

Volatile Organic Compound Analysis in Water Following HJ810-2016

Using an Agilent 8697 Headspace Sampler -XL Tray
with an Agilent 8860 GC System and 5977B MSD

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Abstract

A group of 55 representative volatile organic compounds (VOCs) in water were analyzed by an Agilent 8697 Headspace -XL Tray coupled with an Agilent 8860 gas chromatograph (GC) and Agilent 5977B single quadrupole mass spectrometer (MSD) system. The system repeatability, linearity, and detectability were evaluated according to the HJ810-2016 method. The results demonstrated excellent system performance, which met or exceeded the HJ810 standard requirements.

Introduction

Ensuring water quality is a great challenge that we face in the modern world. The quality of water is impacted not only by natural phenomenon but also human activities. Water quality is described as water conditions including physical, chemical, and biological characteristics. VOCs are one of the key chemical indexes for water quality. VOCs are organic compounds having high vapor pressure and low water solubility. Most VOCs enter bodies of water via industry dumping, leaks, or spills. Some VOCs are the by-products of disinfection treatment and are easy to evaporate from water. This evaporation aligns with the headspace work principle and makes the headspace technique an ideal approach to extract and introduce VOCs from water to GC or gas chromatography/mass spectrometry (GC/MSD) for identification and quantitation. Purge and trap (P&T) is another widely used VOC introduction technique for water analysis. P&T sweeps the VOCs out of a water sample and concentrates them for analysis. P&T provides a more exhaustive extraction of VOCs, generating much higher sensitivity compared to headspace techniques. However, P&T instrumentation design is more complex, and the use and maintenance of the instrument requires more caution and expertise.¹ By contrast, a headspace sampler is much easier to use and maintain. In China and Europe, the headspace sampler is widely applied to VOCs analysis in water.^{2,3}

The 8697 headspace samplers are the second generation of Agilent headspace products. There are two models, 8697 and 8697 -XL Tray, of which the main differences are sample throughput (48 versus 120 vials) and vial cooling capability. Both models are developed on an intelligent platform. Easy access and execution of multiple smart features such as user-guided maintenance, a gas supply pressure check, a transfer line restriction and leak test, a user vial leak test, and others, were developed. These intelligent maintenance and diagnostic tests were designed based on the polling and analysis of representative customer issues and pain points during headspace use. The tests help the users to know the instrument status, pinpoint the malfunctioning areas quickly and accurately, and maintain the instrument in a timely and effective manner.

In this application note, the 8697 -XL Tray coupled with an 8860 GC and 5977B MSD system were used for water VOCs analysis following the Chinese HJ810-2016 method.⁴ The system performance was evaluated for repeatability, linearity, limit of detection (LOD), limit of quantitation (LOQ), and method recovery rate.

Experiment

Chemicals and standards

All chemicals and standards were purchased from Alta Scientific Co. Ltd. These chemicals included 1,000 mg/L VOCs in methanol, 1,000 mg/L internal calibration standards (IS) of fluorobenzene, and 1,4-dichlorobenzene-d₄ (in methanol), and sodium chloride (analytical grade).

VOCs standard working solution

The VOC stock solution was diluted with methanol to 100 and 10 mg/L. The IS stock solution was diluted to 200 and 25 mg/L with methanol for later use.

Calibration standards and water sample preparation

First, 4 g of NaCl salt were weighed into a 20 mL headspace vial before the addition of 10 mL of deionized water. After the VOCs standard and IS working solutions were spiked into the salt solution, the vials were capped immediately and vortexed vigorously for 10 to 20 seconds.

The calibration standards analyzed by MSD scan mode were prepared at six calibration levels: approximately 10, 20, 40, 100, 200, and 400 µg/L with internal standards of 200 µg/L. The calibration standards ranging from 1 to 40 µg/L (i.e., 1, 2, 4, 10, 20, 40 µg/L) with 20 µg/L IS, were prepared for selected ion monitoring (SIM) mode analysis. For each set of calibrants, six replicates at three different calibration levels were prepared for repeatability test. Eight replicates of 4 and 0.5 µg/L standards were used for LOQ evaluation in scan and SIM modes.

The water sample was collected and prepared from a local lake according to the sample collection/preparation procedure described in HJ810-2016. The real-world water samples were spiked at the middle and high concentration levels for the recovery test.

Instrumentation and analytical conditions

An 8697 -XL Tray was coupled to an 8860/5977B GC/MSD system for analysis (Figure 1). An extract ion source was used with a 6-mm drawout lens. An Agilent J&W DB-624 GC column, 60 m × 250 μm, 1.4 μm, was used for VOCs separation.

The headspace and GC/MSD test parameters are shown in Table 1. This experiment was aligned with HJ810-2016 recommendations, and results are reported in the following figures.

Agilent MassHunter Acquisition software for GC/MS systems version 10.0 was used for data collection. MassHunter Qualitative Analysis version 10.0 software and MassHunter Quantitative Analysis version 10.0 software were used for data analysis. Quantitation for scan and SIM methods was based on the same set of target ions.

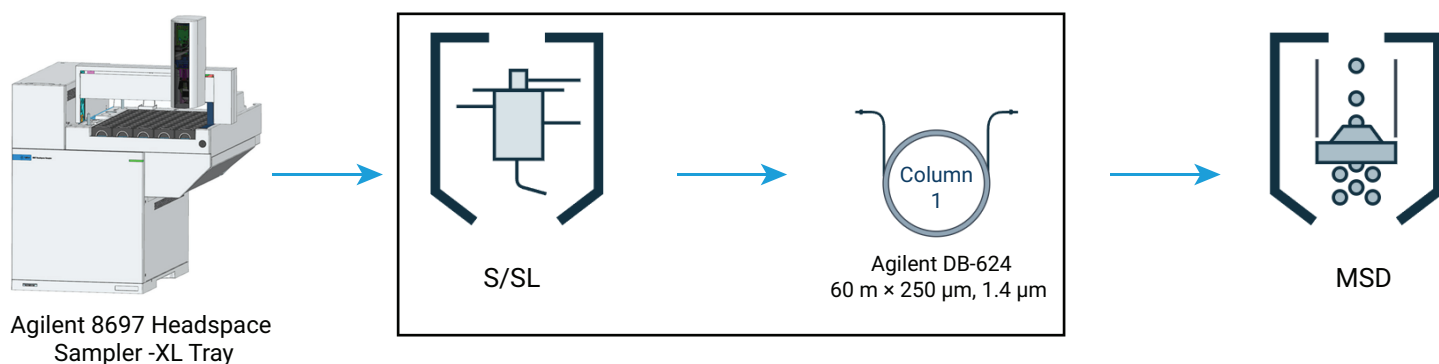


Figure 1. System schematics of the Agilent 8697 -XL Tray and the Agilent 8860/5977B GC/MSD system.

Table 1. Analytical conditions of the Agilent 8697 -XL Tray and the Agilent 8860/5977B GC/MSD system.

Agilent 8860 GC and 5977B MSD System with Inert Extract Ion Source		Agilent 8697 Headspace Sampler -XL Tray	
Parameters	Setpoints	Parameters	Setpoints
Inlet Temperature	250 °C	8697 Loop Size	1 mL
Liner	Deactivated quartz liner, splitless, 2 mm id (p/n 5181-8818)	Vial Pressurization Gas	N ₂
Carrier Gas	Helium	Hs Oven Temperature	65 °C
Column Flow	Constant flow mode, 1.2 mL/min	Hs Loop Temperature	80 °C
Split Ratio	5:1	Hs Transfer Line Temperature	120 °C
Oven Program	40 °C (2 min), 5 °C/min to 120 °C (3 min), then 10 °C/min to 230 °C (4 min)	Vial Equilibration Time	40 min
Column	Agilent J&W DB-624 GC column, 60 m × 0.25 mm, 1.4 μm (p/n 121-1364)	Vials Size	20 mL, PTFE/silicone septa (p/n 8010-0413)
MSD Transfer Line	250 °C	Vial Shaking	Level 7, 136 shakes/min with acceleration of 530 cm/s ²
MS Source	280 °C	Vial Fill Mode	Default
MS Quad	150 °C	Vial Fill Pressure	15 psi
Scan Range	35 to 350 Da	Loop Fill Mode	Custom
Dwell Time for Ions in SIM Method	20 ms	Loop Ramp Rate	20 psi/min
Gain Factor	0.4	Loop Final Pressure	3 psi
Drawout Plate	6 mm, inert (p/n G2589-20045)	Loop Equilibration Time	0.1 min
		Carrier Control Mode	GC carrier control
		Vent After Extraction	On

Results and discussion

User vial leak test

A vial leak will cause poor response repeatability. There is no absolute leak-free vial. Control of the vial leak rate at a proper level is critical to achieve high-precision results. The 8697 headspace samplers can automate the vial leak test on five capped vials and recommends an acceptable leak rate threshold based on the statistical results. The recommended threshold then can be set in the test method and used for the real-time system leak check for the subsequent analysis. A passed leak check means effective vial sealing. If the leak check fails, a preset operation including abort, continue, or skip will be executed on the test vial automatically. If abort or skip is executed, the precious samples can be saved and analyzed later after the leak issue is fixed. The vial leak test helps find a proper leak threshold based on specific application conditions, which guarantees the analytical precision and reduces the risk of leak check fail. This test is important for compliance labs who have complained

that sometimes even though the test results were good, the message of a leak test failure would appear. A pop-up message of a leak test fail, caused by the improper setting of leak rate threshold, could cause analysts to spend time troubleshooting the noncompliance issue. Such cases can be significantly reduced by the vial leak test feature.

In this work, five capped 40 µg/L calibration samples were tested under the analytical conditions described in Table 1. The response and precision of the five samples met the analytical requirement. Then, the user vial leak test was run automatically on another set of five capped samples by initiating the user vial leak test from the 8860 GC browser user interface.

When the test was finished, a leak rate threshold of 0.2 mL/min was recommended. This recommended value was saved in the analytical method. The following analysis was performed under this leak rate threshold. Satisfactory results were generated without a leak test failure pop-up message.

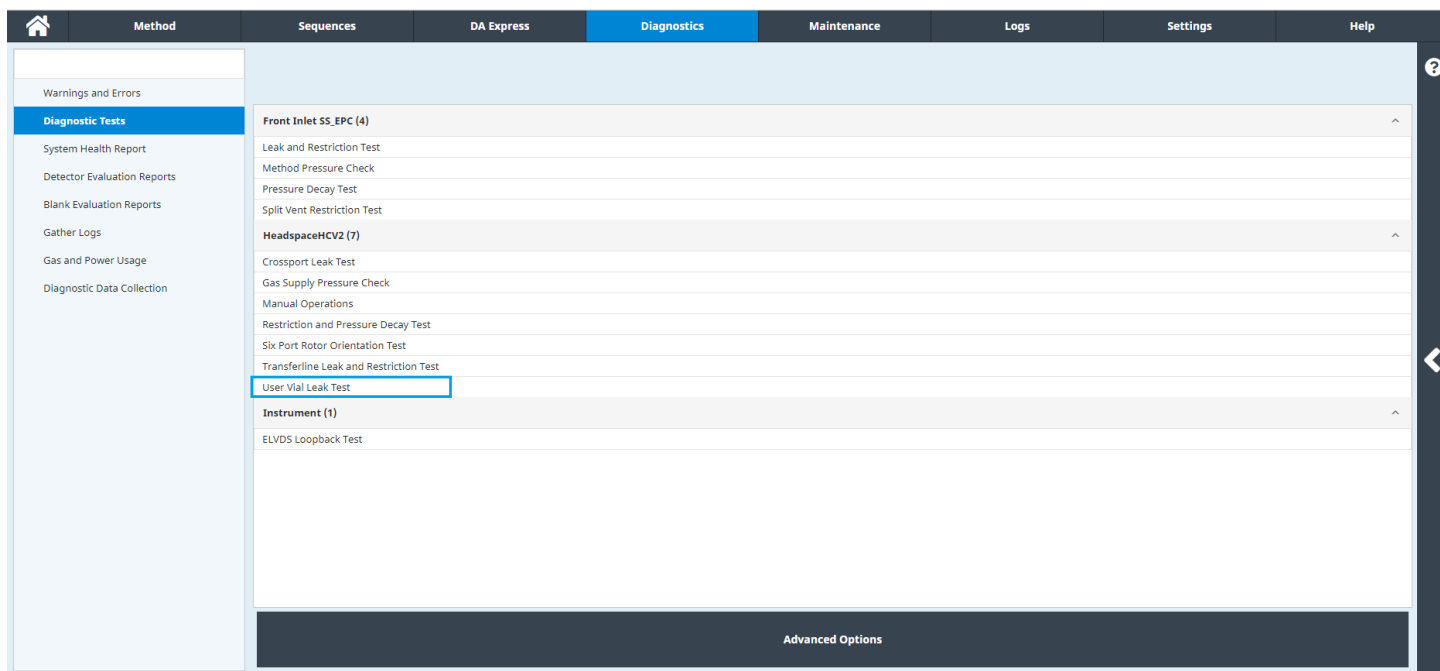


Figure 2. User vial leak test initiated from the browser user interface.

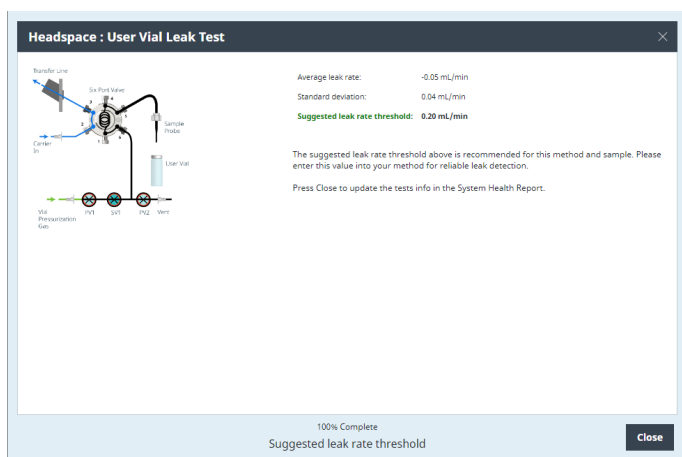


Figure 3. Leak rate threshold recommended by user vial leak test.

MSD performance evaluation

According to HJ810-2016, MSD performance should be checked before each batch of real samples is run to ensure MS data validity and reliability. The MSD was autonomously tuned by selecting the Etune method. Then, 20 μL of 25 $\mu\text{g}/\text{mL}$ BFB sample was spiked into 10 mL VOC-free water, capped, and analyzed. Table 2 shows the tune evaluation result for BFB.

Table 2. MSD Etune result conformity assessment.

Target Mass	Rel. to Mass	Lower Limit %	Upper Limit %	Rel. Abn. %	Raw Abn.	Pass/Fail
95	95	100	100	100.0	10,603	Pass
96	95	5	9	5.8	617	Pass
173	174	0	2	0.0	0	Pass
174	95	50	100	74.8	7,936	Pass
175	174	5	9	7.0	553	Pass
176	174	95	105	95.1	7,550	Pass
177	176	5	10	6.2	466	Pass

As described in HJ810-2016, the MSD scan mode is the primary detection mode for water VOCs analysis. If the sensitivity is not adequate for target VOCs detection, a SIM mode-based detection will be used. In this work, a comprehensive performance evaluation was made under two MSD detection modes based on two sets of calibration standards.

Scan results

The total ion chromatogram (TIC) of 40 $\mu\text{g}/\text{L}$ calibration standard is shown in Figure 4. Most compounds obtained baseline separation. Six pairs of compounds coeluted; they are labeled with superscripts in Appendix Table A1. These coeluted compounds were identified and quantitated by their unique qualifier and quantifier ions. The peak identities based on elution order are listed in Table A1.

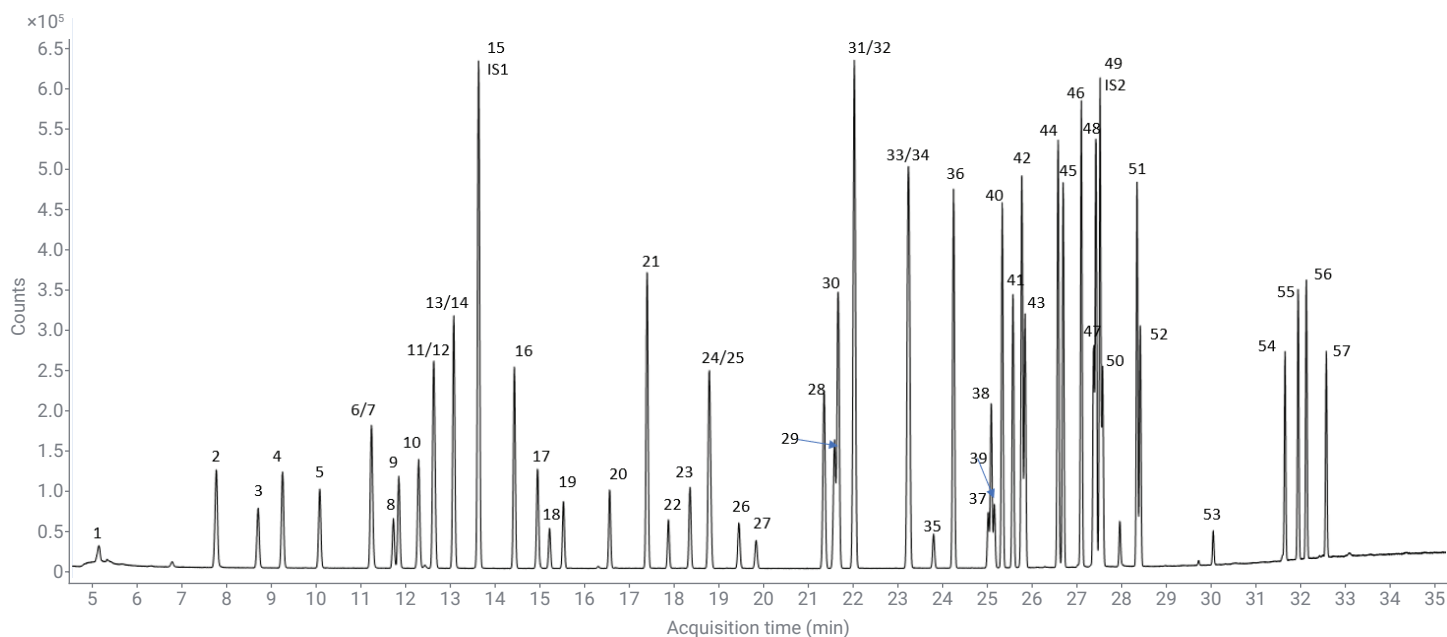


Figure 4. TIC of 40 $\mu\text{g}/\text{L}$ VOCs standard obtained in scan mode.

The system repeatability was evaluated based on the analyte absolute responses. The quantitation of each compound was based on the EIC of target ions (as listed in Table A1). Six replicates of 10, 40, and 200 µg/L calibrants were analyzed. The average response %RSD of 55 VOCs was 1.8% ranging

from 0.8 to 6.2% (Figure 5). The average response RSD % for 200 µg/L fluorobenzene (IS1) and 1,4-dichlorobenzene-d₄ (IS2) in three calibration levels was 1.5 and 2.9%. The repeatability performance demonstrated excellent sampling and detection precision.

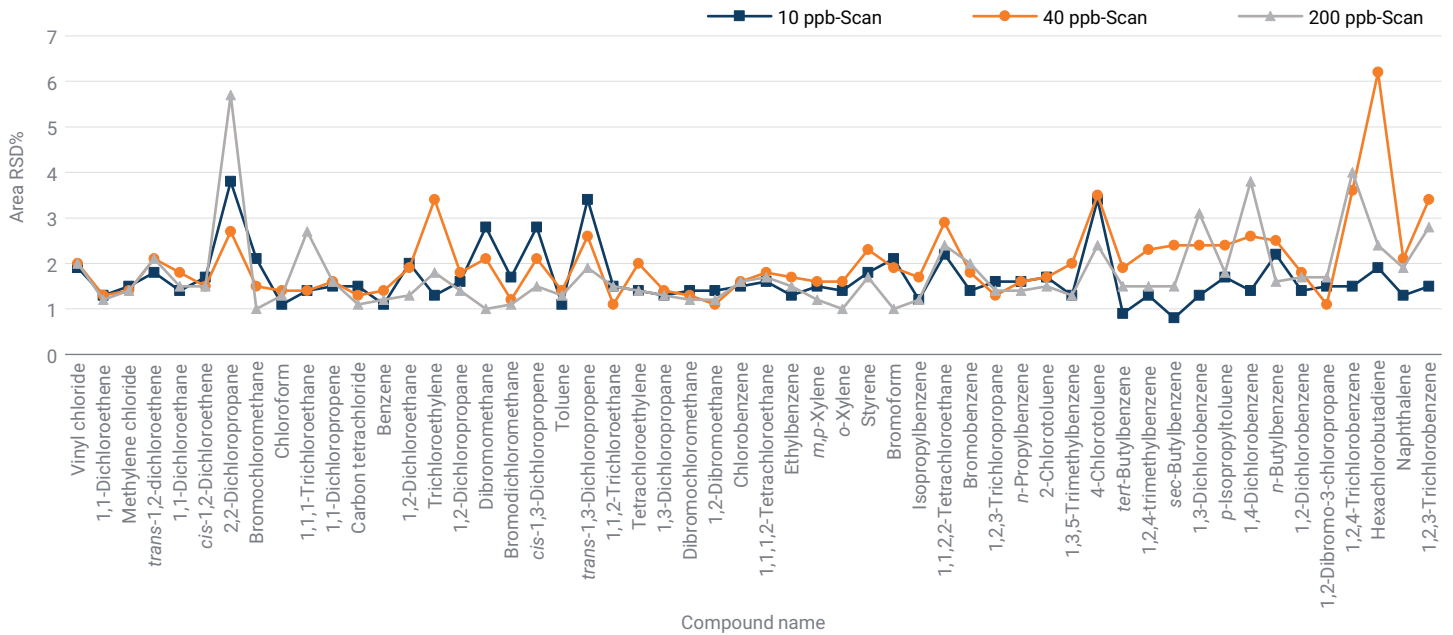


Figure 5. The area %RSD of 55 VOCs at different concentration levels in scan mode.

Linearity was evaluated based on the relative response of each analyte to internal standard across the tested concentration range of 10 to 400 µg/L. The correlation coefficient R^2 of target analytes was from 0.9947 to 0.9999 with an average of 0.9990. Among them, only one compound, 2,2-dichloropropane, had an R^2 less than 0.9950. The linearity performance met the HJ810-2016 requirement of $R^2 \geq 0.990$. The linearity plots of four representative compounds are shown in Figure 6. The %RSD of relative response factor (RRF) of each analyte was also calculated across six calibration levels. The average RRF %RSD was 5.2% ranging from 0.98 to 12.7%, locating within the HJ810-2016 RRF %RSD threshold of 20% (detailed RRF %RSD results are shown in Table A1).

The MDLs for the 55 targeted VOCs were calculated by applying the formula shown in Equation 1 on eight trial analyses of 4 µg/L standards. The MDLs ranged from 0.132

to 1.105 µg/L (corresponding to µg/kg in a real water sample). The LOQs were from 0.44 to 3.68 µg/L.

Equation 1. Formula for MDL calculation.

$$\text{MDL} = S \times t (n - 1, 1 - \alpha = 99)$$

n: number of trials (n = 8)

S: standard deviation of n trials

t: t-value for the 99% confidence level with n - 1 degrees of freedom (when n = 8, t = 2.998)

The method recovery was assessed on a spiked lake water sample at 40 and 100 µg/L. The recovery rate for 40 µg/L spiked sample was from 90.8 to 122.3% and 90.9 to 105.7% for a 100 µg/L sample. The recovery performance was comparable with the reference recovery results demonstrated in the HJ810-2016 method.

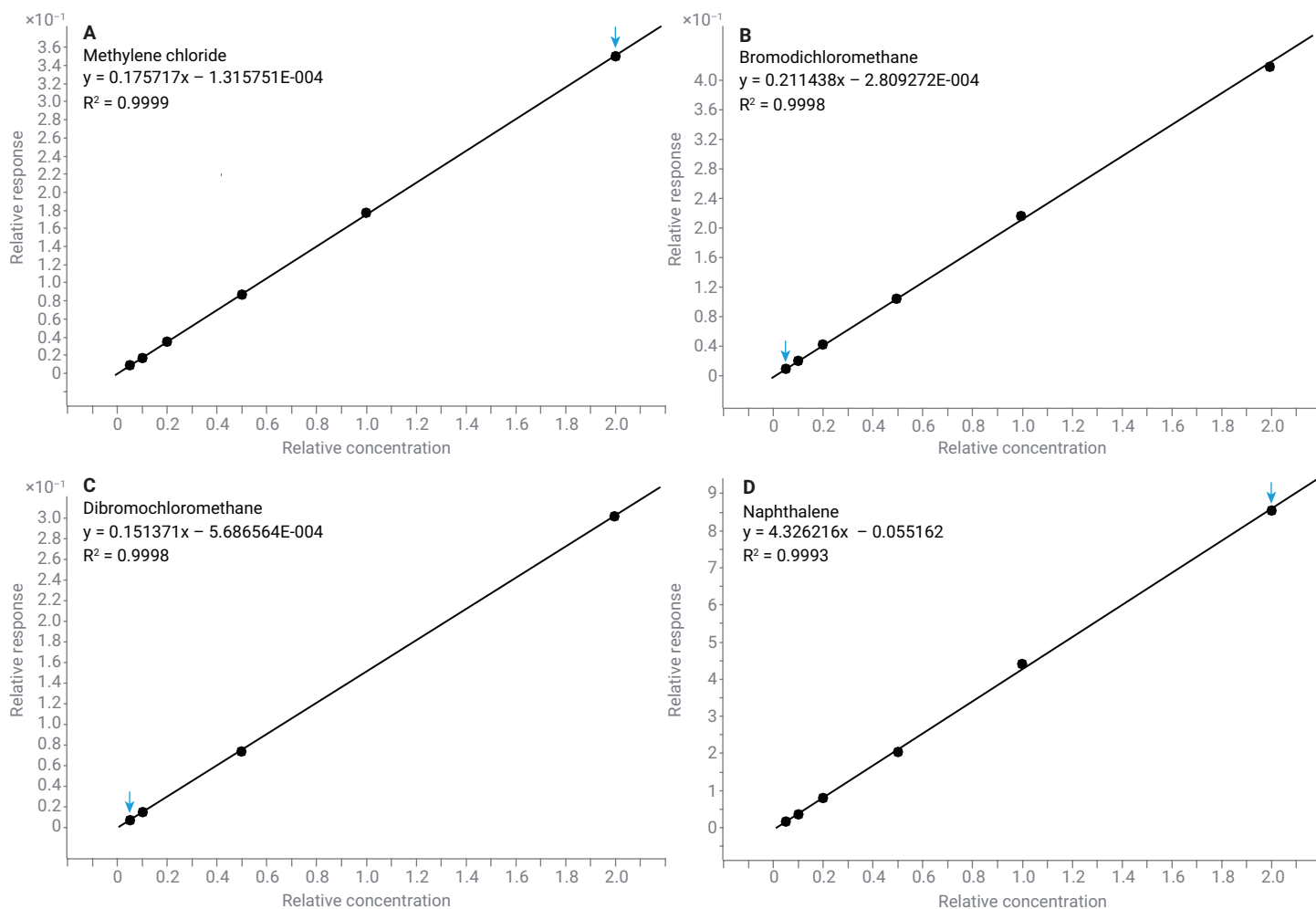


Figure 6. Linear calibration curves in scan mode (10 to 400 µg/L) of four compounds eluting at the early, middle, and late part of the chromatogram, CF weight: 1/x. Compounds: (A) methyl chloride, R^2 0.9999; (B) bromodichloromethane, R^2 0.9998; (C) chlorodibromomethane, R^2 0.9998; (D) naphthalene, R^2 0.9993.

SIM results

Six replicates of 4, 10 and 40 µg/L calibrants were analyzed to assess the response repeatability obtained by SIM detection. The quantitation of each compound was based on the quantifier ions listed in Appendix Table A2. The response %RSD of 55 VOCs were in the range of 0.6 to 4.8% (Figure 8). The average response %RSD of 20 µg/L fluorobenzene (IS1) and 1,4-dichlorobenzene-d₄ (IS2) in three calibration levels was 2.3 and 3.8%, respectively.

The results of the SIM mode calibration are listed in Table A2. SIM provided excellent calibration linearity for all compounds in the range of 1 to 40 µg/L with an average R² of 0.9996. The average relative response factor (RRF) %RSD of 55 analytes was from 0.86 to 17.15% on average of 5.5%, locating within the 20% threshold specified in HJ810-2016 method.

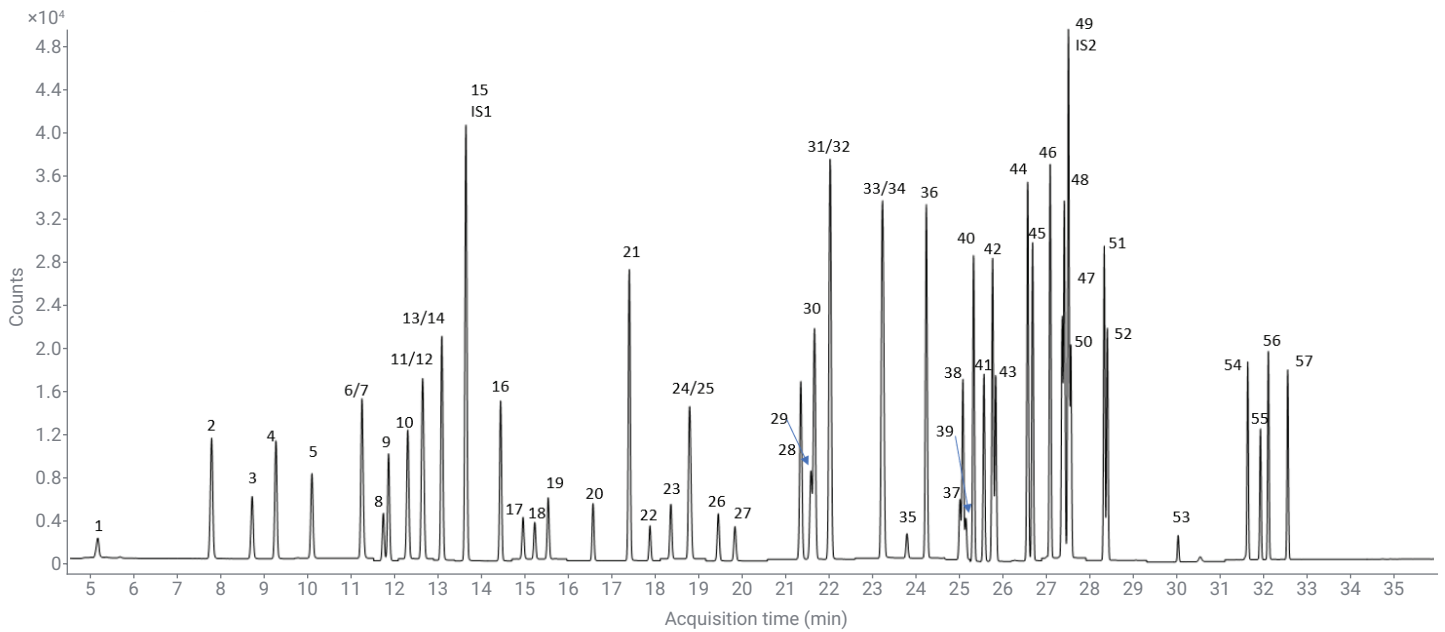


Figure 7. The total ion chromatogram of 4 µg/L VOCs calibration sample acquired by SIM mode.

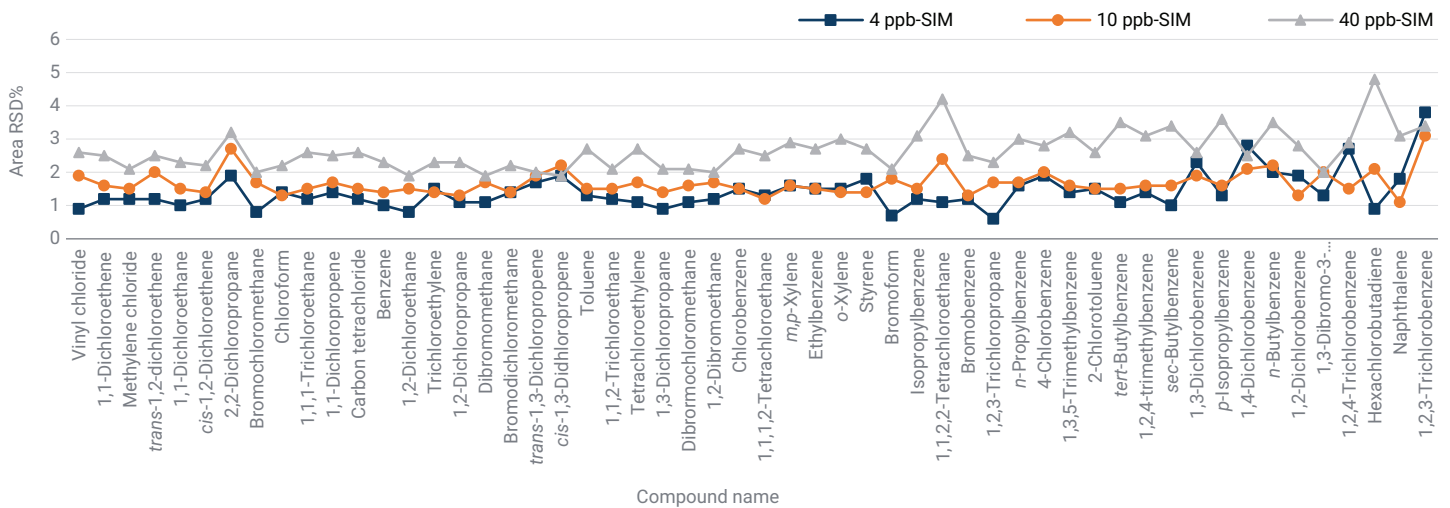


Figure 8. The absolute response precision of 55 VOCs at 4, 10, and 40 µg/L in SIM mode.

The MDLs of SIM mode were calculated based on analysis of eight replicas of 0.5 µg/L standards. The MDLs ranged from 0.007 to 0.073 µg/L (corresponding to µg/kg in a real water sample). The LOQ ranged from 0.0229 to 0.243 µg/L, which was much better than the HJ810-2016 requirement.

SIM method recovery rate was also tested by spiked local lake water sample at two concentration levels. The recovery rate was 93.6 to 113.5% for a 20 µg/L spiked sample and 90.5 to 110.3% for a 4 µg/L spike sample.

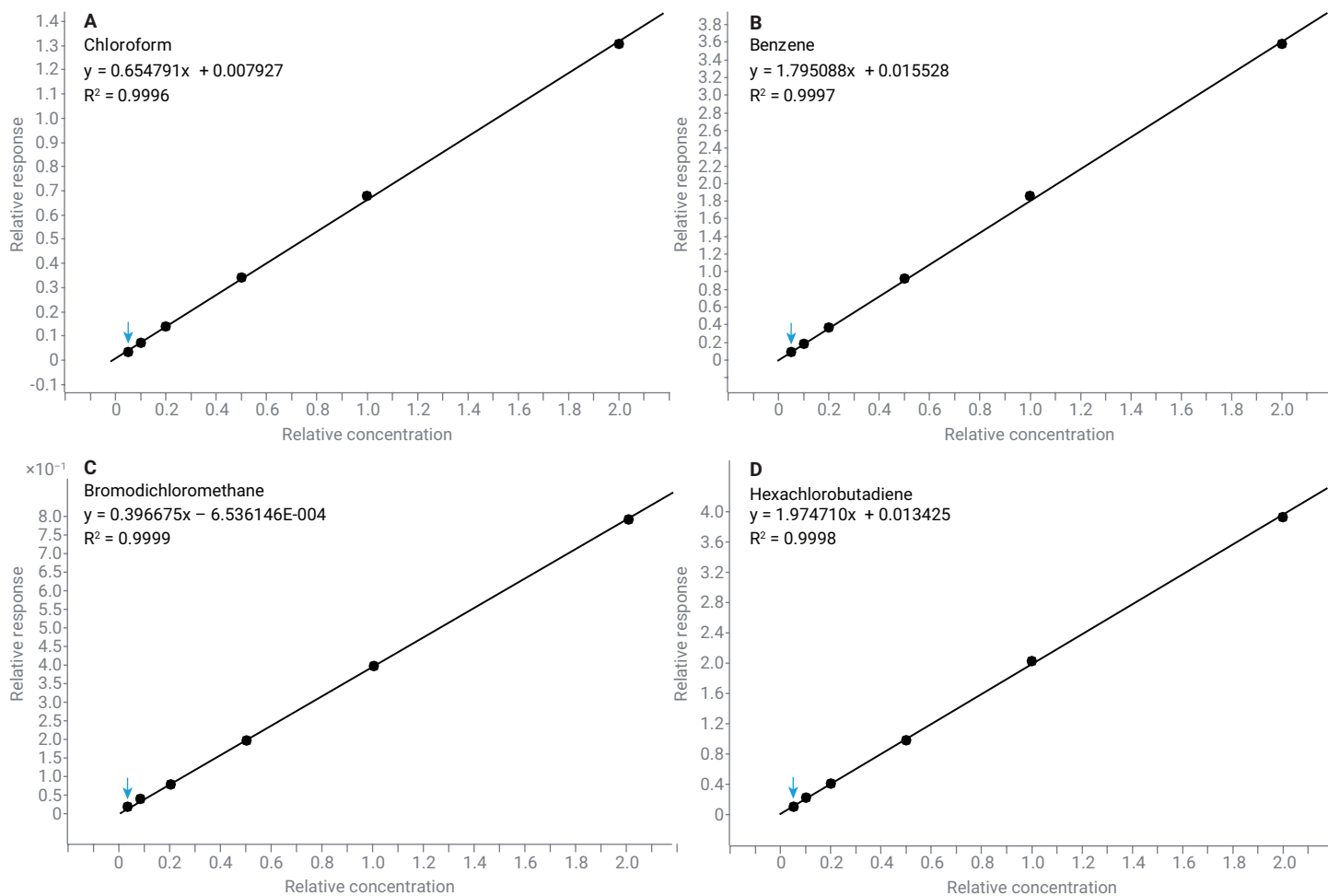


Figure 9. Linear calibration curves of four representative analytes (1 to 40 µg/L) in SIM mode, CF weight: none. Compounds: (A) chloroform, R^2 0.9996; (B) benzene, R^2 0.9997; (C) bromodichloromethane, R^2 0.9999; (D) hexachlorobutadiene, R^2 0.9998.

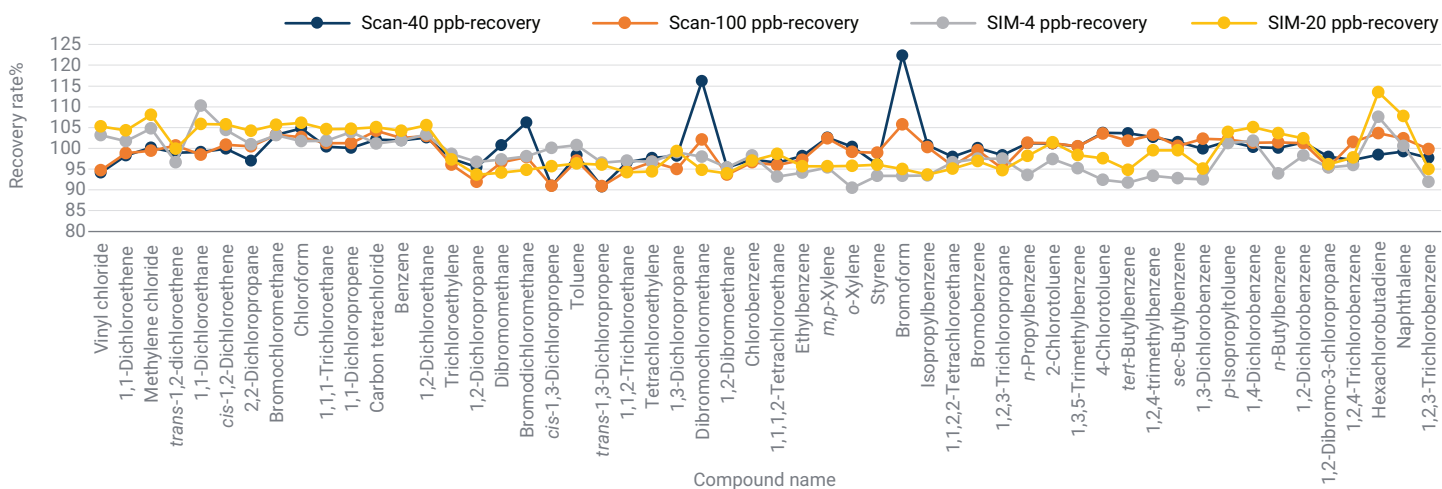


Figure 10. Recovery performance of scan and SIM based method.

Conclusion

In this application note, the system performance of an 8697 -XL Tray with a 8860/5977B GC/MSD system was evaluated for VOCs analysis in water based on the HJ810-2016 standard. The response precision achieved by MSD scan mode and SIM mode was in the range of 0.6 to 6.2%, which demonstrates excellent headspace sampling and GC/MSD detection repeatability. The linearity performance of all target components across the tested concentration range exceeded the HJ810 requirement for linear regression coefficient R^2 (≥ 0.99). The average RRF %RSDs of all target compounds in two MSD detection modes were below the 20% threshold specified in the HJ810-2016 method. The LOQs obtained in MSD scan and SIM mode were from 0.44 to 3.68 $\mu\text{g/L}$ and 0.0228 to 0.243 $\mu\text{g/L}$ respectively, much better than the reference LOQs in HJ810-2016 standard. The recovery rates on spiked local lake water samples were between 90 and 125%. All test results proved that the 8697 -XL Tray can effectively and reproducibly extract and introduce VOCs from a water matrix to a GC/MSD system for reliable identification and accurate quantitation with high confidence levels.

References

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3. Rothweiler, B. Analysis of Volatile Organic Compounds in Environmental Waters Using the Agilent 7697A Headspace and 7890B/5977A GC/MS, *Agilent Technologies application note*, publication number 5991-3927EN, **2014**.
4. Water quality—Determination of Volatile Organic Compounds—Headspace/Gas Chromatography Mass Spectrometry, HJ 810-2016, published by Ministry of Ecology and Environment of the People's Republic of China. 2016-10-01.

Appendix

Table A1. RT, linearity, LOD, and LOQ of the scan-based method (coeluted compounds are labeled with the same superscript).

Peak No.	Name	RT	CF R ²	CF Formula	Avg. RRF RSD	LOD (µg/L)	LOQ (µg/L)	Target Ion for EIC Quantitation	IS
1	Vinyl chloride	5.135	0.9999	$y = 0.126972x + 3.503640E-004$	1.42	0.325	1.083	62	IS1
2	1,1-Dichloroethene	7.760	1.0000	$y = 0.287535x - 6.883461E-004$	1.77	0.378	1.260	96	
3	Methylene chloride	8.695	0.9999	$y = 0.175717x - 1.315751E-004$	1.07	0.288	0.959	84	
4	<i>trans</i> -1,2-Dichloroethene	9.238	1.0000	$y = 0.290481x - 4.032902E-004$	1.28	0.366	1.219	96	
5	1,1-Dichloroethane	10.069	0.9997	$y = 0.370494x + 0.001974$	2.70	0.355	1.184	63	
6	<i>cis</i> -1,2-Dichloroethene ¹	11.215	1.0000	$y = 0.262305x - 5.676062E-004$	1.78	0.320	1.068	96	
7	2,2-Dichloropropane ¹	11.237	0.9947	$y = 0.229538x + 2.058373E-005$	7.79	1.012	3.372	77	
8	Bromochloromethane	11.713	0.9998	$y = 0.108911x + 1.088656E-004$	1.42	0.598	1.993	128	
9	Chloroform	11.827	0.9997	$y = 0.351395x + 7.031272E-004$	1.23	0.306	1.020	83	
10	1,1,1-Trichloroethane	12.278	0.9998	$y = 0.349041x + 4.844261E-004$	0.98	0.278	0.926	97	
11	1,1-Dichloropropene ²	12.603	0.9994	$y = 0.354595x - 1.713302E-005$	2.41	0.215	0.717	75	
12	Carbon tetrachloride ²	12.629	0.9993	$y = 0.317708x + 7.545995E-004$	2.15	0.395	1.317	117	
13	Benzene ³	13.056	0.9989	$y = 0.975904x + 0.004011$	2.53	0.258	0.860	78	
14	1,2-Dichloroethane ³	13.064	0.9979	$y = 0.119321x + 0.001719$	6.86	0.444	1.481	62	
15	Fluorobenzene (IS1)	13.613						96	
16	Trichloroethylene	14.409	0.9997	$y = 0.332354x + 7.836946E-004$	1.47	0.582	1.940	95	IS1
17	1,2-Dichloropropane	14.926	0.9998	$y = 0.207195x + 7.853720E-004$	2.10	0.261	0.870	63	
18	Dibromomethane	15.193	0.9999	$y = 0.080913x - 2.946909E-004$	3.15	0.949	3.163	93	
19	Bromodichloromethane	15.508	0.9998	$y = 0.211438x - 2.809272E-004$	1.41	0.318	1.060	83	
20	<i>cis</i> -1,3-Dichloropropene	16.539	0.9990	$y = 0.271367x - 0.003129$	6.91	0.644	2.146	75	
21	Toluene	17.372	0.9987	$y = 1.218899x - 6.724743E-004$	4.40	0.209	0.698	91	
22	<i>trans</i> -1,3-Dichloropropene	17.849	0.9991	$y = 0.171387x - 0.001696$	6.17	0.877	2.924	75	
23	1,1,2-Trichloroethane	18.333	0.9998	$y = 0.148842x - 4.405210E-005$	1.83	0.447	1.491	83	
24	Tetrachloroethylene ⁴	18.758	0.9998	$y = 0.375692x + 7.865872E-004$	1.41	0.534	1.778	166	
25	1,3-Dichloropropane ⁴	18.788	0.9994	$y = 0.213894x + 4.938890E-004$	1.94	0.235	0.782	76	
26	Dibromochloromethane	19.427	0.9998	$y = 0.151371x - 5.686564E-004$	2.75	0.341	1.137	129	
27	1,2-Dibromoethane	19.805	0.9996	$y = 0.118271x - 7.610758E-004$	4.17	0.318	1.060	107	

Peak No.	Name	RT	CF R ²	CF Formula	Avg. RRF RSD	LOD (µg/L)	LOQ (µg/L)	Target Ion for EIC Quantitation	IS	
28	Chlorobenzene	21.322	0.9992	y = 3.361692x - 0.050788	9.43	0.396	1.320	112	IS2	
29	1,1,1,2-Tetrachloroethane	21.561	0.9988	y = 1.031673x - 0.016123	9.48	0.638	2.128	131		
30	Ethylbenzene	21.642	0.9997	y = 5.796045x - 0.095480	12.66	0.323	1.076	91		
31/32	<i>m,p</i> -Xylene ⁵	22.000	0.9982	y = 8.881587x - 0.028249	7.06	0.353	1.176	106		
33	<i>o</i> -Xylene ⁶	23.198	0.9995	y = 4.482819x - 0.052524	9.89	0.407	1.355	106		
34	Styrene ⁵	23.227	0.9995	y = 3.494952x - 0.046133	11.34	0.318	1.061	104		
35	Bromoform	23.766	0.9981	y = 0.372236x - 0.006807	11.25	0.771	2.570	173		
36	Isopropylbenzene	24.215	0.9996	y = 6.061658x - 0.076808	10.45	0.510	1.700	105		
37	1,1,2,2-Tetrachloroethane	24.986	0.9985	y = 0.890392x - 0.012181	8.16	0.719	2.397	83		
38	Bromobenzene	25.050	0.9993	y = 1.281626x - 0.012817	5.72	0.466	1.555	156		
39	1,2,3-Trichloropropane	25.125	0.9990	y = 0.591367x - 0.004143	4.42	0.520	1.733	75		
40	<i>n</i> -Propylbenzene	25.303	0.9992	y = 6.827220x - 0.067985	10.01	0.419	1.395	91		
41	2-Chlorotoluene	25.540	1.0000	y = 1.500561x - 0.012329	6.49	0.298	0.992	91		
42	1,3,5-Trimethylbenzene	25.740	0.9997	y = 2.688176x - 0.028858	9.49	0.464	1.546	105		
43	4-Chlorotoluene	25.809	0.9989	y = 4.029700x - 0.004739	4.80	1.035	3.450	91		
44	<i>tert</i> -Butylbenzene	26.548	0.9997	y = 4.668966x - 0.049583	9.40	0.465	1.550	119		
45	1,2,4-Trimethylbenzene	26.658	0.9987	y = 5.240525x - 0.017612	6.62	0.439	1.464	105		
46	<i>sec</i> -Butylbenzene	27.065	0.9999	y = 1.477040x - 0.013188	7.16	0.583	1.942	105		
47	1,3-Dichlorobenzene	27.344	1.0000	y = 2.640657x - 0.003993	1.50	0.506	1.687	146		
48	<i>p</i> -Isopropyltoluene	27.393	0.9997	y = 1.603523x - 0.010740	6.78	0.612	2.041	119		
49	1,4-Dichlorobenzene-D4 (IS2)	27.485						115		
50	1,4-Dichlorobenzene	27.542	1.0000	y = 2.442603x + 0.007424	2.19	0.302	1.006	146		IS2
51	<i>n</i> -Butylbenzene	28.310	0.9999	y = 1.549466x - 0.013981	6.34	0.678	2.259	91		
52	1,2-Dichlorobenzene	28.379	0.9999	y = 2.374979x + 0.003092	1.75	0.586	1.955	146		
53	1,2-Dibromo-3-chloropropane	30.012	0.9971	y = 0.185372x - 0.002942	9.57	0.704	2.346	157		
54	1,2,4-Trichlorobenzene	31.613	0.9990	y = 1.919704x - 0.016428	4.64	0.526	1.754	180		
55	Hexachlorobutadiene	31.909	0.9970	y = 0.714420x - 0.011222	8.84	0.800	2.666	225		
56	Naphthalene	32.093	0.9993	y = 4.326216x - 0.055162	9.10	0.282	0.939	128		
57	1,2,3-Trichlorobenzene	32.538	0.9990	y = 1.680303x - 0.011443	3.79	0.405	1.349	180		

Table A2. RT, linearity, LOD, and LOQ of the SIM-based method.

Peak No.	Name	RT	CF R ²	CF Formula	Avg. RRF %RSD	LOD (µg/L)	LOQ (µg/L)	Quantifier (m/z)	Qualifier (m/z)	IS
1	Vinyl chloride	5.133	0.9999	y = 0.281442x - 2.687199E-004	1.54	0.0366	0.1221	62	64	IS1
2	1,1-Dichloroethene	7.754	0.9998	y = 0.648000x + 0.002310	1.29	0.0139	0.0464	96	61.63	
3	Methylene chloride	8.689	0.9999	y = 0.342324x + 0.002340	2.92	0.0164	0.0547	84	86.49	
4	<i>trans</i> -1,2-Dichloroethene	9.238	0.9994	y = 0.609515x + 0.007889	2.66	0.0156	0.052	96	61.98	
5	1,1-Dichloroethane	10.067	0.9995	y = 0.723088x + 0.008328	2.31	0.0105	0.0352	63	65.83	
6	<i>cis</i> -1,2-Dichloroethene ¹	11.217	0.9997	y = 0.535136x + 0.004580	1.92	0.0069	0.0229	96	61.98	
7	2,2-Dichloropropane ¹	11.235	1.0000	y = 0.413206x + 0.001122	2.14	0.0401	0.1336	77	41.97	
8	Bromochloromethane	11.715	0.9996	y = 0.216656x + 0.002607	3.28	0.0119	0.0396	128	49.130	
9	Chloroform	11.833	0.9996	y = 0.654791x + 0.007927	3.17	0.0094	0.0315	83	85.47	
10	1,1,1-Trichloroethane	12.28	0.9998	y = 0.657788x + 0.005203	1.86	0.01	0.0332	97	99.61	
11	1,1-Dichloropropene ²	12.601	1.0000	y = 0.635295x - 0.001033	1.13	0.0171	0.0571	75	110.77	
12	Carbon tetrachloride ²	12.633	0.9996	y = 0.628067x + 0.007055	2.79	0.0107	0.0355	117	119.121	
13	Benzene ³	13.054	0.9997	y = 1.795088x + 0.015528	1.95	0.0074	0.0246	78	77.51	
14	1,2-Dichloroethane ³	13.066	0.9991	y = 0.229826x + 0.005075	6.23	0.0155	0.0518	62	64.98	
15	Fluorobenzene (IS1)	13.613		NA				96	77	

Peak No.	Name	RT	CF R ²	CF Formula	Avg. RRF %RSD	LOD (µg/L)	LOQ (µg/L)	Quantifier (m/z)	Qualifier (m/z)	IS
16	Trichloroethylene	14.412	0.9997	y = 0.625227x + 0.005265	2.15	0.0176	0.0587	95	130.132	IS1
17	1,2-Dichloropropane	14.932	0.9999	y = 0.393225x + 6.140449E-004	0.97	0.0107	0.0358	63	41.112	
18	Dibromomethane	15.191	1.0000	y = 0.121111x + 1.503549E-004	1.56	0.0192	0.064	93	95.174	
19	Bromodichloromethane	15.508	1.0000	y = 0.396675x - 6.536146E-004	0.98	0.0108	0.0358	83	85.127	
20	cis-1,3-Dichloropropene	16.539	0.9997	y = 0.446259x - 0.005669	3.92	0.0249	0.083	75	39.77	
21	Toluene	17.376	0.9998	y = 2.151509x - 0.013350	4.28	0.0452	0.1508	91	92	
22	trans-1,3-Dichloropropene	17.851	0.9997	y = 0.276712x - 0.003420	3.79	0.0233	0.0775	75	39.77	
23	1,1,2-Trichloroethane	18.329	1.0000	y = 0.280903x - 7.321405E-005	1.05	0.0212	0.0705	83	97.85	
24	Tetrachloroethylene ⁴	18.758	0.9997	y = 0.699240x + 0.007796	3.05	0.0125	0.0416	166	168.129	
25	1,3-Dichloropropane ⁴	18.79	1.0000	y = 0.391944x + 0.001236	1.36	0.0169	0.0564	76	41.78	
26	Dibromochloromethane	19.423	1.0000	y = 0.293262x - 2.788273E-004	1.03	0.0125	0.0417	129	127.131	
27	1,2-Dibromoethane	19.805	0.9999	y = 0.213981x - 0.001164	1.66	0.0264	0.088	107	109.188	
28	Chlorobenzene	21.328	0.9998	y = 5.624883x - 0.061726	3.62	0.0134	0.0446	112	77.114	
29	1,1,1,2-Tetrachloroethane	21.555	0.9999	y = 1.834390x - 0.003029	1.68	0.0149	0.0498	131	133.119	
30	Ethylbenzene	21.642	0.9992	y = 9.604301x - 0.254832	12.35	0.0203	0.0676	91	106	
31/32	m,p-Xylene ⁵	22.006	0.9996	y = 15.927853x - 0.242611	13.36	0.0244	0.0813	106	91	
33	o-Xylene ⁶	23.196	0.9995	y = 7.906416x - 0.190460	13.54	0.021	0.0699	106	91	
34	Styrene ⁶	23.229	0.9994	y = 6.011384x - 0.156803	16.55	0.0119	0.0398	104	78.103	
35	Bromoform	23.77	1.0000	y = 0.624120x - 6.509101E-004	2.52	0.0286	0.0952	173	175.254	
36	Isopropylbenzene	24.215	0.9993	y = 10.764866x - 0.285476	14.26	0.0108	0.0361	105	120	
37	1,1,2,2-Tetrachloroethane	24.988	0.9997	y = 1.575668x - 0.016306	2.74	0.0466	0.1554	83	85.131	
38	Bromobenzene	25.056	0.9999	y = 3.204360x - 0.019287	2.97	0.0501	0.1671	156	77.158	
39	1,2,3-Trichloropropane	25.123	0.9988	y = 0.273946x + 0.004546	5.13	0.073	0.2432	75	77.110	
40	n-Propylbenzene	25.309	0.9994	y = 11.651015x - 0.284331	14.89	0.0274	0.0912	91	120	
41	2-Chlorotoluene	25.546	0.9998	y = 6.579881x - 0.093063	9.36	0.0217	0.0724	91	126	
42	1,3,5-Trimethylbenzene	25.74	0.9996	y = 9.412703x - 0.216021	16.06	0.0224	0.0748	105	120	
43	4-Chlorotoluene	25.811	0.9998	y = 7.059042x - 0.065293	9.27	0.0283	0.0945	91	126	
44	tert-Butylbenzene	26.552	0.9994	y = 8.436241x - 0.211647	14.96	0.0101	0.0338	119	91.134	
45	1,2,4-Trimethylbenzene	26.662	0.9997	y = 9.332961x - 0.181817	15.90	0.0298	0.0994	105	120	
46	sec-Butylbenzene	27.071	0.9996	y = 12.869653x - 0.281401	14.22	0.0124	0.0412	105	134	
47	1,3-Dichlorobenzene	27.344	0.9999	y = 4.738672x + 0.011042	0.86	0.0277	0.0922	146	111.148	
48	p-Isopropyltoluene	27.393	0.9995	y = 10.115025x - 0.221348	17.15	0.0156	0.052	119	134.91	
49	1,4-Dichlorobenzene-d ₄ (IS2)	27.485		NA				115	150.152	IS2
50	1,4-Dichlorobenzene	27.546	0.9999	y = 4.371155x + 0.018148	1.04	0.0301	0.1002	146	111.148	
51	n-Butylbenzene	28.31	0.9994	y = 8.951068x - 0.218214	14.61	0.0134	0.0446	91	92.134	
52	1,2-Dichlorobenzene	28.385	0.9995	y = 4.289234x + 0.039700	1.77	0.0221	0.0738	146	111.148	
53	1,2-Dibromo-3-chloropropane	30.01	0.9998	y = 0.349032x - 0.003252	3.09	0.0533	0.1776	157	75.155	
54	1,2,4-Trichlorobenzene	31.619	0.9999	y = 3.312049x + 0.010646	1.18	0.0409	0.1365	180	182.145	
55	Hexachlorobutadiene	31.907	0.9998	y = 1.974710x + 0.013425	3.10	0.0652	0.2174	225	223.227	
56	Naphthalene	32.093	0.9997	y = 7.577165x - 0.127161	7.29	0.0445	0.1483	128		
57	1,2,3-Trichlorobenzene	32.54	0.9994	y = 2.998406x + 0.033306	2.45	0.0396	0.1318	180	182.145	

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