Application note | 002337

Environmental

Reducing the helium consumption for analysis of VOCs in accordance with EPA Method 8260D without compromising performance using HeSaver-H_2Safer technology

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Keywords

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Goal

To describe the use of the Thermo Scientific™ ISQ™ 7610 single quadrupole mass spectrometer coupled with a Thermo Scientific™ TRACE™ 1610 gas chromatograph (GC) and the Teledyne Tekmar Atomx XYZ P&T for U.S. EPA Method 8260

Introduction

Volatile organic compounds (VOCs) have a high vapor pressure and low water solubility. Many VOCs are human-made chemicals that are used and produced in the manufacturing industry. They can also be generated as by-products of chlorination used in water treatment.[1] Many of these compounds are environmental contaminants and therefore are considered a hazard to human health when present at elevated levels. Analytical testing laboratories often perform testing to ensure these analytes do not exceed the allowed limits in the environment globally. There are regulations in place for a number of environmental sample types, with one of the most prominent ones being United States Environment Protection Agency (EPA) Method 8260D[2] that is commonly used to monitor a variety of solid waste matrices for the presence of VOCs.

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The analytical method of choice for the analysis of VOCs is gas chromatography coupled to single quadrupole mass spectrometry combined with Purge and Trap (P&T) sampling. The sample is purged with an inert gas, causing volatile compounds to be swept out of the sample. The volatile compounds are firstly retained in an adsorbent trap, then desorbed by heating the trap, and finally transferred to the GC column for analysis.

Helium is commonly used as a carrier gas for gas chromatography thanks to its high chromatographic efficiency and inertness. Recent price rises in helium and supply issues caused by shortages have led GC manufacturers, researchers, and analysts to investigate possible mitigation options that entail either switching to alternative carrier gases or reducing the helium consumption. The Thermo Scientific™ HeSaver-H_2Safer™ carrier gas saving technology[3] offers an innovative and smart approach to dramatically reduce carrier gas consumption, especially during GC operation. It consists of a modified SSL body connected to two gas lines. Whereas an inexpensive gas (e.g., nitrogen or argon) is used for inlet pressurization, analyte vaporization, and transfer to the analytical column, 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 carrier gas, the limited consumption allows mitigation of shortage issues while maintaining GC-MS performance without the need of instrument method re-optimization otherwise required in case of migration to a different carrier gas.

A TRACE 1610 gas chromatograph equipped with a Thermo Scientific™ iConnect™ split/splitless injector, upgraded to work in HeSaver-H_2Safer mode, was coupled to the ISQ 7610 single quadrupole mass spectrometer and a Teledyne Tekmar Atomx XYZ P&T and used to analyze water and soil samples according to EPA Method 8260D. To perform EPA Method 8260D, 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. Details of the material and the methods used for sample preparation, as well as complete lists of reagents and consumables, are reported in a previous application note.[4] Instrument settings are reported in Appendix 1.

Results and discussion

One of the key benefits of the HeSaver-H_2Safer inlet is that the method transfer (for methods using the standard SSL injector) required minimal effort and the chromatographic performance remained unaffected independent of the analyzed matrix (soil or water). Typical chromatograms for 20 µg/L (in water) and 20 µg/kg (in soil) VOC standards are shown in Figure 1.

Linearity was assessed using a calibration curve from 0.5 to 200 µg/L (ppb) for water, whereas for soil matrix, the calibration curve ranged from 1 to 200 µg/kg (ppb). The average response factor RSD for the calibration solutions was in compliance with the EPA method requirements with calculated values <20% for all compounds across the specified concentration range for both water and soil matrices as reported in Appendix 2 and Appendix 3, respectively. Examples of extracted ion chromatograms (XICs), as well as spectrum comparison with the NIST library and calibration curves obtained for some selected compounds are shown in Figure 2 for water and soil samples spiked with 0.5 µg/L and 5 µg/kg VOC standard solutions, respectively.

The method detection limit (MDL) and precision were assessed using n=7 replicates of a 0.5 µg/L VOC standard spiked in a water sample and n=7 replicates of a 2 µg/kg VOC standard spiked in a soil sample. Calculated MDLs were ≤0.14 µg/L and ≤0.42 µg/kg for water and soil, respectively, with calculated precision of less than 20% for all compounds in both the analyzed matrices (Appendix 2 and Appendix 3, respectively).

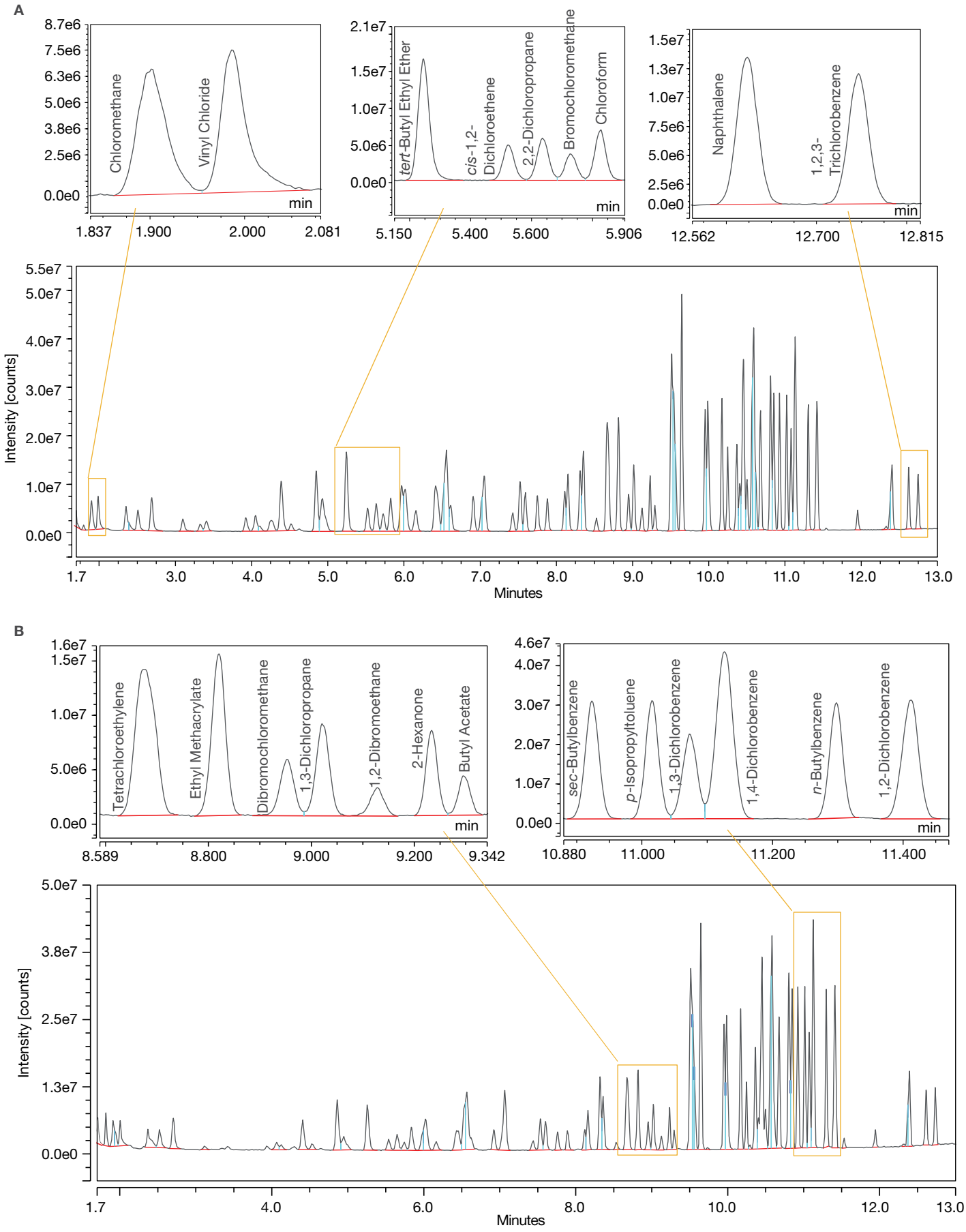

Figure 1. Chromatographic performance achieved with the HeSaver-H_2Safer technology for VOC standard in water (A) and soil (B) samples spiked at 20 µg/L and 20 µg/kg, respectively

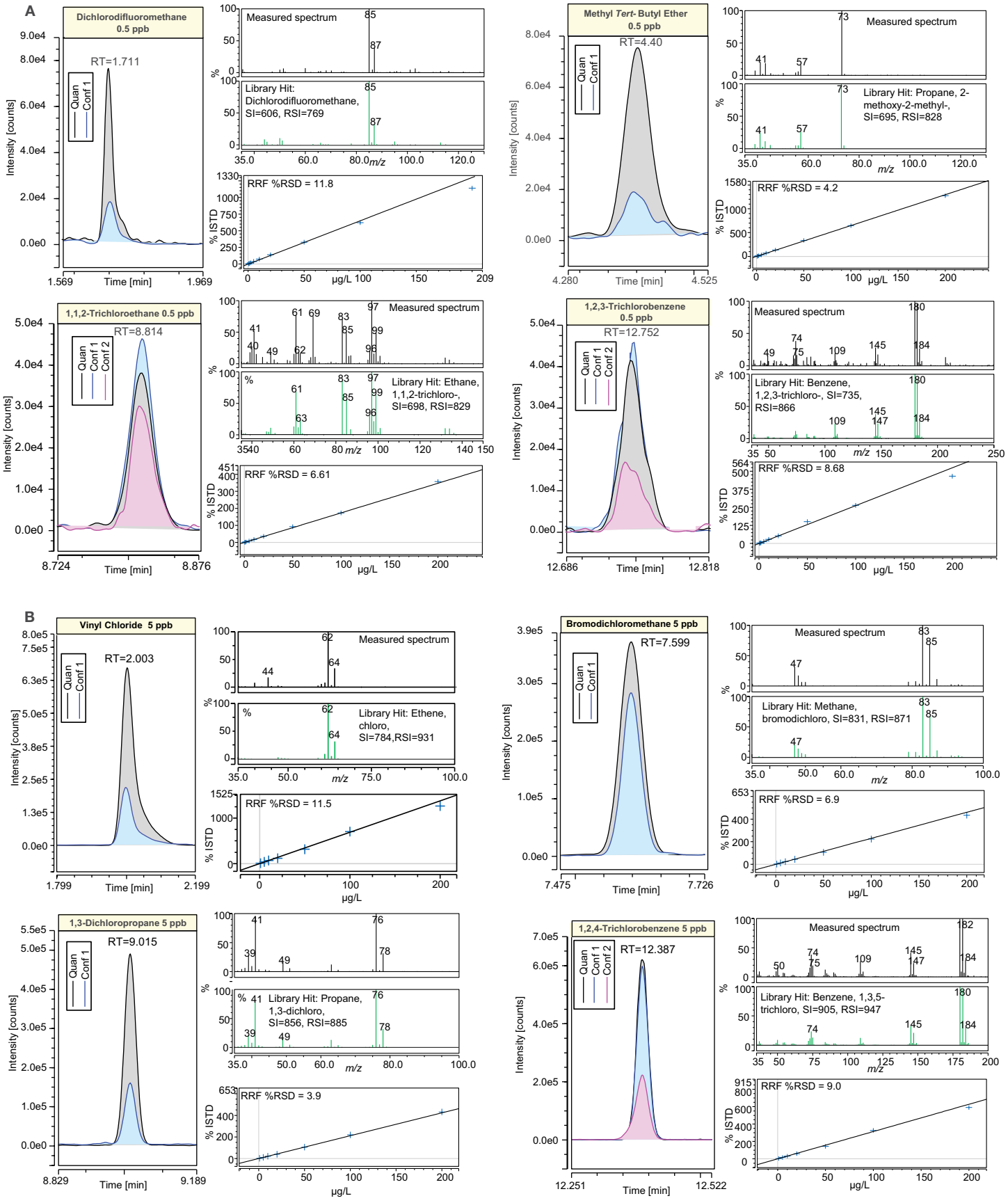

Figure 2. Examples of XICs for quantifier and qualifier ions, spectrum comparison with the NIST spectral library and calibration curves obtained for dichlorodifluoromethane, methyl *tert*-butyl ether, 1,1,2-trichloroethane, and 1,2,3-tricholrobenzene in a water sample spiked with a 0.5 µg/L VOC standard solution (A) as well as vinyl chloride, bromochloromethane, 1,3-dicholoropropane, and 1,2,4-dicholorobenzene in soil spiked with a 5 µg/kg VOC standard solution (B)

Accuracy and precision when analyzing water and soil matrices were evaluated by injecting n=10 replicates of a 10 µg/L (for water) or 10 µg/kg (for soil) of matrix-matched standard. For all compounds assessed, the precision (%RSD) was ≤20 with accuracy ranging from 78% to 130% for both the analyzed matrices, meeting the requirements of EPA Method 8260D (Appendix 2 and Appendix 3, respectively).

The HeSaver-H_2Safer concept of decoupling the inlet pressurizing gas and the carrier gas reduces contamination from the injector into the column: the pressuring gas flushing the liner and the injector is discharged only through the split line for most of the time, entering the column just for the limited time of the injection phase and therefore limiting the transfer of contaminants (septum/sample matrix/by-products). This was demonstrated by running a 240-sample injection sequence over three days. To monitor system performance, n=40 quality controls (QCs), consisting of water standards at 20 µg/L, were prepared and injected at regular intervals. The water standards were acquired with no user intervention at all on the entire analytical system, including the P&T, GC, or MS system. Excellent system stability was demonstrated with QC precision within ±30% the expected amount and accuracy ranging from 70% to 117%. The results obtained for some selected compounds covering the entire VOCs boiling point range are shown as an example in Figure 3. Details of the results can be found in Appendix 4.

Reduced helium consumption and cost savings

The HeSaver-H_2Safer technology offers significant gas savings not only when the GC is idle, but mainly during sample injection and analysis. When used with helium as carrier gas, it translates into an extended helium cylinder lifetime from months to years, depending on the instrument method and usage, and how many GCs are connected. The Thermo Scientific™ Helium Saver Calculator tool[5] offers an easy-to-use and intuitive interface to estimate the helium consumption and cost impact. The user is only required to insert the column geometry, the carrier and split flow settings, as well as helium and nitrogen costs and the tool provides an estimation of both the helium cylinder lifetime and the cost savings. The use of the HeSaver-H_2Safer technology for the analysis of VOCs according to EPA Method 8260D[2] allows the use of a low carrier gas flow (0.3 mL/min) compared to a standard P&T method, which would require a helium flow of 0.8 mL/min if a standard SSL were used. This would allow a helium cylinder to last about 4 times longer in comparison to a standard SSL injector (Figure 4).

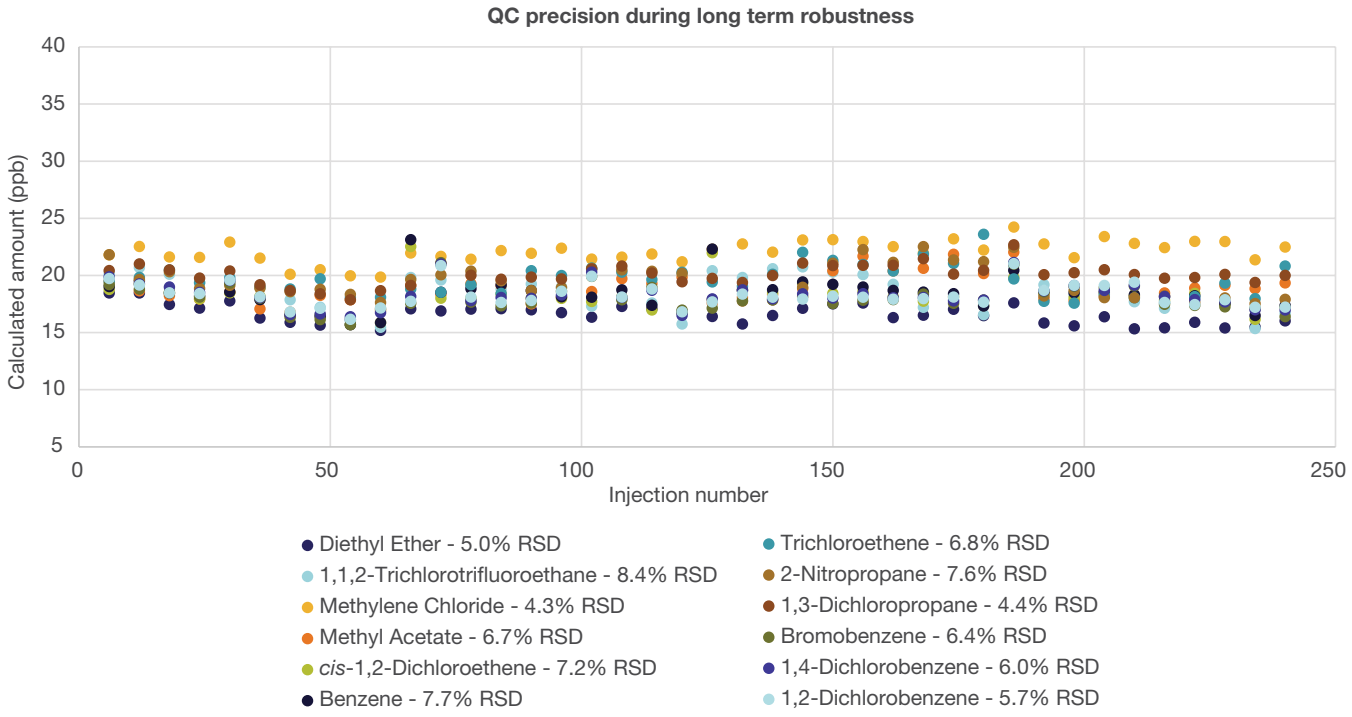

Figure 3. Precision of QC water samples spiked at 20 µg/L VOC standard assessed over n=240 consecutive injections over three days of analysis

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

Column length (m)*	20	Column flow (sccm)*	0.8
Column ID (mm)*	0.18	Total time per sample (mins)	26.85
Film thickness (µm)*	1	Cost of helium cylinder (UHP 5.0)	350
Split flow setting (sccm)*	60	Cost of nitrogen cylinder (UHP 5.0)	50

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	Helium usage featuring Helium Saver Technology	Standard helium usage
He volume used per sample:	0.21 Liters	0.88 Liters
N_2 volume ued per sample:	0.68 Liters	0
Estimated lifetime of helium cylinder (if using 24/7/365):	1.7993 Years	0.4212 Years
Estimated lifetime of helium cylinder (if using 8 hrs x 5 days/wk for 365):	7.3912 Years	1.7645 Years
Annual cost savings (if using 24/7/365):	$545.11	$0.00
Lifetime cost savings (assuming 14 years of GC-MS instrument life time):	$7,631.49	$0.00

The information and calculations included here are intended to serve as estimates only. Further attributes and detail can be considered on a case-by-case basis for a more complete and in-depth analysis.

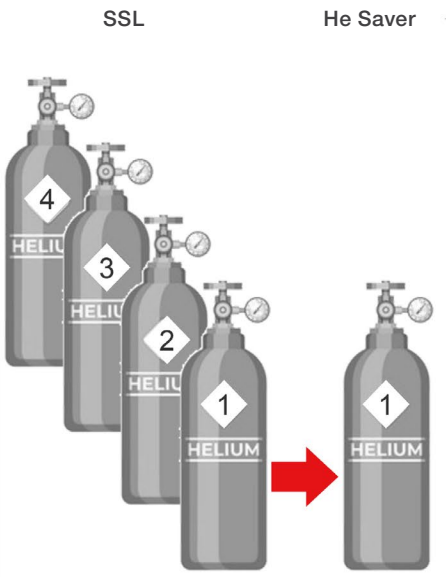

Figure 4. Gas Saver Calculator reporting the helium savings for EPA Method 8260D. The cylinder's cost is indicative and country dependent.

Conclusion

The HeSaver-H_2Safer technology offers the advantage of reduced helium gas consumption without compromising GC-MS performance for the analysis of VOCs in environmental samples, through a smooth and simple upgrade of a standard iConnect SSL injector module.

- The transition from the injection phase using an inexpensive pressurizing gas to the separation process using the best carrier gas is extremely fast (within a few milliseconds), ensuring a rapid gas replacement into the column and thus analogous performance compared to the standard SSL injector.
- HeSaver-H_2Safer technology provides consistent analytical performance compared to the standard SSL injector in terms of analyte transfer, linearity, precision, accuracy, and robustness in compliance with EPA Method 8260D suitability requirements.
- Moreover, the HeSaver-H_2Safer technology provides additional advantages, such as maintaining the column flow during the inlet maintenance, protecting the column from possible contaminants.
- The Helium Saver Calculator tool allows for easy and immediate estimation of helium cylinder lifetime and cost savings when using the Helium Saver technology.

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Appendix 1. Experimental conditions

Part 1, Atomix XYZ method water matrix

P&T and GC-MS experimental conditions for the analysis of VOCs according to EPA Method 8260D. Atomx XYZ method parameters for water matrix

Standby	**Variable**
Valve oven temp. (°C)	150
Transfer line temp. (°C)	150
Sample mount temp. (°C)	90
Water heater temp. (°C)	90
Sample cup temp. (°C)	20
Soil valve temp. (°C)	50
Standby flow (mL/min)	10
Purge ready temp. (°C)	40
Purge	**Variable**
Sample equilibrate time (min)	0
Pre-sweep time (min)	0.25
Prime sample fill volume (mL)	3
Sample volume (mL)	5
Sweep sample time (min)	0.25
Sweep sample flow (mL/min)	100
Sparge vessel heater	Off
Purge time (min)	11
Purge flow (mL/min)	40
Purge temp. (°C)	20
MCS purge temp. (°C)	20
Dry purge time (min)	1
Dry purge flow (mL/min)	100
Dry purge temp. (°C)	20
Desorb	**Variable**
Methanol needle rinse	Off
Water needle rinse volume (mL)	7
Sweep needle time (min)	0.25
Desorb preheat temp. (°C)	245
GC start signal	Begin Desorb
Desorb time (min)	0.5
Drain flow (mL/min)	300
Desorb temp. (°C)	250
Bake	**Variable**
Methanol glass rinse	Off
Water bake rinses	5
Water bake rinse volume(mL)	10
Bake rinse sweep time (min)	0.25
Bake rinse sweep flow (mL/min)	100
Bake rinse drain time (min)	0.4
Bake time (min)	4
Trap bake temp. (°C)	280
MCS bake temp. (°C)	200
Bake flow (mL/min)	200
Trap	9
Chiller tray	Off
Purge gas	Nitrogen

Part 2, Atomix XYZ method soil matrix

P&T and GC-MS experimental conditions for the analysis of VOCs according to EPA Method 8260D method. Atomx XYZ method parameters for soil matrix

Standby	**Variable**
Valve oven temp. (°C)	150
Transfer line temp. (°C)	150
Sample mount temp. (°C)	90
Water heater temp. (°C)	90
Sample cup temp. (°C)	20
Soil valve temp. (°C)	100
Standby flow (mL/min)	10
Purge ready temp. (°C)	40
Purge	**Variable**
Pre-purge time (min)	0
Pre-purge flow (min)	0
Pre-heat mix speed	Slow
Sample pre-heat time (min)	0
Pre-sweep time (min)	0.25
Water volume (mL)	10
Sweep water time (min)	0.25
Sweep water flow (mL/min)	100
Sparge vessel heater	Off
Purge mix speed	Medium
Purge time (min)	11
Purge flow (mL/min)	40
Purge temp. (°C)	20
MCS purge temp. (°C)	20
Dry purge time (min)	2
Dry purge flow (mL/min)	100
Dry purge temp. (°C)	20
Desorb	**Variable**
Methanol needle rinse	Off
Water needle rinse volume (mL)	7
Sweep needle time (min)	0.25
Desorb preheat temp. (°C)	245
GC start signal	Begin Desorb
Desorb time (min)	0.5
Drain flow (mL/min)	300
Desorb temp. (°C)	250
Bake	**Variable**
Bake time (min)	4
Bake flow (mL/min)	200
Bake temp. (°C)	270
MCS bake temp. (°C)	200
Trap	9
Purge gas	Nitrogen

Part 3, GC-MS conditions

TRACE 1610 GC and ISQ 7610 single quadrupole parameters

Parameter	Value
Inlet module and mode	SSL upgraded to HeSaver-H_2Saver, split
Liner	Direct straight liner (P/N 453A1335)
Inlet temperature (°C)	200
Split ratio	60:1 (Nitrogen)
Septum purge mode, flow (mL/min)	Constant, 5 (Nitrogen)
Carrier gas, mode, flow (mL/min)	He, constant flow, 0.3
Helium delay (min)	0.4
Oven temperature program	
Temperature 1 (°C)	35
Hold time (min)	4
Rate (°C/min)	12
Temperature 2 (°C)	85
Rate (°C/min)	25
Temperature 3 (°C)	225
Hold time (min)	2
GC total run time (min)	14.767

Parameter	Value
ISQ 7610 single quadrupole parameters:	
Ion source	Thermo Scientific™ ExtractaBrite™
Transfer line temperature (°C)	230
Source temperature (°C)	280
Ionization mode	EI
Electron energy (eV)	70
Emission current (µA)	30
Acquisition mode	Full Scan
Mass range (*m/z*)	35–260
Solvent delay (min)	1.55
Dwell/Scan time (s)	0.1
Chromatographic column	Thermo Scientific™ TraceGOLD™ TG-VMS (P/N 26080-4950) 20 m × 0.18 mm, 1 µm

Appendix 2. Precision and accuracy, water samples

Calculated relative response factors (RRFs), MDLs, as well as precision and accuracy for mid-point check at 10 µg/L for water samples

	Calibration (0.5–200 µg/L)				Method detection limit (n=7, 0.5 µg/L)		Mid-point check (n=10, 10 µg/L)	
Compound	RT (min)	Quan ion (*m/z*)	RRF (≤20% RSD R^2 ≥0.99)	Avg. RRF	MDL	Precision ≤20% RSD	Precision ≤20% RSD	Accuracy ±30%
Dichlorodifluoromethane	1.70	85	11.85	1.76	0.10	5.80	6.80	97
Chloromethane	1.91	50	10.14	2.54	0.11	6.61	6.28	100
Vinyl Chloride	2.00	62	8.05	2.29	0.06	3.54	6.37	102
Bromomethane	2.36	94	7.12	1.19	0.06	3.49	4.64	102
Chloroethane	2.52	64	5.63	1.45	0.11	7.08	9.01	94
Trichlorofluoromethane	2.70	101	6.12	2.04	0.09	5.28	6.49	101
Diethyl ether	3.12	74	3.90	0.37	0.05	3.07	4.10	97
1,1-Dichloroethene	3.34	61	8.82	0.40	0.19	10.16	5.70	102
1,1,2-Trichlorotrifluoroethane	3.42	101	9.52	0.38	0.14	8.46	5.81	103
Iodomethane[1]	3.49	142	1.00	0.06	1.22	2.97	2.77	130
Carbon disulfide	3.89	76	9.98	0.25	0.12	7.30	4.99	95
Allyl chloride	3.93	76	8.06	0.25	0.15	8.35	5.72	96
Methylene chloride[2]	4.06	49	1.00	1.01	0.19	5.66	2.57	122
Acetone[2]	4.12	58	0.99	0.08	0.59	11.16	5.55	120
trans-1,2-dichloroethene	4.26	96	10.62	0.27	0.13	6.99	6.06	95
Methyl acetate	4.30	43	12.31	0.95	0.14	8.84	4.22	96
Methyl tert-butyl ether	4.40	73	4.24	1.62	0.08	5.25	2.73	102
tert-Butyl alcohol	4.54	59	8.14	0.07	0.69	8.02	8.08	95
Diisopropyl ether	4.86	45	4.32	1.89	0.07	4.76	2.56	100
Acetonitrile	4.86	41	6.18	0.69	0.10	6.29	2.39	103

[1]Compound has a quadratic calibration

[2]Compound has a linear calibration

Calculated relative response factors (RRFs), MDLs, as well as precision and accuracy for mid-point check at 10 µg/L for water samples (continued)

	Calibration (0.5–200 µg/L)				Method detection limit (n=7, 0.5 µg/L)		Mid-point check (n=10, 10 µg/L)	
Compound	RT (min)	Quan ion (*m/z*)	RRF (≤20% RSD R^2 ≥0.99)	Avg. RRF	MDL	Precision ≤20% RSD	Precision ≤20% RSD	Accuracy ±30%
Acrylonitrile	4.92	53	2.65	0.45	0.13	8.55	5.45	100
Chloroprene	4.92	53	3.71	0.45	0.12	7.60	5.36	100
1,1-Dichloroethane	4.95	63	6.48	0.82	0.08	4.54	3.81	102
tert-Butyl ethyl ether	5.26	59	6.37	1.83	0.14	10.01	2.71	99
Vinyl Acetate	5.26	43	5.66	1.28	0.12	8.98	10.5	85
cis-1,2-Dichloroethene	5.53	96	7.26	0.35	0.14	8.13	3.61	101
2,2-Dichloropropane	5.65	77	8.05	0.64	0.09	5.49	7.95	88
Bromochloromethane	5.74	128	11.13	0.15	0.12	7.46	1.62	99
Chloroform	5.83	83	7.28	0.93	0.07	4.22	3.39	103
Carbon tetrachloride	5.97	117	6.71	0.36	0.15	9.58	4.67	97
Methyl acrylate	5.98	55	7.16	0.51	0.12	8.49	4.30	97
Ethyl acetate	5.99	43	5.20	0.69	0.11	7.06	4.36	99
Tetrahydrofuran	6.00	42	8.98	0.30	0.16	9.92	4.40	101
Dibromofluoromethane (surr)	6.02	111	3.86	0.77		2.38	1.50	103
1,1,1-trichloroethane	6.03	97	5.33	0.55	0.07	4.56	4.63	104
2-Butanone	6.16	43	7.32	0.14	0.45	9.52	5.30	105
1,1-Dichloropropene	6.17	75	4.49	0.30	0.11	7.15	5.47	97
Benzene	6.42	78	2.98	1.21	0.07	4.22	4.05	100
Propionitrile	6.44	54	10.61	0.12	0.18	9.89	4.09	98
Methacrylonitrile	6.46	41	4.31	0.52	0.10	6.41	3.37	102
Pentafluorobenzene (ISTD)	6.53	168	–	–	–	–	–	–
1,2-Dichloroethane-d_4 (surr)	6.55	65	4.37	0.42		1.82	2.33	103
tert-Amyl methyl ether	6.57	73	5.61	1.53	0.04	2.56	2.30	97
1,2-Dichloroethane	6.62	62	7.03	0.77	0.10	5.34	2.33	106
Isobutyl alcohol	6.92	43	6.58	1.27	0.10	6.38	3.67	100
Isopropyl acetate	6.92	43	5.26	1.27	0.13	8.94	3.56	100
Trichloroethene	7.02	130	6.80	0.62	0.16	9.80	3.14	107
1,4-Difluorobenzene (ISTD)	7.06	114	–	–	–	–	–	–
Dibromomethane	7.44	93	6.74	0.30	0.16	9.87	2.83	105
1,2-Dichloropropane	7.53	63	5.23	0.60	0.05	3.14	2.64	102
Bromodichloromethane	7.60	83	4.38	0.83	0.07	4.57	1.88	103
Methyl Methacrylate	7.76	69	8.93	0.40	0.14	9.51	4.37	96
Propyl Acetate	7.89	43	6.14	0.96	0.10	7.26	4.27	98
2-Chloroethyl vinyl ether	8.12	63	9.21	0.50	0.17	11.65	3.08	96
cis-1,3-dichloropropene	8.16	75	3.89	0.93	0.10	7.27	3.38	98
Toluene-d_8 (surr)	8.32	98	1.97	0.79		1.29	1.92	100
Toluene	8.36	92	6.55	0.85	0.17	10.82	4.88	95
2-Nitropropane	8.66	43	5.06	0.65	0.14	9.44	4.92	97
4-methyl-2-pentanone	8.66	100	6.98	0.03	0.29	7.28	5.15	91
Tetrachloroethylene	8.67	164	10.64	0.36	0.09	4.85	4.49	116
trans-1,3-Dichloropropene	8.69	75	6.05	0.82	0.08	5.66	3.71	96
1,1,2-Trichloroethane	8.81	83	6.61	0.43	0.11	8.09	4.06	102
Ethyl methacrylate	8.82	69	9.74	0.68	0.06	4.70	4.41	97

Calculated relative response factors (RRFs), MDLs, as well as precision and accuracy for mid-point check at 10 µg/L for water samples (continued)

	Calibration (0.5–200 µg/L)				Method detection limit (n=7, 0.5 µg/L)		Mid-point check (n=10, 10 µg/L)	
Compound	RT (min)	Quan ion (*m/z*)	RRF (≤20% RSD R^2 ≥0.99)	Avg. RRF	MDL	Precision ≤20% RSD	Precision ≤20% RSD	Accuracy ±30%
Dibromochloromethane	8.95	129	5.37	0.46	0.07	4.93	3.54	100
1,3-Dichloropropane	9.02	76	4.60	0.88	0.05	3.31	4.14	101
1,2-Dibromoethane	9.13	107	4.05	0.41	0.05	3.47	3.62	101
Butyl acetate	9.23	43	6.63	0.94	0.14	9.69	5.50	98
2-Hexanone	9.30	43	6.05	0.17	0.36	8.92	6.41	97
Chlorobenzene-d_5 (ISTD)	9.51	117	–	–	–	–	–	–
Chlorobenzene	9.52	112	2.10	1.11	0.05	2.88	3.98	98
Ethylbenzene	9.54	91	2.80	1.97	0.07	4.33	4.68	95
1,1,1,2-Tetrachloroethane	9.57	131	5.63	0.40	0.07	5.13	3.65	98
m,p-Xylene	9.65	106	3.26	0.69	0.16	5.42	5.08	97
o-Xylene	9.95	106	2.02	0.72	0.11	7.36	4.24	96
Styrene	9.99	104	6.86	1.23	0.10	7.15	4.35	97
Bromoform	10.01	173	13.12	0.26	0.07	5.76	4.51	99
Isopropylbenzene	10.17	105	2.71	1.84	0.09	6.23	5.42	96
Amyl acetate	10.25	43	11.92	1.03	0.11	8.89	3.60	98
4-Bromofluorobenzene (surr)	10.37	95	3.20	1.27		2.19	2.72	100
cis-1,4-Dichloro-2-butene	10.41	88	12.08	0.51	0.18	15.80	6.19	94
Bromobenzene	10.44	156	5.42	0.83	0.09	5.80	4.20	99
n-Propylbenzene	10.46	91	5.17	4.80	0.09	5.81	4.26	99
1,1,2,2-Tetrachloroethane	10.50	83	10.62	1.27	0.05	3.87	5.27	97
2-Chlorotoluene	10.57	91	4.15	3.66	0.08	4.75	4.43	100
1,3,5-Trimethylbenzene	10.59	105	10.09	3.30	0.10	7.00	3.89	98
1,2,3-Trichloropropane	10.59	75	10.15	1.44	0.17	8.34	4.57	106
trans-1,4-Dichloro-2-butene	10.62	53	7.12	0.67	0.10	6.62	5.35	97
4-Chlorotoluene	10.68	91	4.52	3.34	0.05	3.11	3.91	100
Pentachloroethane	10.81	77	7.35	0.44	0.17	11.98	4.44	100
tert-Butylbenzene	10.81	119	8.92	3.06	0.13	9.37	6.02	92
1,2,4-Trimethylbenzene	10.85	105	9.96	3.37	0.05	4.07	3.92	99
sec-Butylbenzene	10.93	105	7.38	3.84	0.08	5.80	5.37	100
p-Isopropyltoluene	11.02	119	11.27	2.93	0.11	8.87	4.90	100
1,3-Dichlorobenzene	11.08	146	5.73	1.72	0.07	4.41	3.94	99
1,4-Dichlorobenzene-d_4 (ISTD)	11.13	152	–	–	–	–	–	–
1,4-Dichlorobenzene	11.14	146	9.08	1.70	0.10	6.19	4.11	101
n-Butylbenzene	11.31	91	11.17	3.04	0.09	6.40	5.00	97
Hexachloroethane	11.41	117	9.22	0.91	0.05	6.04	4.97	93
1,2-Dichlorobenzene	11.42	146	5.76	1.67	0.08	4.83	4.45	100
1,2-Dibromo-3-chloropropane	11.95	157	8.81	0.20	0.14	9.22	6.39	99
Nitrobenzene	12.33	123	13.04	0.03	0.27	12.45	9.52	89
Hexachlorobutadiene	12.38	225	9.49	0.24	0.19	11.17	7.56	99
1,2,4-Trichlorobenzene	12.4	180	6.84	0.77	0.14	7.92	4.39	101
Naphthalene	12.62	128	9.18	2.20	0.08	5.34	5.37	96
1,2,3-Trichlorobenzene	12.74	180	8.67	0.66	0.15	8.90	5.01	104

Appendix 3. Precision and accuracy, soil samples

Calculated relative response factors (RRFs), MDLs, as well as precision and accuracy for mid-point check at 10 µg/kg for soil samples

Compound	Calibration (1–200 µg/kg)				Method detection limit (n=7, 2 µg/kg)		Mid-point check (n=10, 10 µg/kg)	
	RT (min)	Quan ion (*m/z*)	RRF (≤20% RSD R^2 ≥0.99)	Avg. RRF	MDL	Precision ≤20% RSD	Precision ≤20% RSD	Accuracy ±30%
Dichlorodifluoromethane	1.71	85	13.68	1.36	0.24	3.39	4.74	103
Chloromethane[1]	1.91	50	1.00	2.47	0.19	2.82	5.53	100
Vinyl chloride	2.00	62	11.51	1.77	0.24	3.84	5.21	97
Bromomethane	2.36	94	11.13	0.95	0.20	3.03	5.47	94
Chloroethane	2.51	64	8.39	1.14	0.25	4.08	6.01	92
Trichlorofluoromethane	2.70	101	12.37	1.77	0.21	3.09	5.58	99
Diethyl ether	3.11	74	7.08	0.07	0.21	3.22	7.14	91
1,1-Dichloroethene	3.34	61	13.52	0.05	0.43	5.85	4.97	105
1,1,2-Trichlorotrifluoroethane	3.42	101	13.81	0.13	0.28	3.85	6.87	101
Iodomethane[2]	3.52	142	1.00	0.01	2.42	7.19	8.12	105
Allyl chloride	3.93	76	9.46	0.05	0.45	6.80	9.64	94
Carbon disulfide	3.93	76	7.47	0.05	0.50	7.64	9.55	94
Methylene chloride[1]	4.06	49	1.00	0.62	1.09	17.3	6.77	98
Acetone[1]	4.11	58	1.00	0.09	4.76	6.40	5.35	95
trans-1,2-dichloroethene	4.25	96	10.54	0.04	0.18	2.57	7.28	107
Methyl acetate	4.28	43	12.51	0.33	0.64	8.02	5.42	100
Methyl *tert*-butyl ether	4.40	73	3.54	0.87	0.16	2.61	3.60	93
tert-Butyl alcohol	4.52	59	12.66	0.05	1.57	4.74	2.74	88
Acetonitrile	4.85	41	5.57	0.44	0.38	5.89	6.05	105
Diisopropyl ether	4.86	45	4.72	1.60	0.18	2.92	4.73	95
Acrylonitrile	4.93	53	11.12	0.14	0.17	2.79	4.07	92
Chloroprene	4.93	53	10.84	0.13	0.19	3.17	3.99	93
1,1-Dichloroethane	4.95	63	11.49	0.37	0.34	5.28	5.96	93
Vinyl acetate	5.25	43	4.08	0.60	0.40	7.74	7.78	83
tert-Butyl ethyl ether	5.25	59	3.13	1.03	0.09	1.54	3.55	93
cis-1,2-Dichloroethene	5.53	96	10.13	0.16	0.35	5.56	4.12	92
2,2-Dichloropropane	5.64	77	11.22	0.39	0.29	4.49	3.31	93
Bromochloromethane	5.74	128	8.63	0.05	0.57	8.43	7.47	93
Chloroform	5.83	83	8.73	0.59	0.34	5.26	4.88	94
Carbon tetrachloride	5.97	117	9.46	0.14	0.51	7.72	4.77	96
Methyl acrylate	5.97	55	13.99	0.16	0.21	3.29	3.67	85
Ethyl acetate	5.98	43	11.62	0.34	0.55	7.63	3.51	91
Tetrahydrofuran	5.99	42	6.65	0.14	0.50	7.90	6.86	95
Dibromofluoromethane (surr)	6.02	111	2.66	0.58		2.31	2.54	101
1,1,1-trichloroethane	6.03	97	11.65	0.29	0.14	2.21	4.27	96
2-Butanone	6.14	43	16.49	0.11	0.95	5.47	6.53	85
1,1-Dichloropropene	6.17	75	7.18	0.08	0.38	5.70	5.39	97
Benzene	6.42	78	12.59	0.48	0.10	1.60	4.42	92
Propionitrile	6.43	54	8.56	0.05	0.44	7.16	8.42	94
Methacrylonitrile	6.45	41	12.32	0.31	0.27	4.31	2.99	91
Pentafluorobenzene (ISTD)	6.52	168	–	–	–	–	–	–
1,2-Dichloroethane-d_4 (surr)	6.55	65	4.64	0.29		5.49	2.05	98

[1]Compound has a quadratic calibration

[2]Compound has a linear calibration

Calculated relative response factors (RRFs), MDLs, as well as precision and accuracy for mid-point check at 10 µg/kg for soil samples (continued)

	Calibration (1–200 µg/kg)				Method detection limit (n=7, 2 µg/kg)		Mid-point check (n=10, 10 µg/kg)	
Compound	RT (min)	Quan ion (*m/z*)	RRF (≤20% RSD R^2 ≥0.99)	Avg. RRF	MDL	Precision ≤20% RSD	Precision ≤20% RSD	Accuracy ±30%
tert-Amyl methyl ether	6.57	73	7.49	0.92	0.21	3.44	3.35	90
1,2-Dichloroethane	6.62	62	10.01	0.30	0.62	9.79	3.72	93
Isopropyl acetate	6.91	43	2.79	0.75	0.42	6.65	3.44	95
Isobutyl alcohol	6.92	43	6.02	0.76	0.40	6.60	3.60	93
Trichloroethene	7.03	130	10.59	0.25	0.24	3.40	6.96	105
1,4-Difluorobenzene (ISTD)	7.06	114	–	–	–	–	–	–
Dibromomethane	7.43	93	11.71	0.14	0.32	4.88	8.69	89
1,2-Dichloropropane	7.53	63	8.19	0.36	0.15	2.36	4.64	94
Bromodichloromethane	7.60	83	6.87	0.58	0.27	4.47	4.44	92
Methyl methacrylate	7.75	69	4.80	0.18	0.37	6.19	4.46	90
Propyl acetate	7.88	43	8.81	0.58	0.11	1.78	2.67	92
2-Chloroethyl vinyl ether	8.11	63	7.52	0.21	0.40	8.88	4.88	78
cis-1,3-dichloropropene	8.16	75	3.75	0.58	0.19	3.29	3.88	89
Toluene-d_8 (surr)	8.31	98	2.70	0.83		1.54	1.54	102
Toluene	8.36	92	9.49	0.66	0.45	5.98	4.34	100
2-Nitropropane	8.66	43	10.76	0.47	0.27	4.31	2.64	94
4-methyl-2-pentanone	8.66	100	5.11	0.02	1.78	11.8	3.72	91
Tetrachloroethylene	8.67	164	19.16	0.28	0.39	5.64	15.2	105
trans-1,3-Dichloropropene	8.69	75	5.07	0.52	0.24	4.26	3.01	88
1,1,2-Trichloroethane	8.81	83	3.94	0.29	0.23	3.94	2.97	93
Ethyl methacrylate	8.82	69	6.42	0.42	0.30	4.87	3.76	91
Dibromochloromethane	8.95	129	5.28	0.31	0.19	3.42	4.28	91
1,3-Dichloropropane	9.02	76	3.88	0.53	0.23	3.92	3.21	93
1,2-Dibromoethane	9.12	107	7.87	0.23	0.26	4.62	2.98	90
Butyl acetate	9.23	43	8.94	0.72	0.22	3.60	3.28	91
2-Hexanone	9.29	43	14.25	0.13	1.09	6.74	3.63	91
Chlorobenzene-d_5 (ISTD)	9.50	117	–	–	–	–	–	–
Chlorobenzene	9.52	112	10.54	0.94	0.16	2.44	3.68	94
Ethylbenzene	9.54	91	11.70	1.83	0.15	2.30	3.77	94
1,1,1,2-Tetrachloroethane	9.56	131	6.95	0.33	0.19	3.29	3.50	95
m,p-Xylene	9.64	106	11.07	0.68	0.28	2.22	3.94	93
o-Xylene	9.95	106	10.44	0.73	0.16	2.54	3.73	92
Styrene	9.98	104	7.32	1.26	0.16	2.75	4.14	91
Bromoform	10.00	173	6.18	0.20	0.30	5.69	3.67	85
Isopropylbenzene	10.17	105	10.21	2.03	0.20	3.36	3.75	94
Amyl acetate	10.24	43	6.28	0.86	0.42	7.58	3.48	85
4-Bromofluorobenzene (surr)	10.36	95	2.19	1.10		1.38	1.88	105
cis-1,4-Dichloro-2-butene	10.40	88	7.88	0.25	0.41	7.75	5.00	88
Bromobenzene	10.43	156	10.08	0.74	0.29	4.47	5.26	95
n-Propylbenzene	10.45	91	7.50	4.54	0.20	3.09	5.46	98
1,1,2,2-Tetrachloroethane	10.49	83	4.69	0.76	0.27	4.40	7.08	94
2-Chlorotoluene	10.56	91	7.48	3.24	0.26	4.08	5.03	97

Calculated relative response factors (RRFs), MDLs, as well as precision and accuracy for mid-point check at 10 µg/kg for soil samples (continued)

Compound	Calibration (1–200 µg/kg)				Method detection limit (n=7, 2 µg/kg)		Mid-point check (n=10, 10 µg/kg)	
	RT (min)	Quan ion (*m/z*)	RRF (≤20% RSD R^2 ≥0.99)	Avg. RRF	MDL	Precision ≤20% RSD	Precision ≤20% RSD	Accuracy ±30%
1,3,5-Trimethylbenzene	10.58	105	6.38	3.12	0.24	3.88	5.55	96
1,2,3-Trichloropropane	10.59	75	11.71	0.83	0.57	8.78	6.93	101
trans-1,4-Dichloro-2-butene	10.61	53	5.36	0.34	0.28	4.45	5.77	94
4-Chlorotoluene	10.67	91	7.57	3.00	0.23	3.59	6.31	94
Pentachloroethane	10.80	77	8.41	0.41	0.15	2.43	5.52	99
tert-Butylbenzene	10.80	119	7.94	3.03	0.33	5.25	6.89	95
1,2,4-Trimethylbenzene	10.85	105	5.82	3.14	0.24	3.92	6.05	95
sec-Butylbenzene	10.92	105	8.16	4.02	0.20	3.15	5.29	98
p-Isopropyltoluene	11.01	119	8.49	3.03	0.22	3.65	5.34	95
1,3-Dichlorobenzene	11.07	146	9.54	1.70	0.37	5.68	5.10	95
1,4-Dichlorobenzene-d_4 (ISTD)	11.12	152	–	–	–	–	–	–
1,4-Dichlorobenzene	11.13	146	5.76	1.74	0.25	3.77	5.00	94
n-Butylbenzene	11.29	91	8.73	3.39	0.26	4.29	4.67	93
Hexachloroethane	11.40	117	10.08	1.19	0.11	3.42	5.58	96
1,2-Dichlorobenzene	11.41	146	5.73	1.55	0.31	4.73	5.18	95
1,2-Dibromo-3-chloropropane	11.94	157	7.63	0.13	0.50	8.85	4.50	88
Nitrobenzene[1]	12.31	123	1.00	0.02	0.87	10.4	7.55	93
Hexachlorobutadiene	12.37	225	14.24	0.05	0.29	4.07	5.30	99
1,2,4-Trichlorobenzene	12.39	180	8.96	0.79	0.39	6.09	5.33	88
Naphthalene	12.61	128	7.25	1.42	0.33	5.29	4.95	93
1,2,3-Trichlorobenzene	12.73	180	6.76	0.60	0.47	7.24	5.23	91

[1]Compound has a quadratic calibration

Appendix 4. Long term study, water samples

Precision and accuracy of QC water samples spiked at 20 µg/L VOC standard assessed over n=240 consecutive injections over three days of analysis

Compound	Long term study (n=10, 20 ppb)	
	Precision	Accuracy
Dichlorodifluoromethane	12.2	85
Chloromethane	11.6	82
Vinyl chloride	10.6	86
Bromomethane	9.2	85
Chloroethane	8.9	87
Trichlorofluoromethane	8.4	92
Diethyl ether	5.0	83
1,1-Dichloroethene	7.7	81
Carbon disulfide	14.1	72
1,1,2-Trichlorotrifluoroethane	8.4	93
Iodomethane	24.1	111
Allyl chloride	9.2	75
Methylene chloride	4.3	110
Acetone	8.9	117
trans-1,2-dichloroethene	6.9	76
Methyl acetate	6.7	94
Methyl *tert* butyl ether	6.6	96
tert-Butyl alcohol	11.6	93
Acetonitrile	5.7	109
Diisopropyl ether	6.8	97
Acrylonitrile	10.6	85
Chloroprene	10.8	86
1,1-Dichloroethane	7.8	97
Vinyl acetate	23.2	76
tert-Butyl ethyl ether	7.8	93
cis-1,2-Dichloroethene	7.2	91
2,2-Dichloropropane[1]	29.0	70
Bromochloromethane	6.1	95
Chloroform	7.5	102
Carbon tetrachloride	11.0	101
Methyl acrylate	7.9	94
Ethyl acetate	8.2	101
Tetrahydrofuran	8.3	99
Dibromofluoromethane (surr)	3.6	108
1,1,1-trichloroethane	8.5	99
2-Butanone	10.1	109
1,1-Dichloropropene	10.4	84
Benzene	7.7	92
Propionitrile	9.3	100
Methacrylonitrile	6.9	104
Pentafluorobenzene (ISTD)	–	–
1,2-Dichloroethane-d_4 (surr)	6.3	110
tert-Amyl methyl ether	8.6	91
1,2-Dichloroethane	6.3	105
Isobutyl alcohol	7.7	101
Isopropyl acetate	7.8	101
Trichloroethene	6.8	98
1,4-Difluorobenzene (ISTD)	–	–
Dibromomethane	6.1	102
1,2-Dichloropropane	6.7	100
Bromodichloromethane	6.8	106
Methyl methacrylate	8.4	90
Propyl acetate	8.6	98
2-Chloroethyl vinyl ether	19.0	75
cis-1,3-dichloropropene	9.0	91
Toluene-d_8 (surr)	2.1	99
Toluene	7.9	83
4-methyl-2-pentanone	8.2	86
2-Nitropropane	7.6	97
Tetrachloroethylene	11.9	110
trans-1,3-Dichloropropene	7.8	88
1,1,2-Trichloroethane	5.0	105
Ethyl methacrylate	8.2	87
Dibromochloromethane	4.9	104
1,3-Dichloropropane	4.4	100
1,2-Dibromoethane	4.6	100
Butyl acetate	7.9	90
2-Hexanone	8.5	96
Chlorobenzene-d_5 (ISTD)	–	–
Chlorobenzene	4.9	92
Ethylbenzene	7.0	87
1,1,1,2-Tetrachloroethane	5.6	102
m,p-Xylene	7.2	89
o-Xylene	6.9	86
Styrene	6.8	91
Bromoform	4.9	107
Isopropylbenzene	8.1	88
Amyl acetate	7.7	95
4-Bromofluorobenzene (surr)	2.7	94
cis-1,4-Dichloro-2-butene	13.2	84
Bromobenzene	6.4	90
n-Propylbenzene	8.9	87
1,1,2,2-Tetrachloroethane	8.9	99
2-Chlorotoluene	7.7	87

[1]Reactive compound and degraded during anlysis, n=25 samples analyzed

Precision and accuracy of QC water samples spiked at 20 µg/L VOC standard assessed over n=240 consecutive injections over three days of analysis (continued)

Compound	Long term study (n=10, 20 ppb)	
	Precision	Accuracy
1,3,5-Trimethylbenzene	8.9	85
1,2,3-Trichloropropane	9.1	106
trans-1,4-Dichloro-2-butene	9.9	86
4-Chlorotoluene	7.4	88
Pentachloroethane	11.5	87
tert-Butylbenzene	13.2	81
1,2,4-Trimethylbenzene	9.6	84
sec-Butylbenzene	9.5	88
p-Isopropyltoluene	10.3	85
1,3-Dichlorobenzene	6.5	90
1,4-Dichlorobenzene-d_4 (ISTD)	–	–

Compound	Long term study (n=10, 20 ppb)	
	Precision	Accuracy
1,4-Dichlorobenzene	6.0	91
n-Butylbenzene	11.4	82
Hexachloroethane	15.9	117
1,2-Dichlorobenzene	5.7	91
1,2-Dibromo-3-chloropropane	7.5	97
Nitrobenzene	11.2	83
Hexachlorobutadiene	9.7	90
1,2,4-Trichlorobenzene	8.7	83
Naphthalene	9.2	81
1,2,3-Trichlorobenzene	7.7	89

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