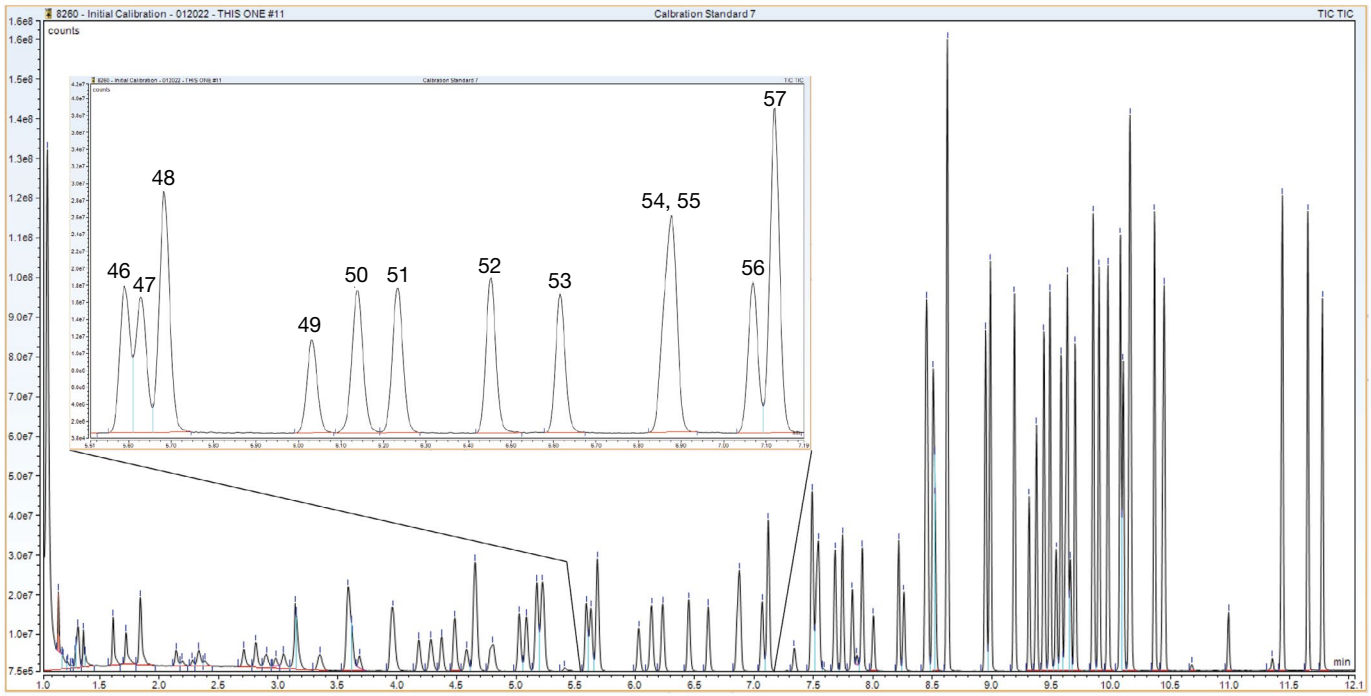


Figure 1. Total ion chromatogram (TIC) of a water method 10 ppb VOC standard with an inset indicating consistent peak shapes and separation with minimal water interference

Peaks:

- |                              |                          |                                     |
|------------------------------|--------------------------|-------------------------------------|
| 46. Isopropyl acetate        | 50. 1,2-Dichloropropane  | 54. 1-Chloroethyl vinyl ether       |
| 47. Trichloroethene          | 51. Bromodichloromethane | 55. <i>cis</i> -1,3-Dichloropropene |
| 48. 1,4-Difluorobenzene (IS) | 52. Methyl methacrylate  | 56. Toluene-d <sub>8</sub>          |
| 49. Dibromomethane           | 53. Propyl acetate       | 57. Toluene                         |

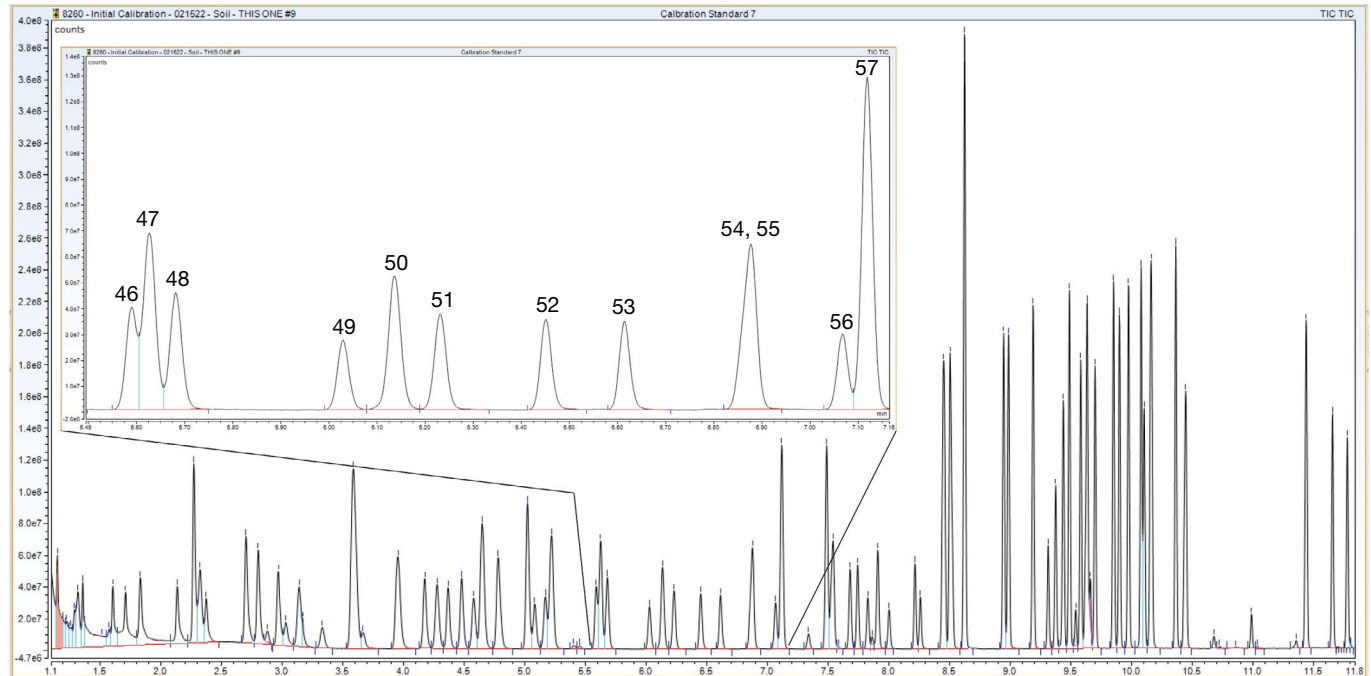


Figure 2. Total ion chromatogram (TIC) of a soil method 10 ppb VOC standard with an inset indicating consistent peak shapes and separation with minimal water interference

Peaks:

- |                              |                          |                                     |
|------------------------------|--------------------------|-------------------------------------|
| 46. Isopropyl acetate        | 50. 1,2-Dichloropropane  | 54. 1-Chloroethyl vinyl ether       |
| 47. Trichloroethene          | 51. Bromodichloromethane | 55. <i>cis</i> -1,3-Dichloropropene |
| 48. 1,4-Difluorobenzene (IS) | 52. Methyl methacrylate  | 56. Toluene-d <sub>8</sub>          |
| 49. Dibromomethane           | 53. Propyl acetate       | 57. Toluene                         |

## Linearity and sensitivity

The water calibration curve was prepared from 0.2 ppb to 200 ppb ( $\mu\text{g/L}$ ) for all compounds, while the soil calibration curve was prepared from 0.5 ppb to 200 ppb ( $\mu\text{g/kg}$ ). 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.

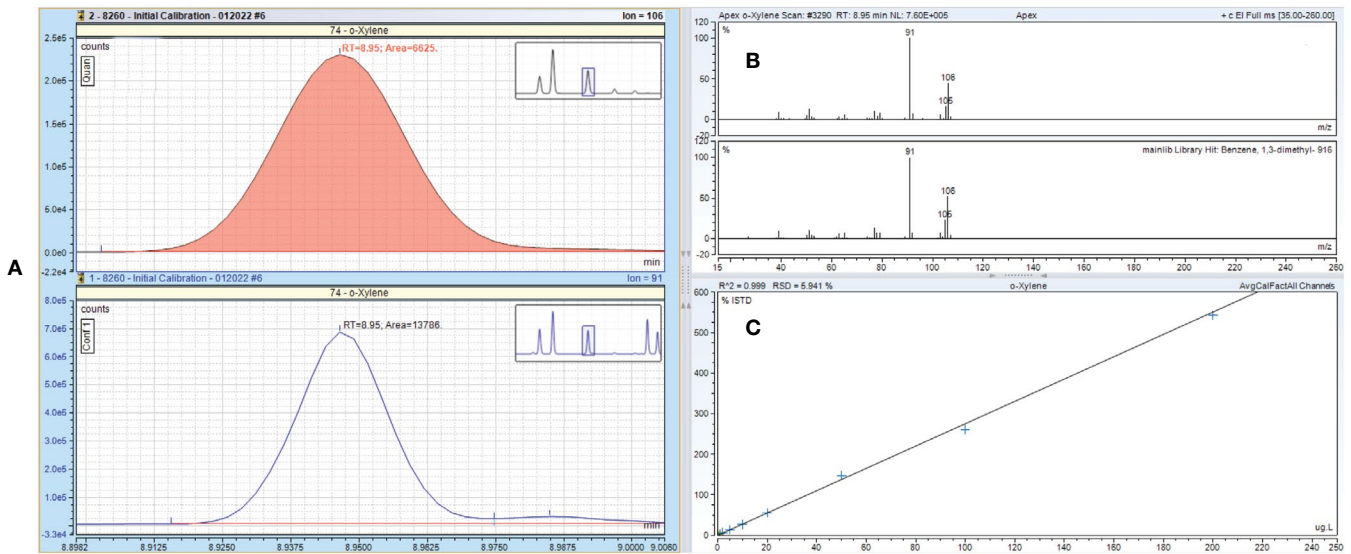


Figure 3. Chromeleon results browser showing extracted ion chromatograms for *o*-xylene in the 0.5 ppb water standard, quantitation ion (mass 106) and one confirming ion (mass 91) (A), an excellent measured spectrum match to the NIST library (B), and a linear calibration over a concentration range of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

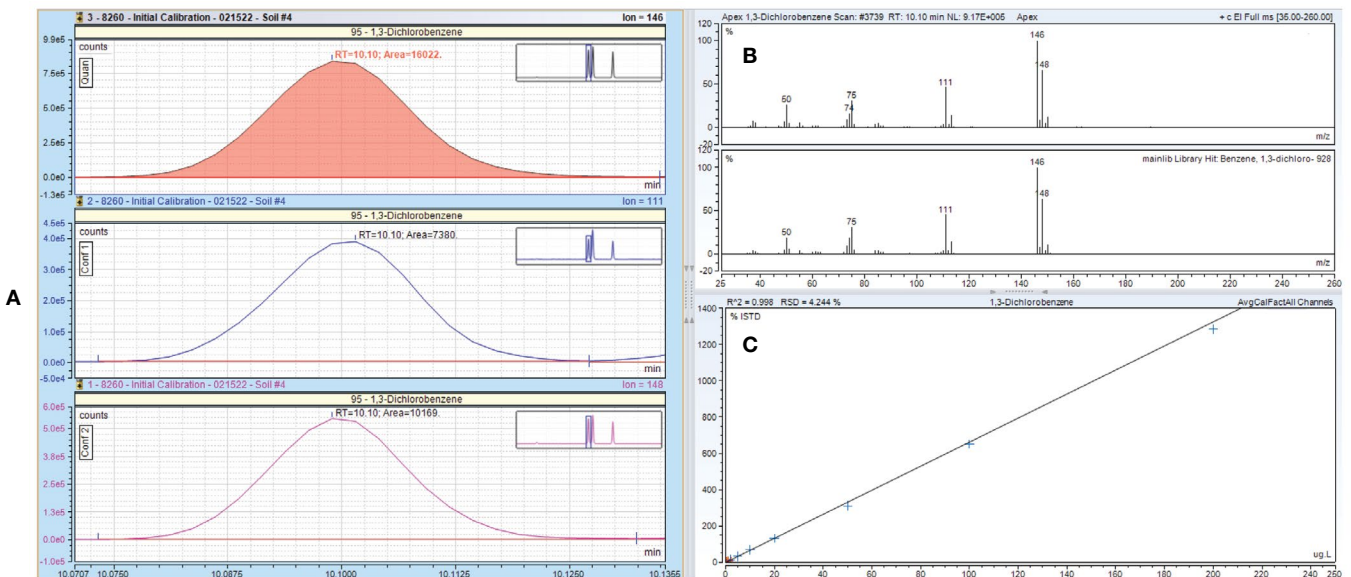


Figure 4. Chromeleon results browser showing extracted ion chromatograms for 1,3-dichlorobenzene in the 0.5 ppb soil standard, quantitation ion (mass 149) and two confirming ions (mass 111, 148) (A), an excellent measured spectrum match to the NIST library (B), and a linear calibration over a concentration 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  $\pm 30\%$  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 Appendixes I and II.

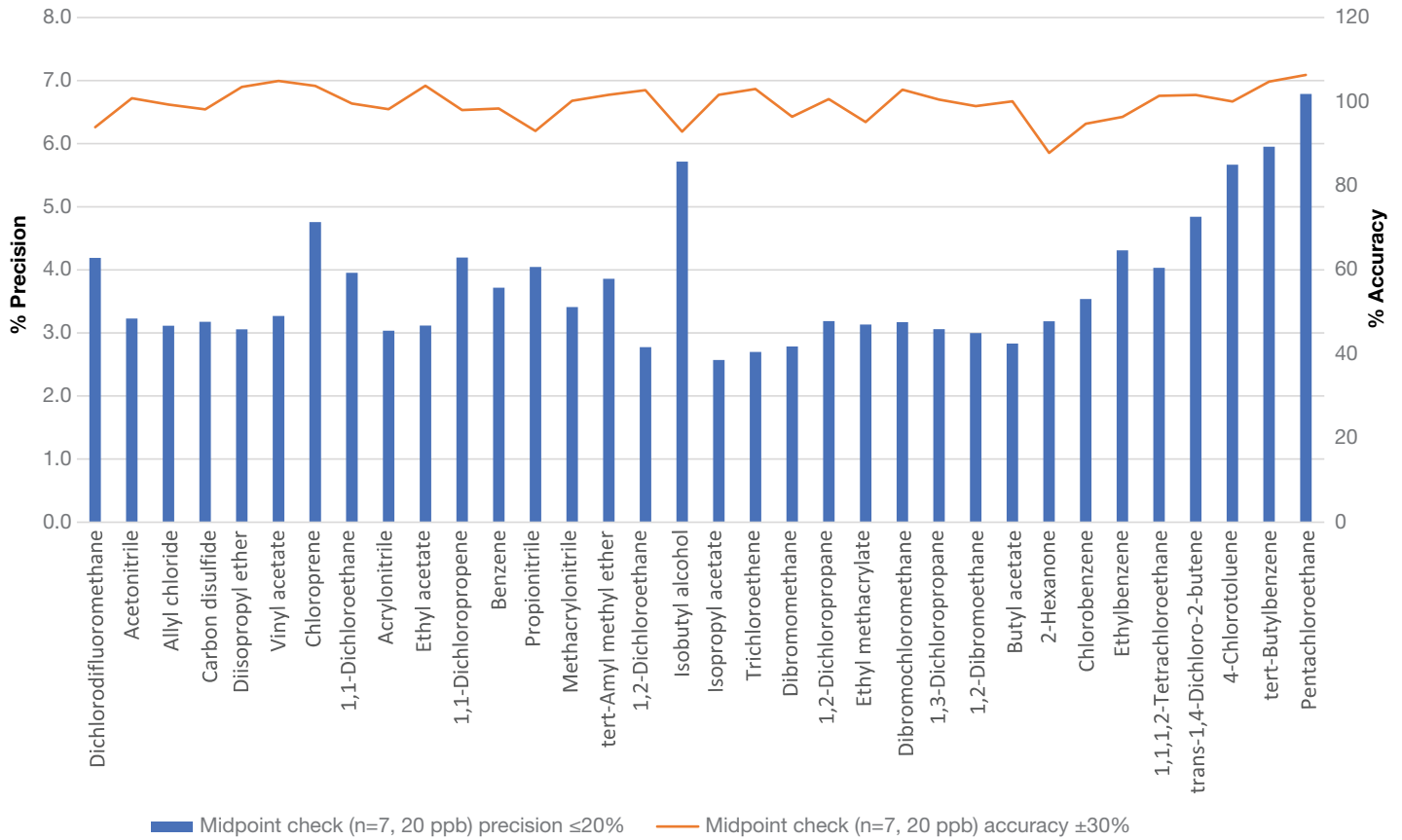


Figure 5. Demonstration of accuracy (% recovery) and precision (calculated concentration) by analyzing n=7 replicates of a 20 ppb soil standard

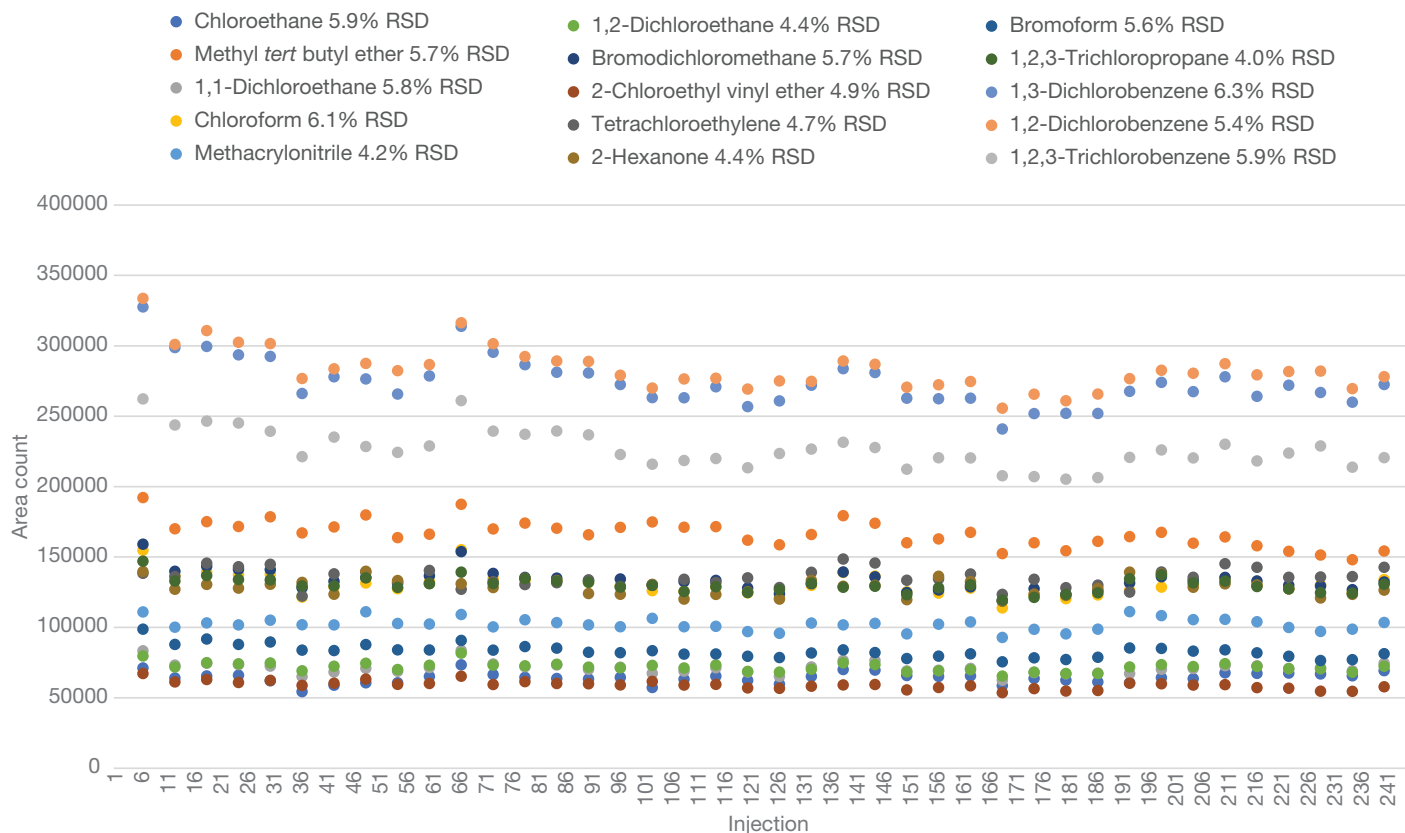


Figure 6. Repeatability (absolute peak area) of a 20 ppb water standard assessed over n=240 consecutive injections corresponding to 3 days of analysis (equivalent to 18 min/sample)

## 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

1. U.S. EPA Method 8260: Measurement of Volatile Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry. [https://www.epa.gov/sites/production/files/2017-04/documents/method\\_8260d\\_update\\_vi\\_final\\_03-13-2017.pdf](https://www.epa.gov/sites/production/files/2017-04/documents/method_8260d_update_vi_final_03-13-2017.pdf)
2. Thermo Scientific AppsLab Library. <https://appslab.thermofisher.com/>
3. Thermo Scientific Application Note 65632: Routine analysis of volatile organic compounds in drinking water with ISQ 7000 GC-MS. <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-65632-gc-ms-volatile-organic-compounds-drinking-water-an65632-en.pdf>

## Appendix I. Calibration, MDL, and IDC results for wastewater

### Appendix 1, part 1

Compound	Calibration (0.2 ppb–200 ppb)				Method detection limit (n=7, 0.2 ppb)		Mid-point check (n=7, 20 ppb)	
	Retention time	Quant. ion	RRF ( $\leq 20\%$ RSD $r^2 \geq 0.99$ )	Avg. RRF	MDL	Precision $\leq 20\%$	Precision $\leq 20\%$	Accuracy $\pm 30\%$
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 <sup>1</sup>	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 <sup>2</sup>	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 <sup>3</sup>	2.88	58	18.5	0.046	0.67	6.4	4.7	76
<i>trans</i> -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 <i>tert</i> butyl ether	3.14	73	6.3	0.757	0.05	7.5	2.6	107
<i>tert</i> -Butyl alcohol <sup>4</sup>	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
<i>tert</i> -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
<i>cis</i> -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

<sup>1</sup>Compound used a linear calibration

<sup>2</sup>Calibration curve from 0.5–200 ppb

<sup>3</sup>Calibration curve from 2.5–500 ppb

<sup>4</sup>Calibration curve from 1–1000 ppb

<sup>5</sup>Calibration curve from 0.5–500 ppb

<sup>6</sup>Calibration curve from 0.4–400 ppb

<sup>7</sup>Calibration curve from 0.25–100 ppb



Appendix 1, part 2

Compound	Calibration (0.2 ppb–200 ppb)				Method detection limit (n=7, 0.2 ppb)		Mid-point check (n=7, 20 ppb)	
	Retention time	Quant. ion	RRF ( $\leq 20\%$ RSD $r^2 \geq 0.99$ )	Avg. RRF	MDL	Precision $\leq 20\%$	Precision $\leq 20\%$	Accuracy $\pm 30\%$
1,1-Dichloropropene	4.78	75	9.1	0.819	0.08	5.3	4.2	98
2-Butanone <sup>2</sup>	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 <sub>4</sub> (surr)	5.16	65	12.2	0.140		3.3	1.4	104
Pentafluorobenzene (ISTD)	5.17	168						
<i>tert</i> -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
<i>cis</i> -1,3-Dichloropropene	6.88	75	9.7	0.905	0.05	3.9	3.0	103
Toluene-d <sub>8</sub> (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 <sup>2</sup>	7.53	100	7.9	0.024	0.30	7.6	3.5	88
<i>trans</i> -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 <sup>2</sup>	8.26	43	13.1	0.202	0.16	3.1	3.2	88
Chlorobenzene-d <sub>5</sub> (ISTD)	8.45	117						

<sup>1</sup>Compound used a linear calibration

<sup>2</sup>Calibration curve from 0.5–200 ppb

<sup>3</sup>Calibration curve from 2.5–500 ppb

<sup>4</sup>Calibration curve from 1–1000 ppb

<sup>5</sup>Calibration curve from 0.5–500 ppb

<sup>6</sup>Calibration curve from 0.4–400 ppb

<sup>7</sup>Calibration curve from 0.25–100 ppb

Appendix 1, part 3

Compound	Calibration (0.2 ppb–200 ppb)				Method detection limit (n=7, 0.2 ppb)		Mid-point check (n=7, 20 ppb)	
	Retention time	Quant. ion	RRF ( $\leq 20\%$ RSD $r^2 \geq 0.99$ )	Avg. RRF	MDL	Precision $\leq 20\%$	Precision $\leq 20\%$	Accuracy $\pm 30\%$
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
<i>m,p</i> -Xylene <sup>4</sup>	8.63	106	9.3	0.947	0.12	3.9	4.1	98
<i>o</i> -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 <sup>1</sup>	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
<i>cis</i> -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
<i>n</i> -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
<i>trans</i> -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
<i>tert</i> -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
<i>sec</i> -Butylbenzene	9.98	105	8.7	3.97	0.09	6.4	5.9	104
<i>p</i> -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- <i>d</i> <sub>4</sub> (ISTD)	10.16	152						
1,4-Dichlorobenzene	10.17	146	8.2	1.72	0.07	3.7	5.3	96
<i>n</i> -Butylbenzene	10.36	91	10.5	3.45	0.06	4.0	6.8	102
Hexachloroethane <sup>5</sup>	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 <sup>6</sup>	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 <sup>6</sup>	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

<sup>1</sup>Compound used a linear calibration

<sup>2</sup>Calibration curve from 0.5–200 ppb

<sup>3</sup>Calibration curve from 2.5–500 ppb

<sup>4</sup>Calibration curve from 1–1000 ppb

<sup>5</sup>Calibration curve from 0.5–500 ppb

<sup>6</sup>Calibration curve from 0.4–400 ppb

<sup>7</sup>Calibration curve from 0.25–100 ppb

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

### Appendix 2, part 1

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 ( $\leq 20\%$ RSD $r^2 \geq 0.99$ )	Avg. RRF	MDL	Precision $\leq 20\%$	Precision $\leq 20\%$	Accuracy $\pm 30\%$
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 <sup>1</sup>	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 <sup>1</sup>	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 <sup>1</sup>	2.81	49	0.999	2.80	0.14	4.3	2.6	121
Acetone <sup>1,2</sup>	2.90	58	0.997	0.138	2.32	6.4	3.1	128
<i>trans</i> -1,2-dichloroethene	2.99	96	10.3	1.51	0.09	4.7	3.2	96
Methyl acetate <sup>1</sup>	3.05	43	0.999	1.81	0.12	5.2	2.6	110
Methyl <i>tert</i> butyl ether	3.15	73	6.0	1.41	0.09	5.7	3.3	111
<i>tert</i> -Butyl alcohol <sup>3</sup>	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
<i>tert</i> -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
<i>cis</i> -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

<sup>1</sup>Compound used linear calibration

<sup>2</sup>Calibration from 1.25–500 ppb

<sup>3</sup>Calibration from 2.5–1000 ppb

<sup>4</sup>Calibration from 1–400 ppb

<sup>5</sup>Calibration from 0.25–100 ppb

<sup>6</sup>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 ( $\leq 20\%$ RSD $r^2 \geq 0.99$ )	Avg. RRF	MDL	Precision $\leq 20\%$	Precision $\leq 20\%$	Accuracy $\pm 30\%$
1,1-Dichloropropene	4.78	75	9.1	0.819	0.08	5.3	4.2	98
2-Butanone <sup>2</sup>	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 <sub>4</sub> (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 <sub>8</sub> (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 <sup>2</sup>	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 <sup>2</sup>	8.26	43	13.1	0.202	0.16	3.1	3.2	88
Chlorobenzene-d <sub>5</sub> (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 <sup>4</sup>	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

<sup>1</sup>Compound used linear calibration

<sup>2</sup>Calibration from 1.25–500 ppb

<sup>3</sup>Calibration from 2.5–1000 ppb

<sup>4</sup>Calibration from 1–400 ppb

<sup>5</sup>Calibration from 0.25–100 ppb

<sup>6</sup>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 ( $\leq 20\%$ RSD $r^2 \geq 0.99$ )	Avg. RRF	MDL	Precision $\leq 20\%$	Precision $\leq 20\%$	Accuracy $\pm 30\%$
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 <sup>1</sup>	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 <sub>4</sub> (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 <sup>5</sup>	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 <sup>6</sup>	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 <sup>6</sup>	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

<sup>1</sup>Compound used linear calibration

<sup>2</sup>Calibration from 1.25–500 ppb

<sup>3</sup>Calibration from 2.5–1000 ppb

<sup>4</sup>Calibration from 1–400 ppb

<sup>5</sup>Calibration from 0.25–100 ppb

<sup>6</sup>Calibration from 1–200 ppb

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