A consolidated method for the analysis of VOCs in soil by HS-GC-MS in analytical testing laboratories

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Goal

To develop and test a consolidated analytical method for the analysis of volatile organic compounds in soil using headspace (HS) gas chromatography (GC) single quadrupole mass spectrometry (MS), following the U.S. EPA 5021 sample preparation guidelines and aligned with the requirements of HJ642-2013 and HJ736-2015 Chinese standard methods.

Introduction

Volatile organic compounds (VOCs) are defined by the United States Environmental Protection Agency (U.S. EPA) as "any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participate in atmospheric photochemical reactions."[1] VOCs are ubiquitous in the environment and they consist of many different classes, including both naturally occurring and man-made. Anthropogenic VOCs are generally used in fragrances, solvents, paints, cleaning materials and as fuels.[2] Many of these compounds are considered toxic for the environment and can cause negative health effects

to humans.[2] Compounds, such as trichloroethene and toluene, are of particular concern for the environment, especially when linked to contaminated soils and sediments which to remove to a safe limit would require costly site remediations. Detecting the level of VOC contamination in these types of samples can trigger the decision to potentially start site remediation, a costly process that relies on the accuracy of VOC measurements.

There are several methods available for the analysis of VOCs including U.S. EPA Method 524.4 for analysis in drinking water,[3] TO-15 for analysis in air,[4] and 8260 for analysis in a wide variety of matrices including water and soil.[5] U.S. EPA Method 5021[6] provides a general purpose method for sample preparation of VOCs in soil and is utilized as the preparation method for Chinese standards HJ642-2013 and HJ736-2015.

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One major challenge for contract testing labs is having to satisfy the requirements of multiple standards. This leads to multiple methods for the analysis of VOCs, increasing the time spent on sample preparation. Multiple instruments and operators are required, adding to the cost per sample that can impact the competitiveness of the lab. As well as cost, sample turn-around times are also impacted due to the additional time required for data processing, instrument maintenance and cross training.

In the experiments described here a robust, cost effective, time efficient and sensitive consolidated analytical method was developed and tested for the analysis of 61 VOCs in soil samples by HS-GC-MS within analytical testing laboratories. The method combines the HJ642-2013, HJ736-2015, and EPA 5021 standards with a significant time saving and reduced cost per sample.

Experimental

Instrument and method setup

The Thermo Scientific™ TRACE™ 1310 gas chromatograph was coupled with a Thermo Scientific™ ISQ™ 7000 single quadrupole mass spectrometer. The Thermo Scientific™ TriPlus™ 500 valve and loop headspace autosampler was used for VOC extraction and sampling into the GC-MS system. Chromatographic separation was achieved on a Thermo Scientific™ TraceGOLD™ TG-624 60 m × 0.25 mm × 1.4 µm column (P/N 26085-3330). The TriPlus 500 HS is directly connected to the analytical column by-passing the GC inlet, significantly reducing the sample path and optimizing the sample transfer. Full instrument conditions can be found in Table 1.

Table 1a. GC instrument conditions

TRACE 1310 parameters			
Carrier gas	He		
Column flow	2 mL/min constant flow		
Inlet mode	Split		
Split flow	40 mL/min		
Column	TG-624, 60 m × 0.25 mm × 1.4 µm		
Oven temp. program			
	Rate (°C/min)	Target temp. (°C)	Hold time (min)
Temperature 1	-	40	5
Temperature 2	6	120	0
Temperature 3	20	250	5
Run time	29.4 min		

Table 1b. Headspace autosampler instrument conditions

TriPlus 500 HS parameters	
Vial incubation temperature	60 °C
Vial incubation time	30 min
Vial shaking	Medium
Vial pressurization mode	Pressure
Vial pressure	160 kPa
Vial pressure equilibration time	1 min
Loop/sample path temperature	110 °C
Loop pressure	100 kPa
Loop equilibration time	1 min
Injection mode	Standard
Injection time	1 min

Table 1c. MS instrument conditions

ISQ 7000 parameters	
Transfer line temperature	240 °C
Ion source temperature	300 °C
Mass range	35–300 *m/z*
Ionization mode	EI @70 eV
Acquisition type	Full scan
Dwell time	0.2 s
Solvent delay	2.5 min

Standard and sample preparation

Separate custom mixed standard solutions of analytes and internal standards, all at 2000 µg/mL in methanol, were purchased from LGC Ltd. UK. A standard stock solution containing 61 VOCs was prepared and diluted in methanol to obtain seven calibration standards ranging from 5 to 250 µg/mL. The internal standard stock solution was diluted in methanol to a final concentration of 25 µg/mL and used to spike the VOCs calibration solutions.

A matrix modifying solution was prepared by adding concentrated phosphoric acid to 1 L of deionized water (resistance 18.2 MΩ) until the pH was 2.0. The solution was saturated with HPLC grade sodium chloride.

Calibration standards were prepared by adding 2 g of quartz sand, 10 mL of matrix modifying solution and a 4 µL aliquot of the appropriate standard solution to a 20 mL headspace vial (P/N 20-CV) and sealed with magnetic caps (P/N 20-MCBC). This produced standards in the range 10–500 µg/kg (ppb) with internal standards at 50 µg/kg.

Samples were prepared by adding 2 g of locally sourced soil to a 20 mL headspace vial and adding 10 mL of matrix modifying solution and 4 µL of internal standard. The vials were then sealed with magnetic caps for analysis.

Data acquisition, processing and reporting

The data were acquired in full scan, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3. Integrated instrument control ensures full automation from instrument setup, to raw data processing, reporting, and storage with all calculations performed within the software. Simplified eWorkflows™ deliver effective data management ensuring ease of use, data integrity, and full traceability. Intelligent run control allows actions to be taken automatically by the software during a sequence in case of SST failure, such as pausing or aborting a sequence, saving the vials to analyze later. Chromeleon CDS also offers the option to scale up the entire analytical process in the laboratory from a single workstation to an enterprise environment.

Results and discussion

Tuning

Before analysis, the ISQ 7000 system was automatically tuned using bromofluorobenzene (BFB). Chromeleon CDS makes the ongoing monitoring of the BFB tune easy with the report designer feature, allowing automatic pass/fail assessment. An example is shown in Figure 1.

Chromatography

Consistent retention times, Gaussian chromatographic peak shape, and repeatable peak areas are essential to provide reliable identification and quantitation. An example of the achieved chromatographic separation is reported in Figure 2.

MS Tune Check Report (BFB)

Sequence Details

Sequence Name:	MDL	Created On:	01/Jun/20 16:23:38
Directory:	Instrument Data\VOC in soil\16 June	Created By:	ukrun.cell.appslab
Data Vault:	ChromeleonLocal	Updated On:	22/Jun/20 16:23:32
No. of Injections:	169	Updated By:	david.lee4
Calibration Source:	MDL		

Injection Details

Injection Name:	Std 5 - 100 ppb	Injection Volume:	1.00
Analysis Type:	n.a.	Dilution Factor:	1.0000
Injection Type:	Calibration Standard	Vial Number:	HS:A19
Injection Date/Time:	16/Jun/20 23:50	Processing Method:	10-500
		Instrument Method:	20 to 1 split

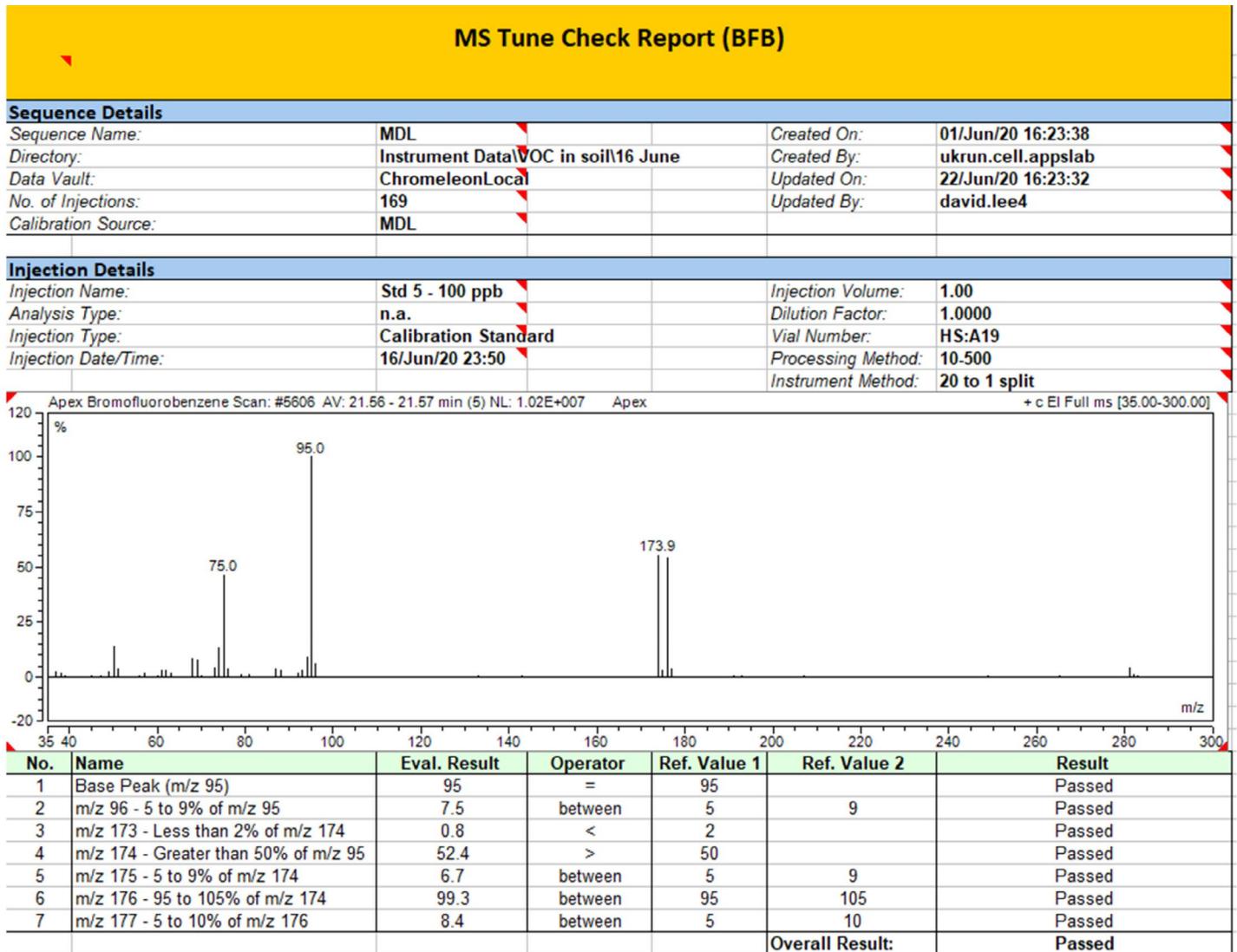| No.	Name	Eval. Result	Operator	Ref. Value 1	Ref. Value 2	Result
1	Base Peak (m/z 95)	95	=	95		Passed
2	m/z 96 - 5 to 9% of m/z 95	7.5	between	5	9	Passed
3	m/z 173 - Less than 2% of m/z 174	0.8	<	2		Passed
4	m/z 174 - Greater than 50% of m/z 95	52.4	>	50		Passed
5	m/z 175 - 5 to 9% of m/z 174	6.7	between	5	9	Passed
6	m/z 176 - 95 to 105% of m/z 174	99.3	between	95	105	Passed
7	m/z 177 - 5 to 10% of m/z 176	8.4	between	5	10	Passed
					Overall Result:	Passed

Figure 1. Screenshot of the BFB tune report showing injection details, obtained mass spectrum, and the criteria and results for a passing BFB tune at the start of analysis
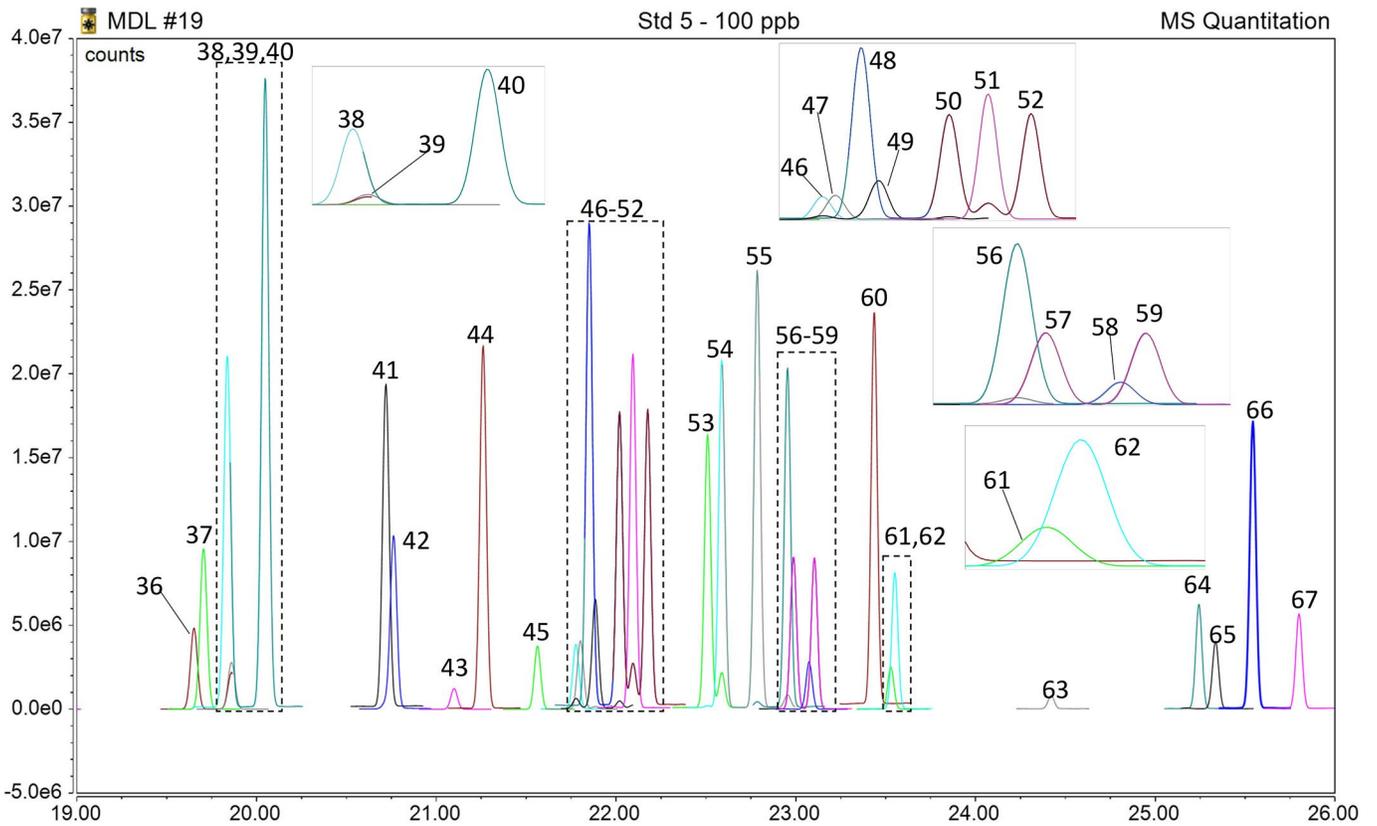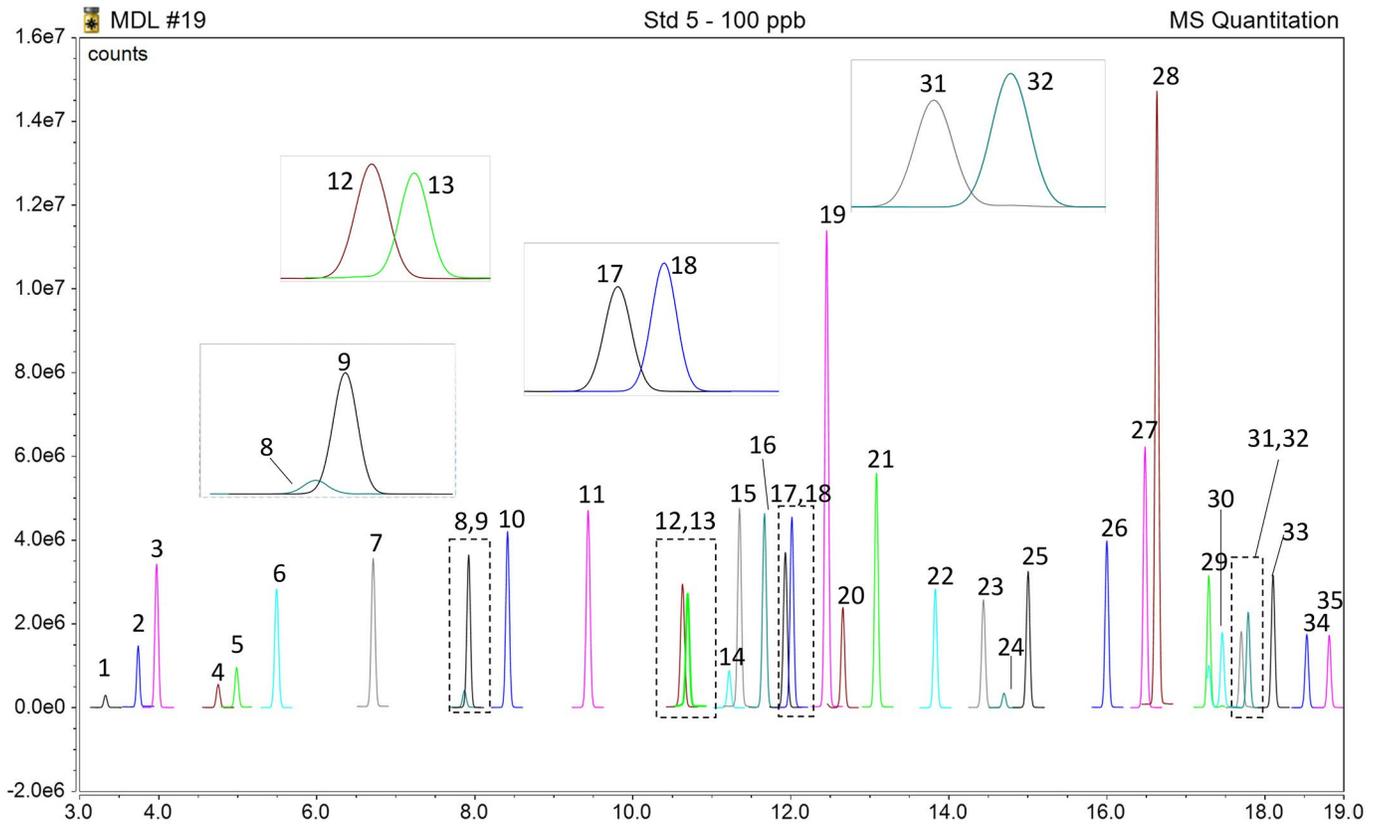
Figure 2. Extracted ion chromatogram of quantitation ions of a 50 µg/kg standard showing retention times 3–19 minutes (top) and 19–26 minutes (bottom). Peak names are given in Appendix 1.

The extraction of the characteristic fragment ions for each compound, combined with the retention time (±0.05 minute window), the ion ratio (within 30% of the expected value), and the NIST 17 spectral library match ensured confident compound identification for all the investigated compounds. The ions selected for quantitation and confirmation are listed in Appendix 1. All the selected ions show no interference from other analytes at similar retention times. NIST library searching can be performed automatically by Chromeleon CDS and results are displayed in the same window (Figure 3). Combined, this allows for sufficient separation of the peaks and ensures correct peak assignment in a GC run under 30 minutes.

The HJ642-2013 and HJ736-2015 methods are both at least 40 minutes long, so combining the compound lists from these two methods into a single analytical method 30 minutes long saves over 24 hours of instrument time for a 20 sample injection run, including calibration and check standards, compared to running both the HJ642-2013 and HJ736-2015 methods.

Linearity

To obtain accurate quantification of results, a calibration curve is essential. Linearity was assessed across the range 10–500 µg/kg. Internal standard correction was performed, and the internal standards associated with each analyte are shown in Appendix 1. For all compounds analyzed, excellent linearity was achieved across the range with R^2 values >0.999 and average calibration factor (AvCF) %RSDs <5 (Appendix 2). This exceeds the linearity criteria stated in the HJ642-2013 and HJ726-2015 methods, which require $R^2 > 0.990$ and AvCF %RSD < 20%. Examples of the calibration curves for 1,1-dichloroethene, 1,1-dichloropropene, chlorobenzene, and naphthalene produced are shown in Figure 4.

Sensitivity

Sensitivity was assessed by performing n=8 consecutive injections of a 10 µg/kg standard and calculating the method detection limit (MDL). The MDLs were calculated considering the Student's-t critical values for the corresponding degrees of freedom (99% confidence) and the standard deviation of the calculated amount. Achieved sensitivity meets the requirement of the HJ methods (2–3 µg/kg) for all the investigated compounds with average MDL of 0.9 µg/kg. The results obtained are shown in Appendix 3.
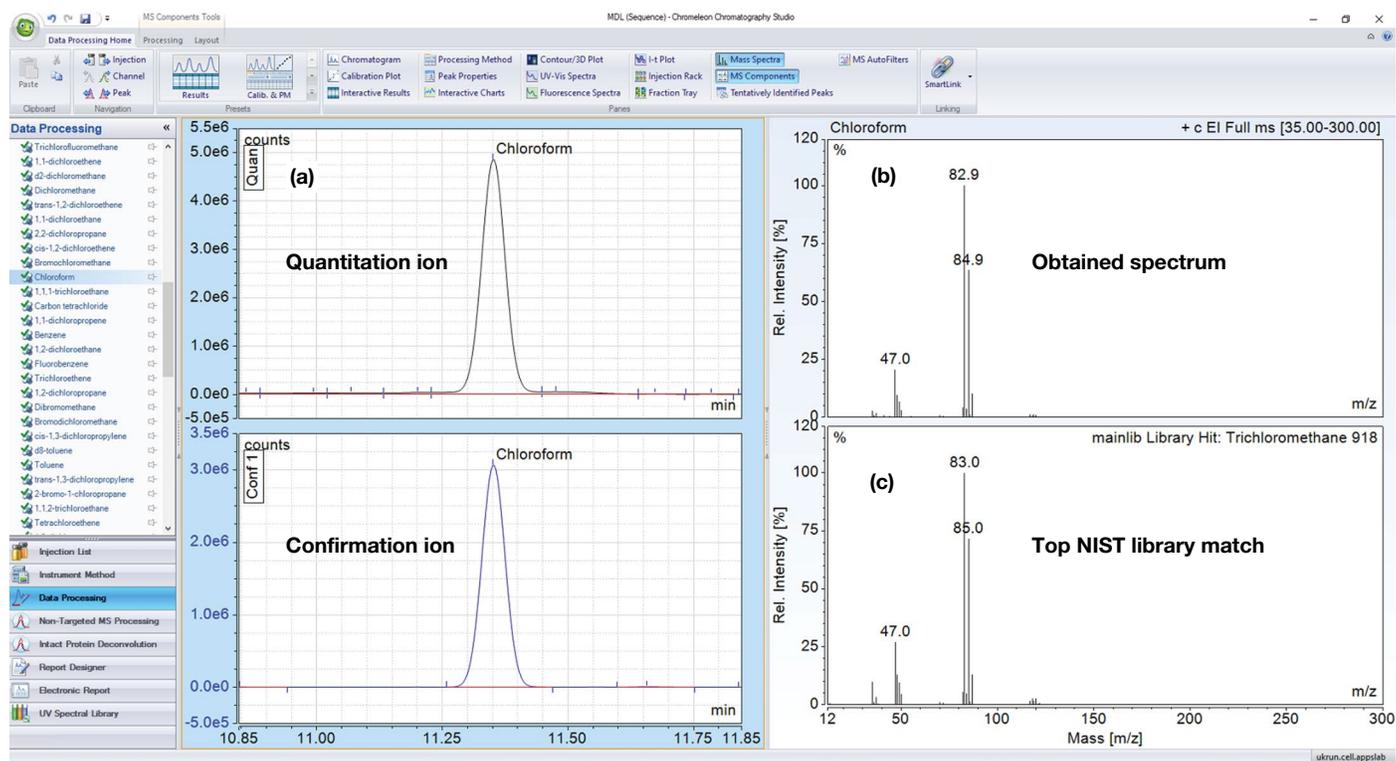

Figure 3. Chromeleon CDS result browser showing quantitation and confirmation extracted ion chromatograms for chloroform (a), the measured mass spectrum (b), and the top NIST library match (c) confirming the identity as trichloromethane (chloroform) with a forward match score (RSI) of 918
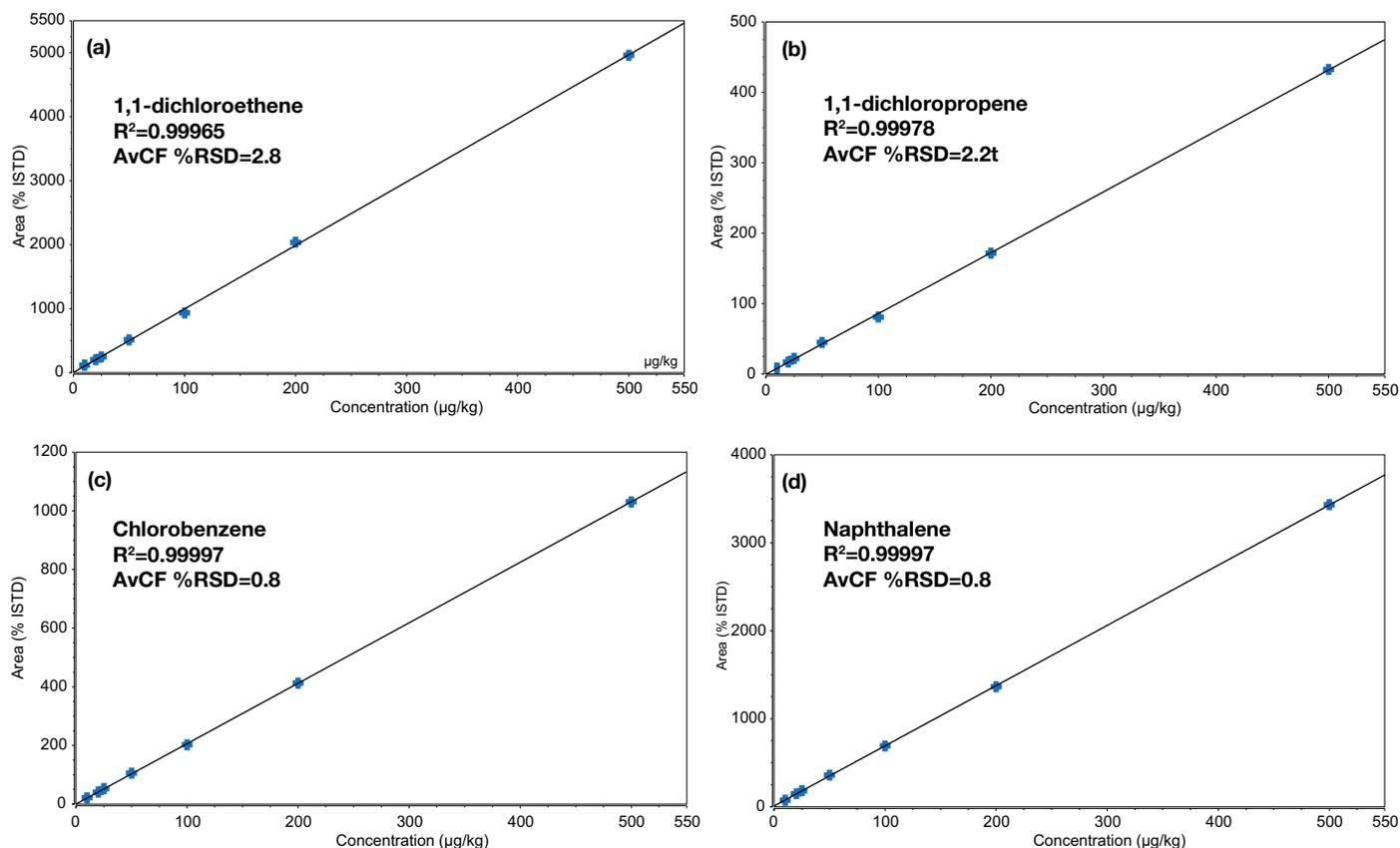
Figure 4. Example of calibration plots for (a) 1,1-dichloroethene, (b) 1,1-dichloropropene, (c) chlorobenzene, and (d) naphthalene assessed over a concentration range of 10–500 µg/kg showing R^2 values of 0.99965, 0.99978, 0.99997, and 0.99997 and AvCF %RSDs of 2.8, 2.2, 0.8, and 0.8, respectively

Precision

Precision was assessed using n=8 standard injections at 100 µg/kg and 200 µg/kg. A %RSD (n=8) of the calculated amounts of <12 was obtained for all compounds. In fact, only four analytes, dichlorodifluoromethane, chloromethane, chloroethene, and bromomethane, had a %RSD >5, comparing favorably with the 20% limit set out in the HJ methods. The values obtained are shown in Appendix 3.

Quantification of target compounds in soil samples

Soil was sampled locally, homogenized, and used for the analysis as spiked (at 100 µg/kg and 200 µg/kg) and unspiked samples in duplicate. The mean % recoveries of target analytes in these samples were within the limits specified in the HJ methods (70–130%) for all analytes, indicating that the method is suitable for the analysis of soil samples. The obtained values are shown in Appendix 4.

Robustness

Method robustness was tested by analyzing a QC standard at 200 µg/kg at defined intervals across n=128 sample injections acquired over 4.5 days without any instrument maintenance or mass spectrometer tuning and monitoring recovery over time. The robustness of the method was assessed by monitoring the accuracy and precision of the analytical results. With the exception of dichlorodifluoromethane and bromomethane (unstable in solution for this length of time), the average recovery was within 70–130% and the %RSD of the calculated amounts for n=10 injections were <20 for all compounds. This can be easily monitored within Chromeleon CDS using interactive charts and examples of this are shown in Figure 5. The full list of values obtained are shown in Appendix 5.

This information could also be used as a system suitability test in conjunction with the intelligent run control feature within Chromeleon CDS. This feature allows actions to be taken automatically by the software during a sequence in case of SST failure. These actions can include pausing or aborting a sequence, thereby saving any further prepared samples for injection once the cause of the SST failure has been established. This saves both time and money that would otherwise need to be spent on re-preparation of the samples.
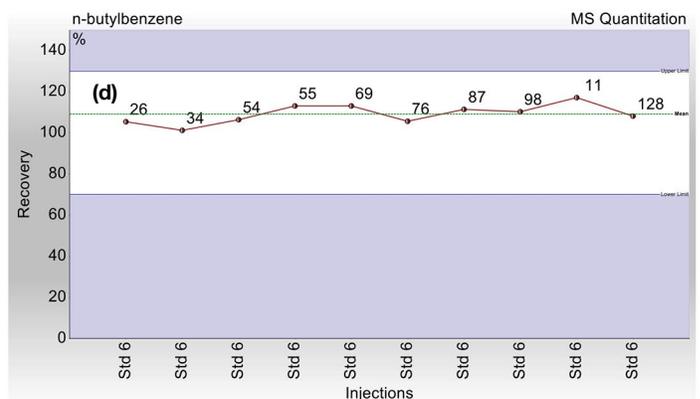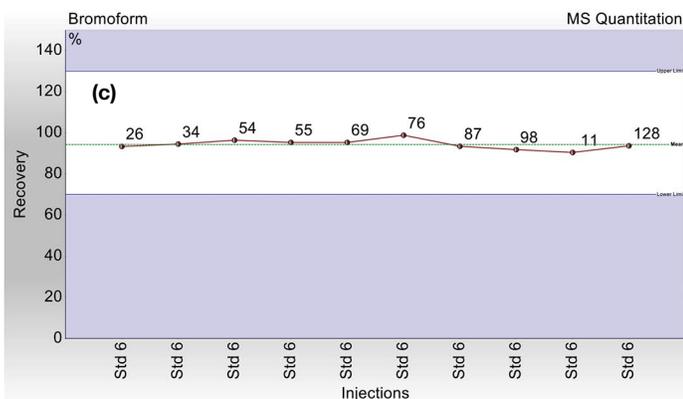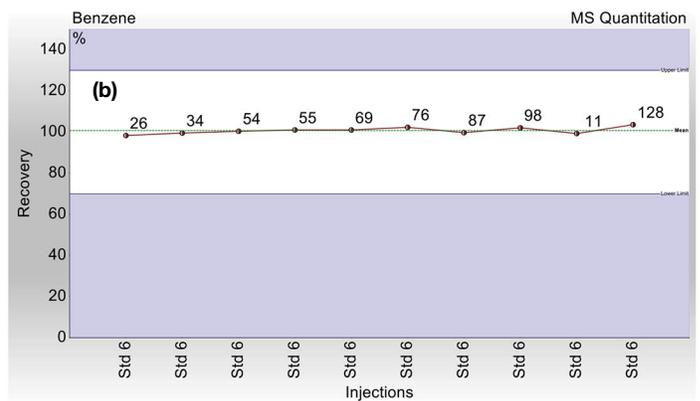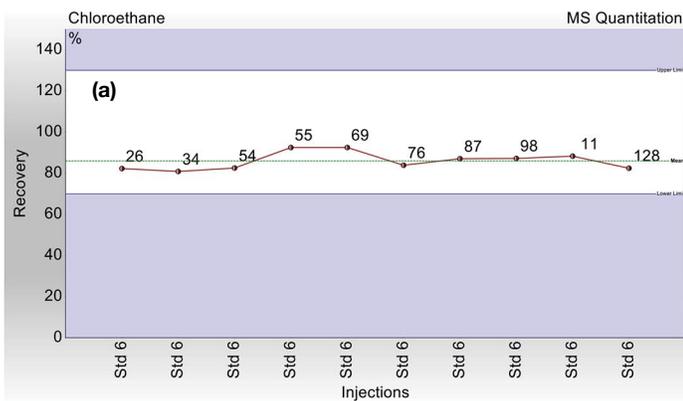
Figure 5. Chromeleon generated control charts showing the 70–130% limits and the recoveries obtained for (a) chloroethane, (b) benzene, (c) bromoform, and (d) n-butylbenzene across 128 consecutive headspace analyses

Retention time alignment

For analytical science labs it is important that the retention time of analytes remains consistent over time. The Thermo Scientific™ Retention Time Alignment (RTA) software tool can be used to account for differences when column maintenance has been performed or a method is transferred to a different GC. Either the column flow or column dimensions can be changed to adjust compound retention times. In the example shown here the column dimensions were adjusted to provide the retention time alignment after approximately 3 m was removed from the injector side of the analytical column. This allows for validated parameters, such as column flow and split flow to remain unchanged. RTA was performed very easily by using pentane (C5) as the reference compound, run

isothermally at 40 °C for 15 min. This reference compound eluted at 5.177 minutes before trimming the column, and the RTA worked to maintain this retention time after the column cut. All other instrument parameters were as shown in Table 1.

Applying the suggested settings from the RTA software tool, after trimming the column and re-injecting pentane using the same conditions, all target analytes were still within the assigned retention time window (±0.05 min) and correctly identified by Chromeleon CDS. If the RTA correction had not been performed, then the peaks would fall outside this expected window. Examples of this for d2-dicloroemethane, d8-toluene and d4-1,2-dichlorobenzene are shown in Figure 6.
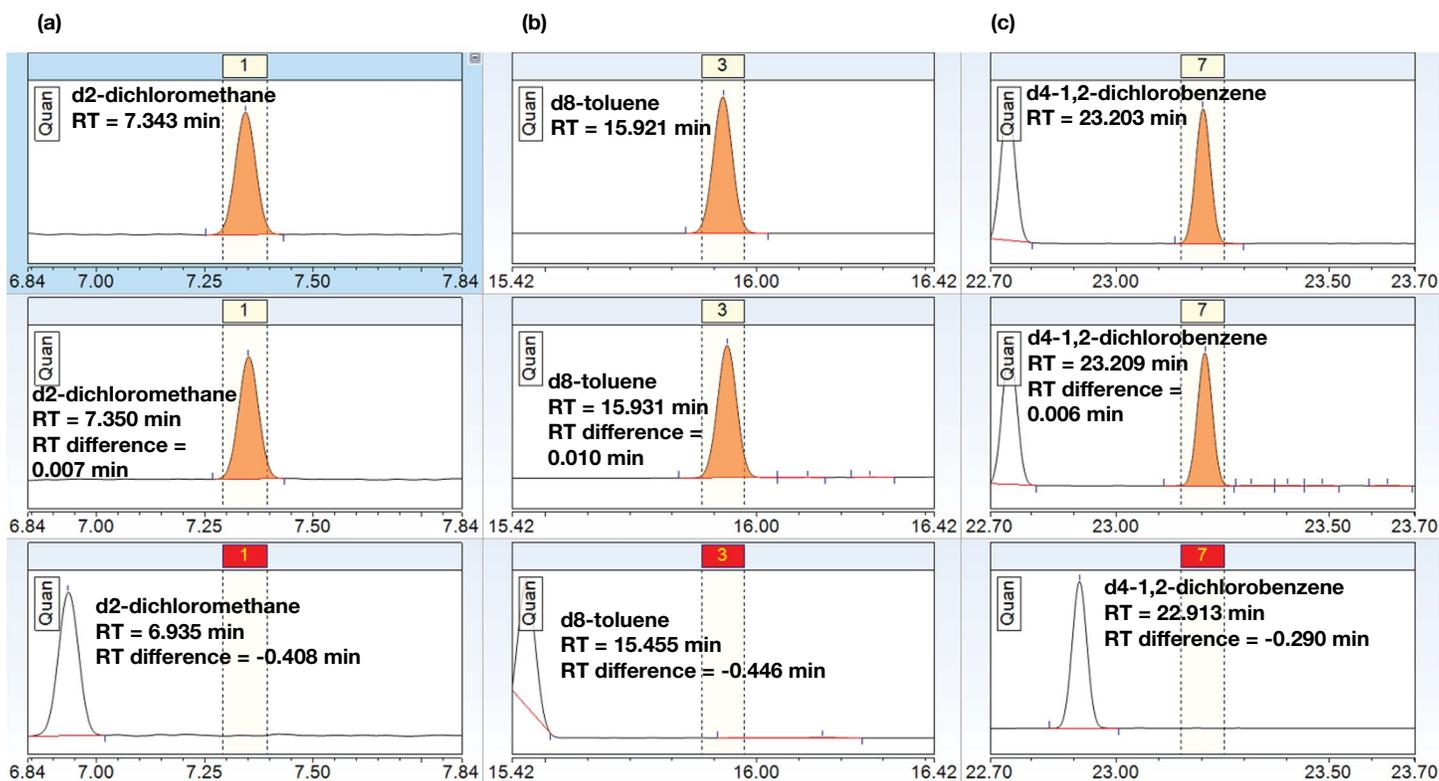
Figure 6. Extracted ion chromatograms, including the peak identification window for (a) d2-dichloromethane, (b) d8-toluene, and (c) d4-1,2-dichlorobenzene, showing the initial retention time before column cut (top), retention time after column cut with RTA applied (middle) and the retention time after column cut without RTA applied (bottom). The retention time difference to the initial retention time is also displayed.

Conclusions

Laboratories analyzing VOCs in environmental samples can consolidate three methods into one, increasing throughput three-fold by running one 30 minute method instead of two methods each >40 minutes, therefore significantly reducing the time from sampling to reporting and the need for multiple GC-MS systems and analysts, decreasing the cost per sample. The HS-GC-MS method presented here allows for simultaneous determination of 61 VOCs in <30 minutes per sample, using the Thermo Scientific TriPlus 500 HS with the TRACE 1310 GC and ISQ 7000 single quadrupole MS. The analytical results obtained in the experiments performed here comply with the HJ methods requirements with the following performance parameters demonstrated:

- Data was acquired in full scan, which simplified the method setup. Additionally, no compromise in the peak shape with sufficient chromatographic resolution of the analytes was achieved.

- Excellent linearity was obtained over the range 10–500 µg/kg with coefficient of determination, R^2, values >0.999 and AvCF %RSD <5 allowing precise quantification of target compounds at low and high concentrations.

- Outstanding sensitivity was obtained with MDLs ≤ 2 µg/kg for 60 compounds.

- Precision values as %RSD of calculated concentration were <12% for all compounds and below 5% for most compounds.

- Quantification of spiked soil samples resulted in calculated concentrations close to the spiking level with compound recoveries between 70% and 130%.

- Instrument robustness was tested over 128 injections across a 4.5 day period with no maintenance or mass spectrometer tuning performed, and mean recoveries of a QC standard within 70–130% and %RSDs of calculated amounts <20 for all compounds.

- The retention time alignment tool allowed for analyte retention times to remain within the expected window even after cutting a significant section from the capillary column, saving analysis time and ensuring consistency of results.

- Users can be up and running quickly and easily using eWorkflows, which allow the user to swiftly set up, run, and process a sequence.

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Appendices

Appendix 1a. Table showing compound names, peak numbers, retention times, quantitation and confirmation ions, and associated internal standards for peaks 1–34

Peak number	Compound name	Retention time (min)	Quantitation ion (*m/z*)	Confirmation ion (*m/z*)	Associated internal standard
1	Dichlorodifluoromethane	3.34	85	87	d2-dichloromethane
2	Chloromethane	3.75	50	52	d2-dichloromethane
3	Chloroethene	3.99	62	64	d2-dichloromethane
4	Bromomethane	4.77	94	96	d2-dichloromethane
5	Chloroethane	5.00	64	66	d2-dichloromethane
6	Trichlorofluoromethane	5.51	101	103	d2-dichloromethane
7	1,1-dichloroethene	6.74	61	96	d2-dichloromethane
8	d2-dichloromethane	7.89	53	90	Internal standard
9	Dichloromethane	7.94	84	49	d2-dichloromethane
10	*trans*-1,2-dichloroethane	8.44	61	96	d2-dichloromethane
11	1,1-dichloroethane	9.46	63	65	d2-dichloromethane
12	2,2-dichloropropane	10.65	77	79	d2-dichloromethane
13	*cis*-1,2-dichloroethene	10.72	96	61	d2-dichloromethane
14	Bromochloromethane	11.24	130	128	Fluorobenzene
15	Chloroform	11.37	83	85	Fluorobenzene
16	1,1,1-trichloroethane	11.69	97	99	Fluorobenzene
17	Carbon tetrachloride	11.95	117	119	Fluorobenzene
18	1,1-dichloropropene	12.03	75	110	Fluorobenzene
19	Benzene	12.47	78	77	Fluorobenzene
20	1,2-dichloroethane	12.68	62	98	Fluorobenzene
21	Fluorobenzene	13.11	96	70	Internal standard
22	Trichloroethene	13.85	130	132	Fluorobenzene
23	1,2-dichloropropane	14.46	63	62	Fluorobenzene
24	Dibromomethane	14.72	172	174	Fluorobenzene
25	Bromodichloromethane	15.02	83	85	d8-toluene
26	*cis*-1,3-dichloropropylene	16.02	75	110	d8-toluene
27	d8-toluene	16.50	98	100	Internal standard
28	Toluene	16.65	91	92	d8-toluene
29	*trans*-1,3-dichloropropylene	17.31	75	110	2-bromo-1-chloropropane
30	2-bromo-1-chloropropane	17.48	77	79	Internal standard
31	1,1,2-trichloroethane	17.72	97	99	2-bromo-1-chloropropane
32	Tetrachloroethene	17.81	164	166	2-bromo-1-chloropropane
33	1,3-dichloropropane	18.12	76	78	2-bromo-1-chloropropane
34	Dibromochloromethane	18.55	129	127	2-bromo-1-chloropropane

Appendix 1b. Table showing compound names, peak numbers, retention times, quantitation and confirmation ions and associated internal standards for peaks 35–67

Peak number	Compound name	Retention time (min)	Quantitation ion (m/z)	Confirmation ion (m/z)	Associated internal standard
35	1,2-dibromoethane	18.83	107	109	d5-chlorobenzene
36	d5-chlorobenzene	19.67	117	119	Internal standard
37	Chlorobenzene	19.72	112	77	d5-chlorobenzene
38	Ethylbenzene	19.85	91	106	d5-chlorobenzene
39	1,1,1,2-tetrachloroethane	19.88	131	133	d5-chlorobenzene
40	m & p-xylene	20.06	91	106	d5-chlorobenzene
41	o-xylene	20.73	91	106	d5-chlorobenzene
42	Styrene	20.78	104	103	d5-chlorobenzene
43	Bromoform	21.11	173	175	d5-chlorobenzene
44	Isopropylbenzene	21.28	105	120	d5-chlorobenzene
45	Bromofluorobenzene	21.58	174	176	d5-chlorobenzene
46	Bromobenzene	21.79	156	158	d5-chlorobenzene
47	1,1,2,2-tetrachloroethane	21.82	83	85	d5-chlorobenzene
48	n-propylbenzene	21.86	91	120	d5-chlorobenzene
49	1,2,3-trichloropropane	21.90	75	110	d5-chlorobenzene
50	2-chlorotoluene	22.03	91	126	d5-chlorobenzene
51	1,3,5-trimethylbenzene	22.11	105	120	d5-chlorobenzene
52	4-chlorotoluene	22.19	91	126	d5-chlorobenzene
53	tert-butylbenzene	22.52	119	134	d5-chlorobenzene
54	1,2,4-trimethylbenzene	22.60	105	120	d5-chlorobenzene
55	sec-butylbenzene	22.80	105	134	d5-chlorobenzene
56	4-isopropyltoluene	22.97	119	134	d5-chlorobenzene
57	1,3-dichlorobenzene	23.00	146	148	d4-1,4-dichlorobenzene
58	d4-1,4-dichlorobenzene	23.09	152	115	Internal standard
59	1,4-dichlorobenzene	23.12	146	148	d4-1,4-dichlorobenzene
60	n-butylbenzene	23.45	91	134	d4-1,2-dichlorobenzene
61	d4-1,2-dichlorobenzene	23.54	152	115	Internal standard
62	1,2-dichlorobenzene	23.56	146	148	d4-1,2-dichlorobenzene
63	1,2-dibromo-3-chloropropane	24.43	157	155	d4-1,2-dichlorobenzene
64	1,2,4-trichlorobenzene	25.25	180	182	d4-1,2-dichlorobenzene
65	Hexachlorobutadiene	25.35	225	227	d4-1,2-dichlorobenzene
66	Naphthalene	25.56	128	129	d4-1,2-dichlorobenzene
67	1,2,3-trichlorobenzene	25.81	180	182	d4-1,2-dichlorobenzene

Appendix 2. Table showing R² and AvCF %RSD values obtained for all compounds

Peak name	R^2	AvCF %RSD	Peak name	R^2	AvCF %RSD
Dichlorodifluoromethane	0.99997	0.9	1,2-dibromoethane	0.99992	1.3
Chloromethane	0.99977	2.4	Chlorobenzene	0.99997	0.8
Chloroethene	0.99914	4.7	Ethylbenzene	0.99997	0.8
Bromomethane	0.99978	2.3	1,1,1,2-tetrachloroethane	0.99983	2.0
Chloroethane	0.99998	0.6	m & p-xylene	0.99994	1.1
Trichlorofluoromethane	0.99996	1.0	o-xylene	0.99994	1.1
1,1-dichloroethene	0.99965	2.8	Styrene	0.99936	3.9
Dichloromethane	0.99988	1.6	Bromoform	0.99904	4.9
trans-1,2-dichloroethene	0.99993	1.2	Isopropylbenzene	0.99990	1.5
1,1-dichloroethane	0.99997	0.8	Bromofluorobenzene	0.99985	1.8
2,2-dichloropropane	0.99990	1.5	Bromobenzene	0.99993	1.2
cis-1,2-dichloroethene	0.99999	0.5	1,1,2,2-tetrachloroethane	0.99994	1.2
Bromochloromethane	0.99975	2.4	n-propylbenzene	0.99978	2.1
Chloroform	0.99985	1.8	1,2,3-trichloropropane	0.99932	3.7
1,1,1-trichloroethane	0.99968	2.7	2-chlorotoluene	0.99971	2.5
Carbon tetrachloride	0.99983	2.0	1,3,5-trimethylbenzene	0.99921	4.1
1,1-dichloropropene	0.99978	2.2	4-chlorotoluene	0.99992	1.3
Benzene	0.99993	1.2	tert-butylbenzene	0.99967	2.7
1,2-dichloroethane	0.99992	1.3	1,2,4-trimethylbenzene	0.99963	2.8
Trichloroethene	0.99990	1.5	sec-butylbenzene	0.99938	3.6
1,2-dichloropropane	0.99996	1.0	4-isopropyltoluene	0.99986	1.7
Dibromomethane	0.99963	2.9	1,3-dichlorobenzene	0.99992	1.3
Bromodichloromethane	0.99995	1.1	1,4-dichlorobenzene	0.99999	0.5
cis-1,3-dichloropropylene	0.99998	0.7	n-butylbenzene	0.99992	1.3
Toluene	0.99996	1.0	1,2-dichlorobenzene	0.99998	0.6
trans-1,3-dichloropropylene	0.99997	0.8	1,2-dibromo-3-chloropropane	0.99948	3.4
1,1,2-trichloroethane	0.99999	0.5	1,2,4-trichlorobenzene	0.99984	1.9
Tetrachloroethene	0.99976	2.4	Hexachlorobutadiene	0.99995	1.0
1,3-dichloropropane	0.99996	0.9	Naphthalene	0.99997	0.8
Dibromochloromethane	0.99965	2.8	1,2,3-trichlorobenzene	0.99987	1.7

Appendix 3. Table showing the calculated MDLs and % RSDs for n=8 injections of standard at 100 µg/kg and 200 µg/kg

Peak name	MDL	%RSD at 100 ppb	%RSD at 200 ppb	Peak name	MDL	%RSD at 100 ppb	%RSD at 200 ppb
Dichlorodifluoromethane	0.8	10.5	11.1	1,2-dibromoethane	1.3	2.0	1.6
Chloromethane	1.6	6.8	8.6	Chlorobenzene	0.6	1.1	1.8
Chloroethene	1.0	4.3	6.9	Ethylbenzene	0.8	1.0	1.7
Bromomethane	2.3	6.5	3.5	1,1,1,2-tetrachloroethane	0.9	1.7	1.4
Chloroethane	1.0	2.1	4.5	m & p-xylene	1.5	1.1	2.1
Trichlorofluoromethane	1.3	2.5	4.2	o-xylene	1.5	1.1	2.0
1,1-dichloroethene	1.2	2.6	3.0	Styrene	0.5	2.0	1.4
Dichloromethane	1.2	1.2	2.2	Bromoform	0.8	2.1	2.0
trans-1,2-dichloroethene	1.1	2.5	2.2	Isopropylbenzene	1.0	0.8	2.2
1,1-dichloroethane	1.0	1.9	2.3	Bromofluorobenzene	0.6	1.9	1.7
2,2-dichloropropane	1.9	3.6	1.4	Bromobenzene	1.5	2.0	2.2
cis-1,2-dichloroethene	0.6	2.1	1.8	1,1,2,2-tetrachloroethane	1.2	3.1	1.5
Bromochloromethane	1.3	2.3	2.1	n-propylbenzene	0.8	1.4	1.6
Chloroform	1.4	2.8	1.5	1,2,3-trichloropropane	1.1	3.2	1.8
1,1,1-trichloroethane	0.9	1.0	0.4	2-chlorotoluene	0.7	1.3	1.4
Carbon tetrachloride	1.2	1.1	0.7	1,3,5-trimethylbenzene	0.8	1.3	1.9
1,1-dichloropropene	1.3	0.5	0.5	4-chlorotoluene	0.8	1.3	2.5
Benzene	0.4	1.0	0.7	tert-butylbenzene	1.0	2.1	1.9
1,2-dichloroethane	0.9	1.4	1.3	1,2,4-trimethylbenzene	1.1	1.1	1.2
Trichloroethene	0.7	0.8	0.7	sec-butylbenzene	1.4	1.8	2.8
1,2-dichloropropane	1.1	1.2	1.2	4-isopropyltoluene	1.0	1.5	1.8
Dibromomethane	1.4	3.0	2.2	1,3-dichlorobenzene	0.8	1.7	1.5
Bromodichloromethane	0.5	2.1	1.7	1,4-dichlorobenzene	0.6	1.7	1.6
cis-1,3-dichloropropylene	0.5	1.7	1.9	n-butylbenzene	1.3	1.4	2.1
Toluene	0.5	0.9	1.3	1,2-dichlorobenzene	1.1	2.3	1.5
trans-1,3-dichloropropylene	0.9	2.0	1.7	1,2-dibromo-3-chloropropane	1.5	3.5	1.6
1,1,2-trichloroethane	1.0	1.5	1.0	1,2,4-trichlorobenzene	1.1	3.0	2.1
Tetrachloroethene	1.1	2.5	2.5	Hexachlorobutadiene	2.0	2.5	3.1
1,3-dichloropropane	1.0	2.2	1.2	Naphthalene	0.6	1.4	1.2
Dibromochloromethane	0.9	1.4	1.2	1,2,3-trichlorobenzene	0.1	2.0	2.2

Appendix 4. Table displaying the obtained recoveries of analytes from soil samples spiked at 100 µg/kg and 200 µg/kg

Peak name	% Recovery at 100 ppb	% Recovery at 200 ppb	Peak Name	% Recovery at 100 ppb	% Recovery at 200 ppb
Dichlorodifluoromethane	104.0	98.5	1,2-dibromoethane	100.0	104.0
Chloromethane	82.7	101.1	Chlorobenzene	94.0	99.4
Chloroethene	100.5	112.5	Ethylbenzene	91.2	96.1
Bromomethane	87.4	110.0	1,1,1,2-tetrachloroethane	92.1	96.8
Chloroethane	105.7	118.4	m & p-xylene	89.7	93.3
Trichlorofluoromethane	73.5	90.4	o-xylene	78.3	84.8
1,1-dichloroethene	87.1	98.1	Styrene	91.4	93.6
Dichloromethane	95.0	104.1	Bromoform	82.4	84.5
trans-1,2-dichloroethene	89.3	98.7	Isopropylbenzene	88.6	93.3
1,1-dichloroethane	93.0	100.8	Bromofluorobenzene	99.4	104.0
2,2-dichloropropane	97.7	109.5	Bromobenzene	100.1	102.5
cis-1,2-dichloroethene	92.5	98.9	1,1,2,2-tetrachloroethane	109.6	110.1
Bromochloromethane	97.6	103.4	n-propylbenzene	97.0	100.9
Chloroform	98.5	102.6	1,2,3-trichloropropane	110.9	114.6
1,1,1-trichloroethane	94.5	98.9	2-chlorotoluene	100.0	103.4
Carbon tetrachloride	90.9	98.3	1,3,5-trimethylbenzene	96.7	102.5
1,1-dichloropropene	91.3	97.5	4-chlorotoluene	99.6	102.6
Benzene	94.9	99.5	tert-butylbenzene	94.5	99.7
1,2-dichloroethane	100.1	103.6	1,2,4-trimethylbenzene	93.8	99.3
Trichloroethene	92.6	98.3	sec-butylbenzene	91.1	94.9
1,2-dichloropropane	96.6	101.0	4-isopropyltoluene	86.2	91.5
Dibromomethane	99.7	103.6	1,3-dichlorobenzene	95.8	99.8
Bromodichloromethane	91.3	92.9	1,4-dichlorobenzene	95.2	99.2
cis-1,3-dichloropropylene	93.4	98.3	n-butylbenzene	78.4	84.5
Toluene	93.3	96.7	1,2-dichlorobenzene	95.0	95.6
trans-1,3-dichloropropylene	93.7	99.7	1,2-dibromo-3-chloropropane	105.6	99.7
1,1,2-trichloroethane	97.8	100.9	1,2,4-trichlorobenzene	86.1	89.8
Tetrachloroethene	90.6	94.7	Hexachlorobutadiene	71.0	74.0
1,3-dichloropropane	99.2	102.9	Naphthalene	96.1	96.4
Dibromochloromethane	85.4	90.4	1,2,3-trichlorobenzene	86.8	88.8

Appendix 5. Table showing the %RSD and the mean % recovery (n=10) for a 200 µg/kg QC standard run at intervals over 128 injections

Peak name	%RSD	Mean % recovery	Peak name	%RSD	Mean % recovery
Chloromethane	14.0	83	Chlorobenzene	1.1	100
Chloroethene	8.4	76	Ethylbenzene	3.1	99
Chloroethane	4.9	85	1,1,1,2-tetrachloroethane	2.1	101
Trichlorofluoromethane	5.6	91	m & p-xylene	4.1	99
1,1-dichloroethene	3.6	96	o-xylene	3.0	97
Dichloromethane	1.3	103	Styrene	9.3	85
trans-1,2-dichloroethene	2.7	98	Bromoform	2.5	96
1,1-dichloroethane	1.6	102	Isopropylbenzene	3.5	99
2,2-dichloropropane	11.0	96	Bromofluorobenzene	3.2	107
cis-1,2-dichloroethene	1.8	99	Bromobenzene	5.3	109
Bromochloromethane	3.1	100	1,1,2,2-tetrachloroethane	11.1	122
Chloroform	3.1	102	n-propylbenzene	6.3	116
1,1,1-trichloroethane	2.4	104	1,2,3-trichloropropane	10.8	125
Carbon tetrachloride	4.3	107	2-chlorotoluene	4.6	111
1,1-dichloropropene	2.2	100	1,3,5-trimethylbenzene	5.6	118
Benzene	1.6	100	4-chlorotoluene	3.8	108
1,2-dichloroethane	4.3	104	tert-butylbenzene	8.3	122
Trichloroethene	1.0	99	1,2,4-trimethylbenzene	3.2	111
1,2-dichloropropane	3.1	103	sec-butylbenzene	7.7	123
Dibromomethane	3.4	99	4-isopropyltoluene	5.5	115
Bromodichloromethane	3.7	104	1,3-dichlorobenzene	1.3	102
cis-1,3-dichloropropylene	4.9	96	1,4-dichlorobenzene	1.3	101
Toluene	1.2	99	n-butylbenzene	4.3	107
trans-1,3-dichloropropylene	8.5	92	1,2-dichlorobenzene	1.6	98
1,1,2-trichloroethane	1.5	99	1,2-dibromo-3-chloropropane	7.4	108
Tetrachloroethene	5.3	94	1,2,4-trichlorobenzene	8.1	88
1,3-dichloropropane	1.4	101	Hexachlorobutadiene	5.1	108
Dibromochloromethane	1.9	100	Naphthalene	2.4	96
1,2-dibromoethane	3.4	104	1,2,3-trichlorobenzene	7.4	87

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