

## 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.<sup>1</sup> U.S. EPA Method 624.1 is an approved test method under the Clean Water Act<sup>2</sup> 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<sub>2</sub>Safe™ 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
Sweep 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<sub>2</sub>Safe 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 <sub>2</sub> Safer 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.<sup>3</sup>

## 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

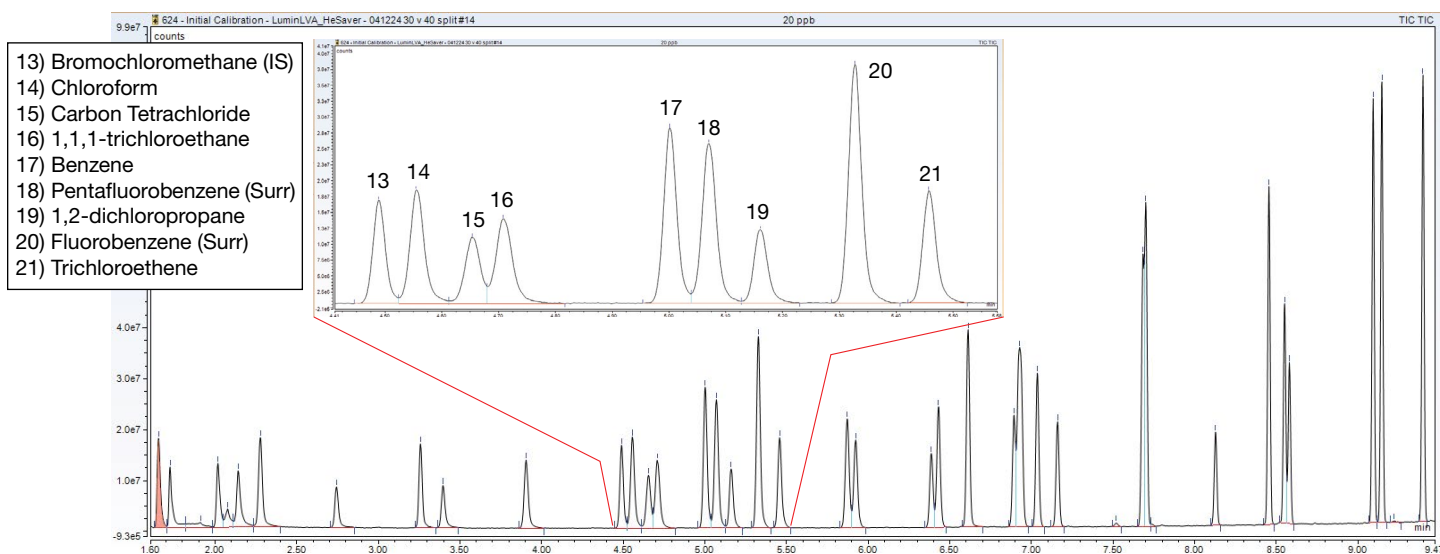


Figure 1. Total ion chromatogram (TIC) of a 20 ppb VOC standard with an inset indicating consistent peak shapes and separation with minimal water interference



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.

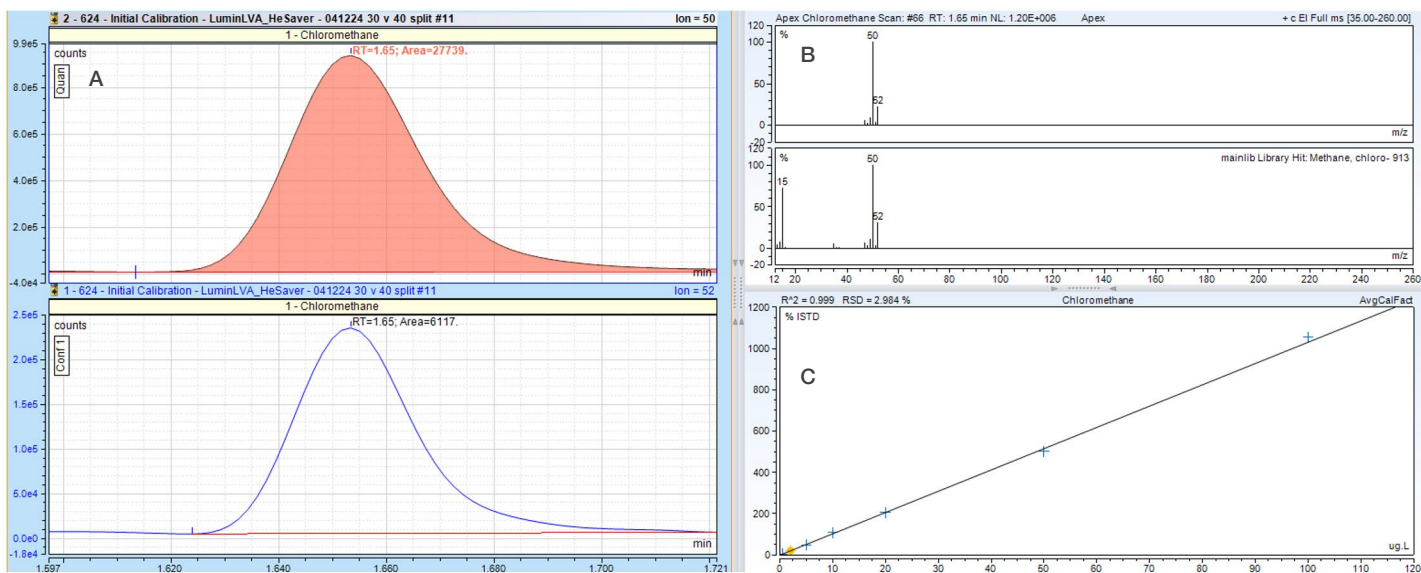


Figure 2. Chromeleon CDS results browser showing extracted ion chromatograms for 1-chloromethane in the 2 ppb standard, quantitation ion (50), and one confirming ion (52) (A), a matching measured spectrum to the NIST library (B), and a linear calibration over a concentration range of 0.5 ppb to 100 ppb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

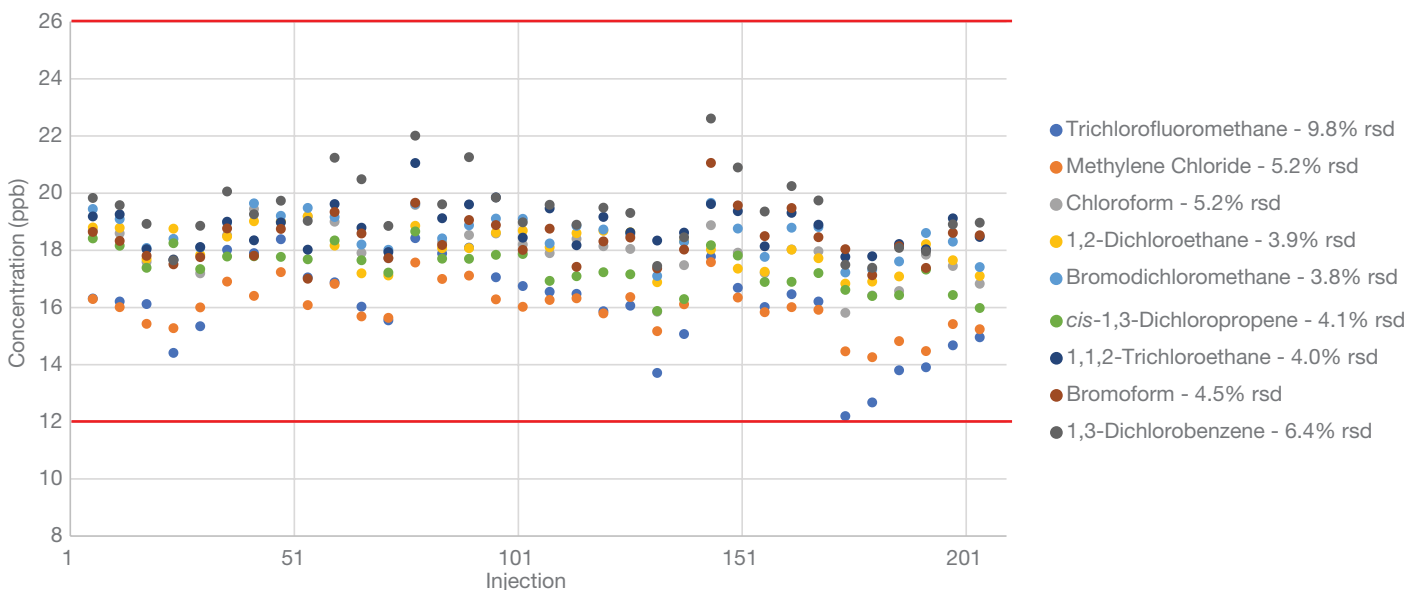


Figure 3. Reproducibility of nine compounds in 20 ppb water standards (n=34) over 209 sample injections

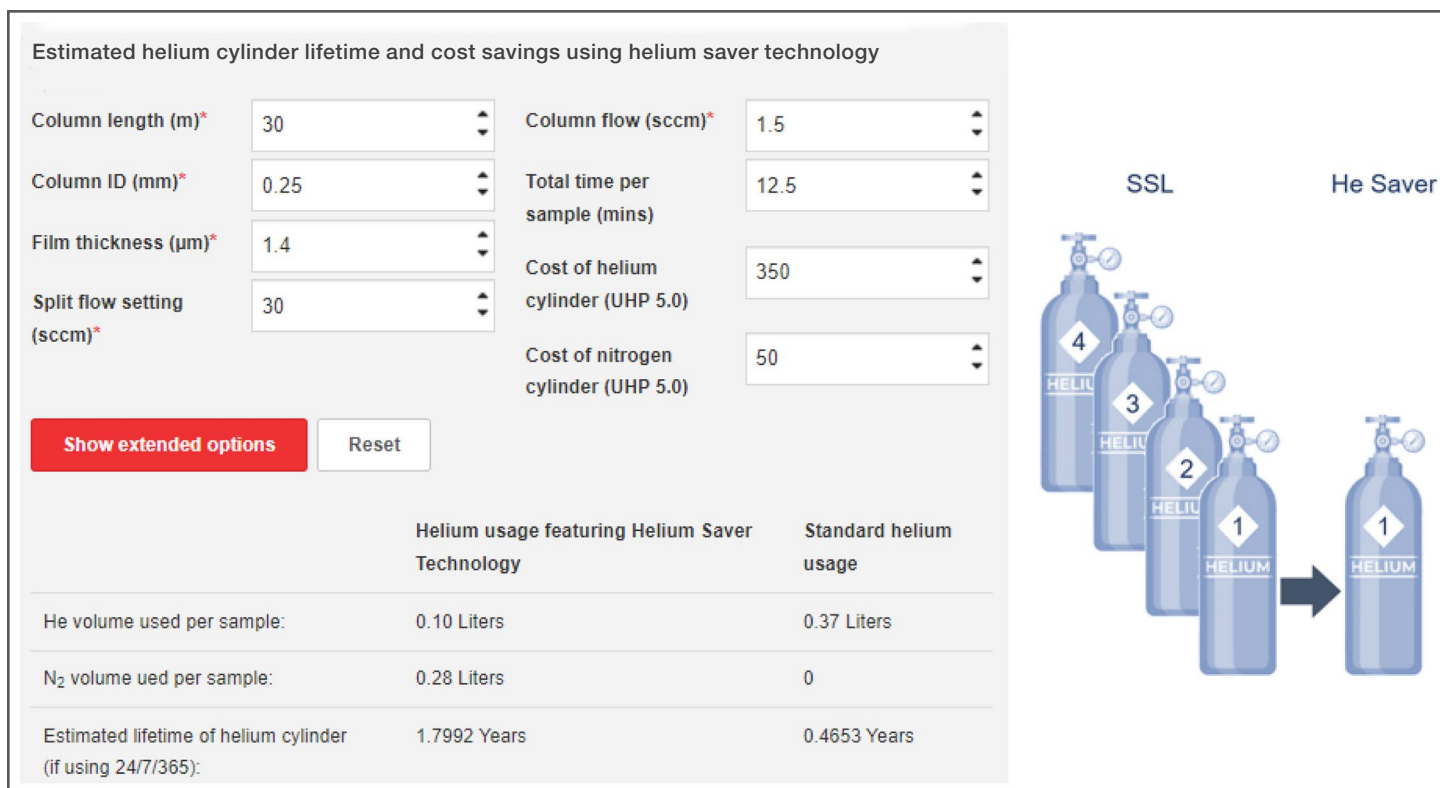


Figure 4. Helium Saver Calculator tool showing 4x savings of carrier gas

### Reduced helium consumption and cost savings

The HeSaver-H<sub>2</sub>Safer 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](#).<sup>4</sup> 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<sub>2</sub>Safer 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.<sup>3</sup>

### References

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## Appendix

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

Compound	Calibration				Method detection limit (n=7, 0.5 ppb)		Mid-point check (n=7, 20 ppb)	
	Retention Time	Quant ion	Relative SD (%RSD)	Average RF	MDL (ppb)	Precision ( $\leq 20\%$ )	Precision ( $\leq 20\%$ )	Accuracy ( $\pm 20\%$ )
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
<i>trans</i> -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
<i>cis</i> -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
<i>trans</i> -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
<i>trans</i> -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

Compound	Analyte recovery (20 ppb n=34, 209 injections)	
	Precision (≤20%RSD)	Accuracy (±30%)
Bromodichloromethane	3.84	93
2-Chloroethyl vinyl ether	3.51	89
Toluene	6.37	83
Tetrachloroethene	8.30	82
<i>cis</i> -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
<i>trans</i> -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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