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Fast Volatile Organic Compound Analysis of Drinking Water Using the Agilent 8697 Headspace Sampler in Tandem with Intuvo 9000 GC and 5977B GC/MSD

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Abstract

This application note describes the volatile organic compound (VOC) analysis of drinking water using the Agilent 8697 headspace sampler, coupled with the Agilent Intuvo 9000 GC and Agilent 5977B GC/MSD system. The system performance in terms of repeatability, linearity, limit of quantitation, and method recovery rate was evaluated, with good results. The sample incubation time at the headspace side was optimized at 20 minutes. The separation of tested compounds under a fast oven program, using hydrogen (H_2) as the carrier gas, took approximately 6 minutes and an additional 2 minutes 30 seconds for column conditioning. With the sample overlapping capability of the headspace sampler and fast analysis on the GC side, the sample throughput can be improved for VOC analysis of drinking water.

Introduction

VOCs are widely used in industry, agriculture, transportation, and in day-to-day household products. They can easily dissolve or leach into groundwater. The private wells located near industrial or commercial areas, gas stations, or landfills are at risk of VOC contamination. If drinking water comes from the city water supply, it is most likely treated with chlorine to kill the waterborne pathogens. The chlorine reacts with the natural organic matter, and subsequently, various VOCs form as disinfection byproducts. To ensure drinking water quality, different countries and regions have set up regulation limits on the amounts of VOCs in drinking water and developed methods to test the VOCs concentration.

To analyze the VOCs in drinking water, a headspace sampler coupled with GC/MSD is a regularly used platform.[1,2] A fixed volume of water sample is sealed and heated in a sample vial. The VOCs in the sample evaporate into the headspace of the vial. After a while, the VOC concentration between the liquid sample and the above headspace gas phase reach equilibrium. Subsequently, the VOC concentration in the headspace gas phase can be measured to determine the corresponding concentration in the liquid sample, given that the concentration in liquid is proportional to that in the gas phase. Headspace samplers provide an easy, reproducible, and clean way to extract and use the VOCs from drinking water for the following GC/MSD analysis. A GC/MSD platform usually uses a 30 to 60 m midpolar column for the VOC separation, prior to MSD identification and quantitation. The GC cycle time is typically longer than 20 minutes. The high-efficiency column, with narrower internal diameter and shorter length, can be used to accelerate the separation. With improved column resolution capability, the oven ramp can be increased accordingly to achieve fast analysis. Even if some coelution happens during the fast separation, with the aid of ion extraction capability in mass spectrometry for compound identification, an accurate qualification can still be made.

In this application note, VOCs in drinking water were analyzed using the 8697 headspace sampler, in tandem with the Intuvo 9000 GC and 5977B GC/MSD system. A high-efficiency source was used to compensate for the sensitivity loss caused by a high split ratio applied on the narrow-bore analytical column. The analysis speed was expedited by using a faster oven temperature program on the high-efficiency column. Three analytical methods were developed; one based on the MSD single ion monitoring (SIM) mode, and the other two based on the MSD scan mode. They focused on different sample concentration ranges. The VOCs tested include: halogenated hydrocarbon; benzene and its derivatives; and the gasoline additive, methyl tert-butyl ether (MTBE). The linearity, repeatability, and limit of quantitation (LOQ) for the targeted 64 VOCs were evaluated to show the system's excellent performance for VOC analysis.

Experimental

Chemicals and standards

All chemicals and standards were purchased from Anpel Laboratory Technologies (Shanghai) Inc. These included (A) a mixture of 60 VOCs in methanol at 1,000 mg/L; (B) internal calibration standards of toluene-d8, 4-bromofluorobenzene and 1,2-dichlorobenzene-d4 in methanol, at 2,000 mg/L; and (C) four single component standards in methanol, with concentrations varying from 100 to 1,000 mg/L.

Analytical grade sodium chloride (NaCl), was weighed and added to the aqueous calibration solutions and real water sample, to increase VOCs partitioning to the headspace, improving sensitivity.

Working solution

The VOC standards were mixed with the single component standards and diluted by methanol to 1 and 10 mg/L working solutions, containing 64 components. The internal standard (IS) stock solution was diluted to 5 and 100 mg/L using methanol, for later use.

Calibration standards and water sample preparation

The NaCl was weighed at 2 g and added to a 20 mL headspace vial, together with 10 mL of deionized water. Aliquots of VOCs and IS working solutions were spiked into the salt solution quickly, then the vials were capped immediately and shaken to mix the standard. The calibration standards, prepared at approximately 2, 4, 10, 20, 40, 100, and 200 µg/L, with internal standards of 50 µg/L, were analyzed in scan mode. The calibration standards, ranging from 0.1 to 20 µg/L (0.1, 0.2, 0.5, 1, 2, 5, 10, and 20), with 2 µg/L IS, were analyzed in SIM mode. Replicates of middle-level and low-level calibration standards in two sets of calibrants were used for repeatability and LOQ evaluation in scan and SIM modes.

The spiked deionized water samples with calibrants and IS solutions were used for recovery tests. The recovery tests were run at three concentration levels for both SIM and scan mode-based analytical methods.

For real-sample analysis, 10 mL of tap water was added to a 20 mL sample vial containing 2 g of salt, then spiked with IS solution. The vial was capped quickly for subsequent analysis using the scan mode-based method.

Instrumentation and analytical conditions

Each prepared solution was analyzed using the 8697 headspace sampler, in tandem with the Intuvo 9000 GC and 5977B GC/MSD system. Both helium (He) and H_2 were used as the carrier gas for scan mode-based method verification. Only He was used for SIM mode-based method verification. The headspace and GC conditions are shown in Table 1.

The Agilent MassHunter acquisition software version 10.0 was used for data collection. The Agilent MassHunter qualitative analysis software version B.08.00 and MassHunter quantitative analysis software version B.08.00 were used for data analysis.

Results and discussion

For the SIM mode-based method, He was used as a carrier gas. The scan mode-based method was verified using both H_2 and He as a carrier gas. A faster oven ramp program (oven program 2, as shown in Table 1) was applied in the scan mode-based method. This is because the MSD could generate a fast enough sampling rate in the applied mass scan range (35 to 300 Da). The faster temperature program was also tested in the SIM mode-based method, however, the MSD sampling rate under SIM mode was challenged. Thus, a slower oven program (oven program 1) was used in the SIM mode-based method. The dwell time for each ion in SIM mode was optimized between 10 and 15 ms, depending on the ion number in each time segment, to achieve fast enough acquisition for accurate and repeatable quantitative analysis.

Table 1. Analytical conditions of the Agilent 8697 headspace sampler, Agilent Intuvo 9000 GC, and Agilent 5977B GC/MSD system.

Agilent Intuvo 9000 GC and 5977B GC/MSD System with High-Efficiency Ion Source	
Parameters	Setpoints
Inlet Temperature	250 °C
Liner	Agilent Ultra Inert inlet liner, split, 4 mm inner diameter (p/n 5190-2295), glass wool removed
Carrier Gas	He for SIM mode; H_2 and He for scan mode
Column Flow	Constant flow rate SIM mode-based method: 1.0 mL/min (He) Scan mode-based method: 0.7 mL/min (H_2) and 1.0 mL/min (He)
Split Ratio	100:1
Oven Program 1 (SIM Mode-Based Method)	35 °C (1.82 min), 41.18 °C/min to 200 °C, 82.37 °C/min to 230 °C (3 min)
Oven Program 2 (Scan Mode-Based Method)	35 °C (1.5 min), 50 °C/min to 200 °C, 100 °C/min to 230 °C (3.5 min)
Column	Agilent J&W DB-624 Ultra Inert Intuvo GC column module, 20 m × 0.18 mm, 1 µm (p/n 121-1324-UI-INT)
MSD Transfer Line	220 °C
MS Source	250 °C
MS Quad	150 °C
Scan Range	35 to 300 Da
Scan Speed	6,250 u/s (n = 0)
Dwell Time for Ions in SIM Method	10 to 15 ms, depending on ion number in each time segment
Gain Factor	0.5
Drawout Plate	3 mm
Agilent 8697 Headspace Sampler Parameters	
8697 Loop Size	1 mL
Vial Pressurization Gas	N_2
HS Loop Temperature	80 °C
HS Oven Temperature	80 °C
HS Transfer Line Temperature	110 °C
Vial Equilibration Time	20 min
Vial Size	20 mL, PTFE/silicone septa (p/n 8010-0413)
Vial Shaking	Level 7, 136 shakes/min with acceleration of 530 cm/S^2
Vial Fill Mode	Default
Vial Fill Pressure	15 psi
Loop Fill Mode	Custom
Loop Ramp Rate	20 psi/min
Loop Final Pressure	4 psi
Loop Equilibration Time	0.1 min
Carrier Control Mode	GC carrier control
Vent After Extraction	On

The total ion chromatograms (TICs) of 1 µg/L calibration standard (acquired in SIM mode), and 20 µg/L standard (acquired in scan mode, with H_2 and He as carrier gas, respectively) are presented in Figures 1 to 3. The separation under the faster oven program took no more than 6 minutes, with an additional 2 minutes 30 seconds for column baking. The separation run under the slower oven program took approximately 7 minutes, plus another 2 minutes 30 seconds for column cleaning.

With He as carrier gas and using oven program 1, a total of 12 compound pairs could not be resolved during the chromatography separation. When using H_2 as the carrier gas and run with oven program 2, the same 12 compound
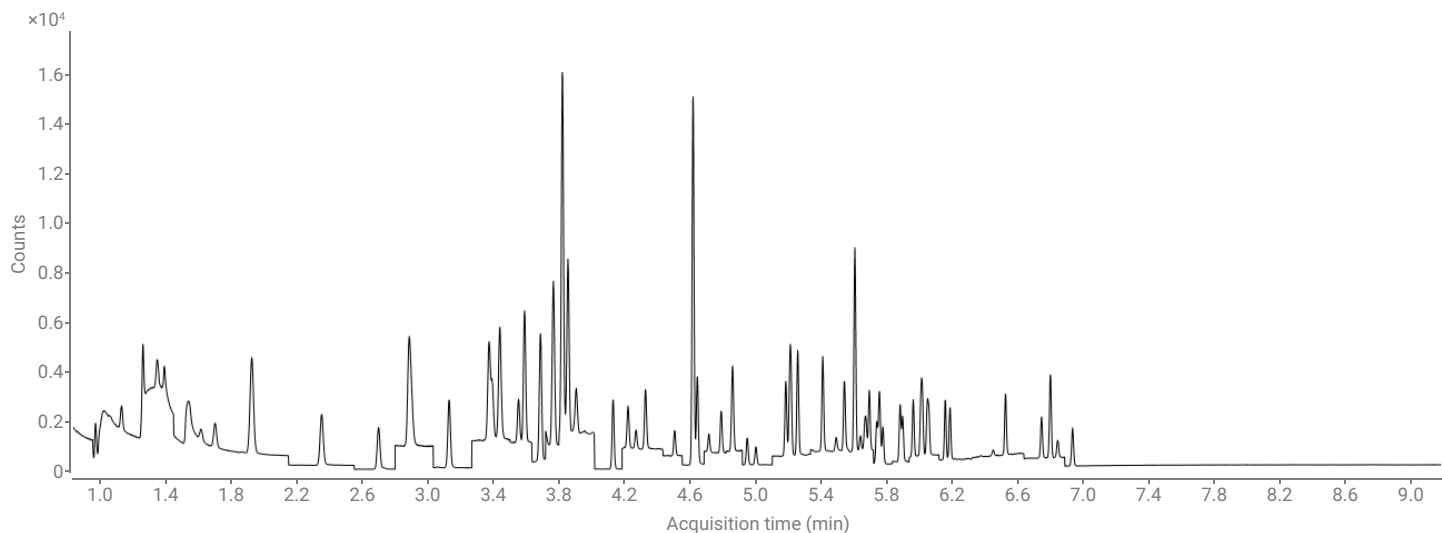
Figure 1. TIC SIM of 1 µg/L VOCs standard in 10 mL aqueous solution containing 20% (w/v) NaCl, using oven program 1 and He as carrier gas.
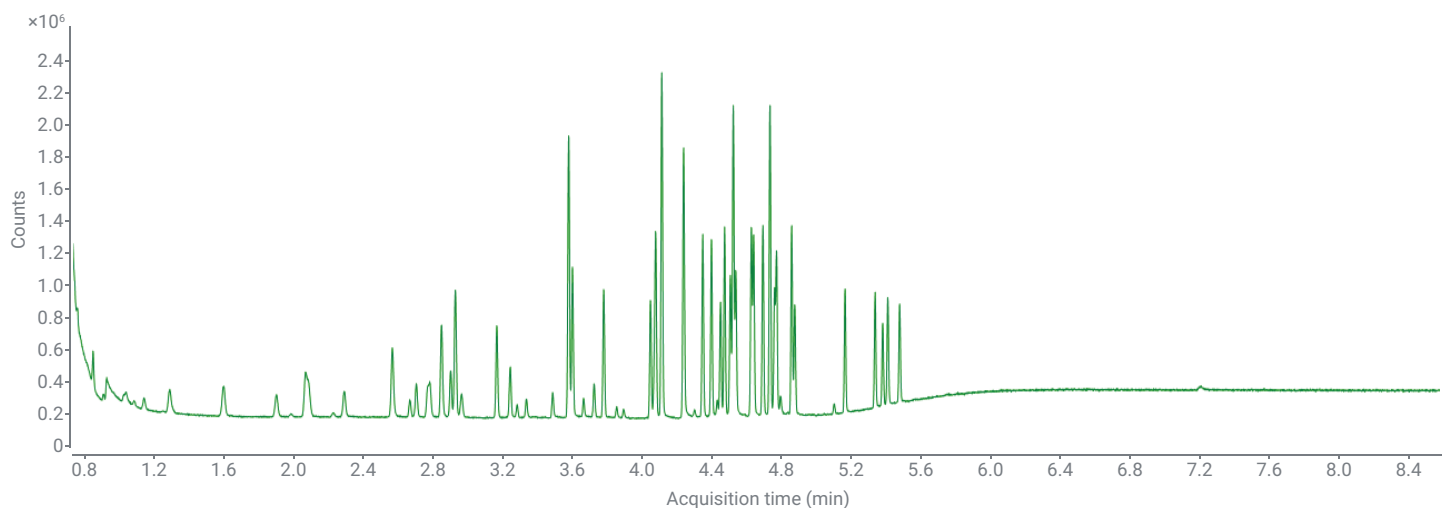

Figure 2. TIC of 20 µg/L VOCs standard in 10 mL aqueous solution containing 20% (w/v) NaCl, using oven program 2 and H_2 as carrier gas.
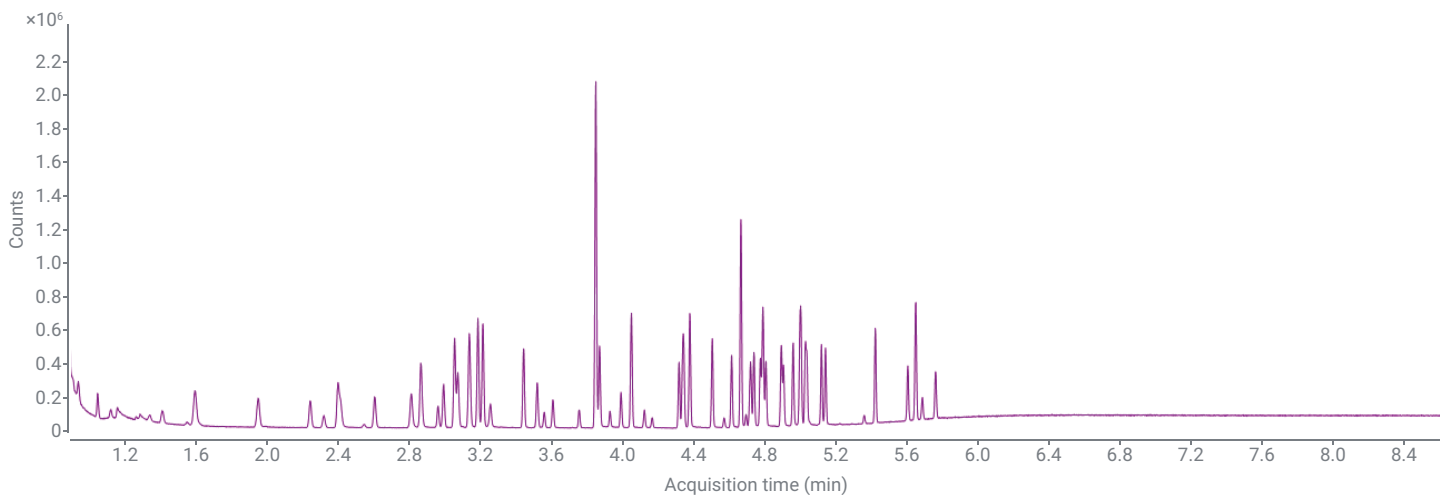
Figure 3. TIC of 20 µg/L VOCs standard in 10mL aqueous solution containing 20% (w/v) NaCl, using with oven program 2 and He as carrier gas.

pairs were also not resolved in the chromatography. These unresolved compounds could be identified and quantified based on their selected or extracted qualifier and quantifier ions at the MSD side. The additional resolving capability of MSD is one of the key reasons for fast VOC analysis on a high-efficiency column. The detailed retention time (RT) information for each compound is shown in Appendixes 1 to 3. (The coeluting compound pairs were labeled with the same number superscript in the Appendix 1 and 2)

The system repeatability in SIM and scan mode-based methods were evaluated based on the analyte absolute responses. Six replicates of 1 µg/L calibrants were analyzed in SIM mode. The response RSD% of 64 VOCs were in the range of 0.4% to 5.9% (Figure 4). The average RSD% was 1.7%, with two compounds' precision greater than 4.0%. For scan mode-based method with H_2 as carrier gas, seven replicates

of 10 µg/L calibrants gave the response precision from 0.5% to 7.2%, with an average RSD% of 2.0%. Four compounds had area precision greater than 4.0%. The response precision of six 20 µg/L replicates obtained by scan mode-based method with He as carrier gas ranged from 1.0% to 5.0%, with five components showing precision greater than 4.0%. The repeatability performance demonstrated excellent sampling and detection precision.
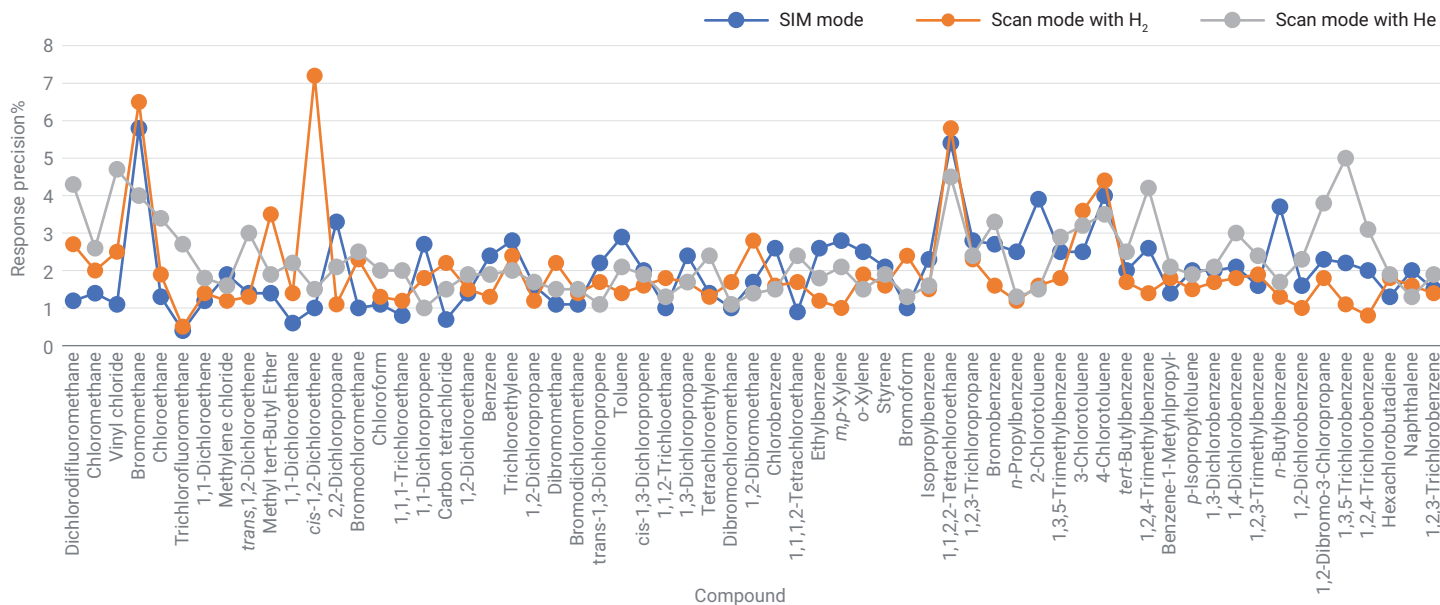

Figure 4. Area precision of calibration standards acquired in SIM and SCAN mode.

Method linearity was evaluated based on the relative response of each component to internal standard across the tested concentration range (i.e., 0.1 to 20 µg/L for the SIM mode-based method, and 2 to 200 µg/L for the scan mode-based method). Due to the different response factor of each compound, some compounds could not be detected at the lowest calibration level. The real linearity range of these compounds is noted in Appendixes 1 to 3.

All 64 VOCs acquired in SIM mode showed good linearity with the coefficients of determination R^2 greater than 0.994, and at an average of 0.998. In the scan mode-based method, when using H_2 as the carrier gas, all compounds had an R^2 greater than 0.995, and the average R^2 was 0.999. With He as the carrier gas, 21 compounds showed linearity with R^2 <0.99 in the tested concentration range. Based on the results, with the described system, it is recommended

that H_2 is used as the carrier gas for the scan mode-based method, if the linearity regression is the preferred quantitation method. In the future investigation, a 6 mm drawout plate will be tested to see if the linearity performance of scan mode-based method using He as the carrier gas can be improved.

Four representative compounds eluting at the early, middle, and late part of the TIC SIM and TIC scan chromatograms are shown in Figures 5 and 6.
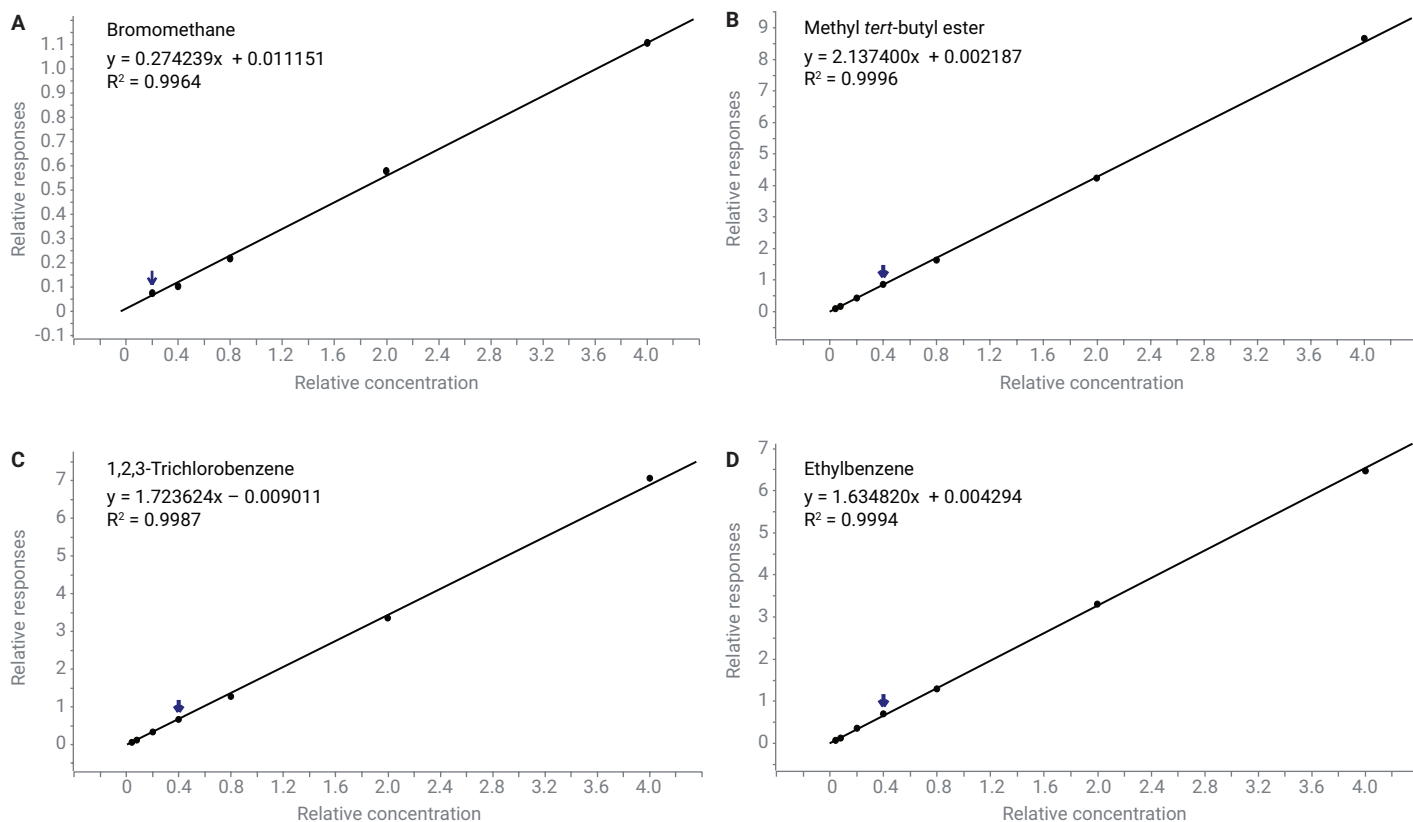

Figure 5. Calibration curves for representative compounds in scan mode using H_2 carrier gas: (A) bromomethane with R^2 0.9963; (B) methyl *tert*-butyl ether with R^2 0.9996; (C) 1,2,3-trichlorobenzene with R^2 0.9987; (D) ethylbenzene with R^2 0.9994. The concentrations ranged from 10 to 200 µg/L for bromomethane, 2 to 200 µg/L for other three compounds and the calibration curve was correlated with weight factor of 1/x.
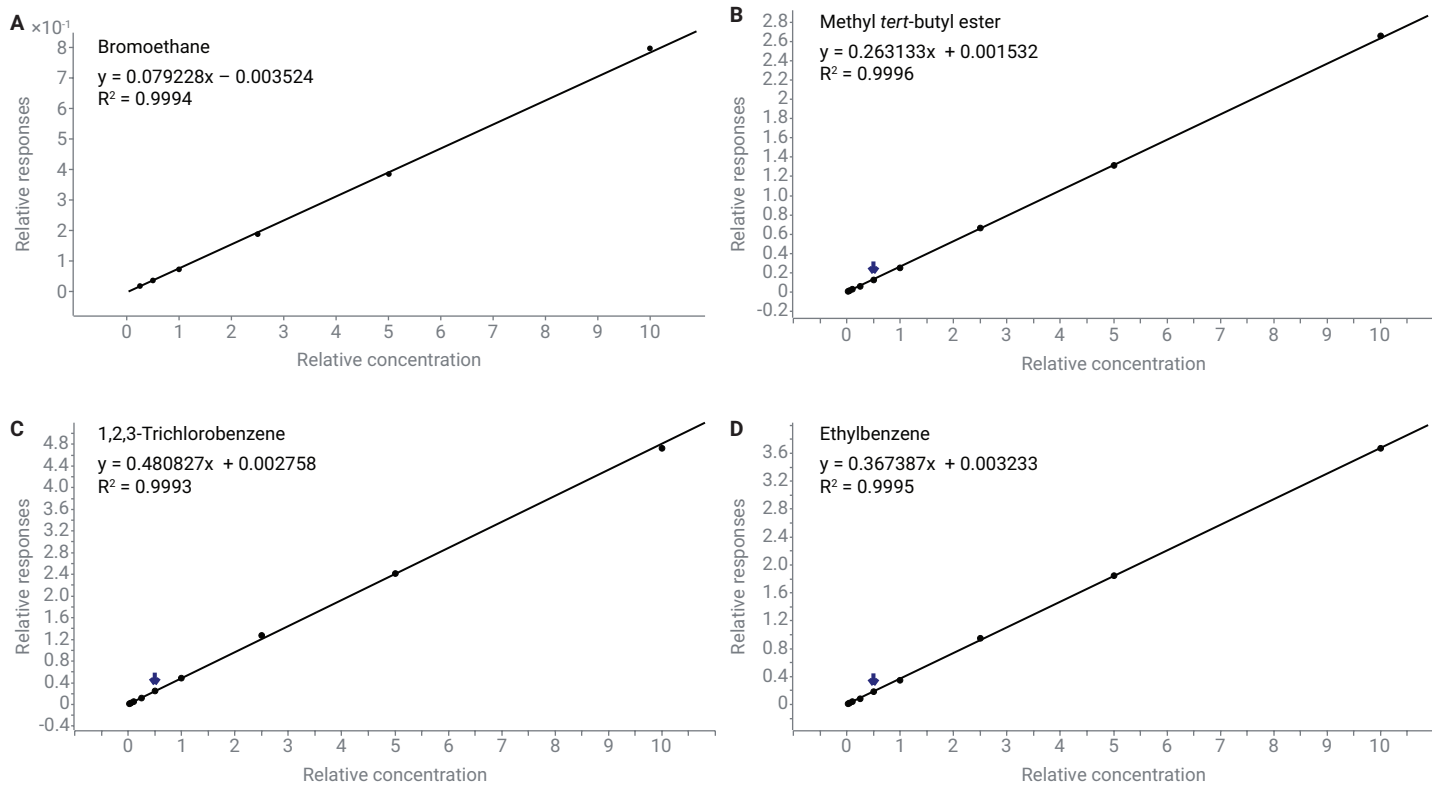
Figure 6. Calibration curves for representative compounds in SIM mode: (A) bromomethane with R^2 0.9994; (B) methyl *tert*-butyl ether with R^2 0.9995; (C) 1,2,3-trichlorobenzene with R^2 0.9993; (D) ethylbenzene with R^2 0.9994. The calibration curve was based on the concentration range of 500 ng/L to 20 µg/L for bromomethane, 100 ng/L to 20 µg/L for other three compounds and correlated with weight factor of 1/x.

The method recovery was assessed on deionized water spiked with different volumes of VOC working solution. The recovery rate in the scan mode-based method with H$_2$ as the carrier gas was tested at 4, 20, and 200 µg/L, with recovery performance ranging from 62 to 113% (Figure 7). The recovery performance in SIM mode was tested at three concentration levels of 100 ng/L, 1 µg/L, and 10 µg/L, and the experimental recovery ratio was from 72 to 116% (Figure 8). Bromomethane tended to show lower recovery than other components and it was the only compound with recovery below 70% in scan mode.

The LOQ for the 64 targeted VOCs were calculated based on the average signal-to-noise ratios (S/N) of seven replicates of 200 ng/L and 10 µg/L standards for SIM and scan mode-based methods, respectively. The LOQ obtained by SIM mode ranged from 0.033 to 1.51 µg/L (µg/L corresponding to µg/kg in a real water sample). The
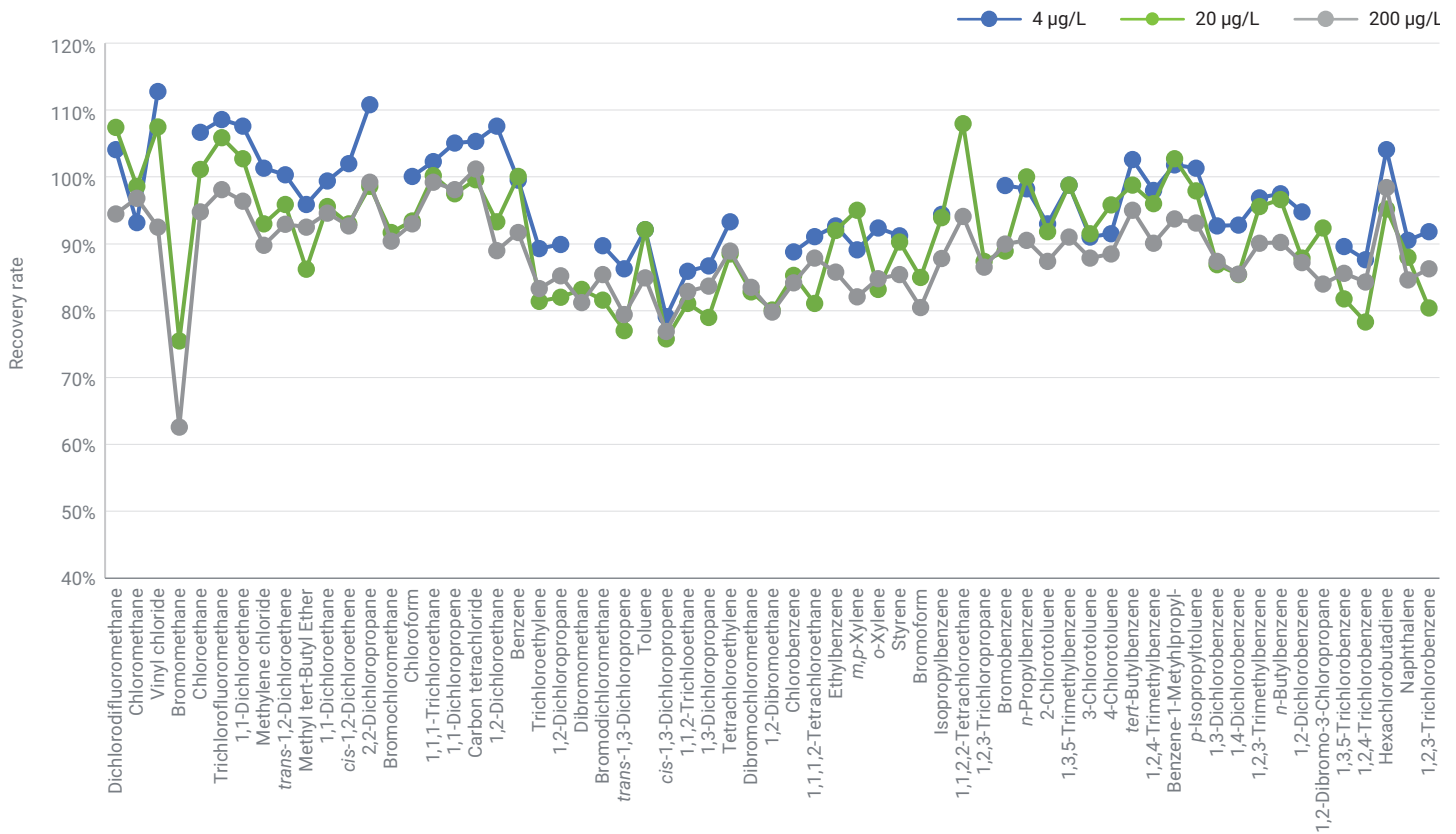

Figure 7. Recovery performance at three concentration levels: 4 (blue), 20 (green), and 200 µg/L (grey) using the scan mode-based method with H$_2$ as carrier gas, some compounds had no recovery results at 4 µg/L because the response at 4 µg/L was very small.
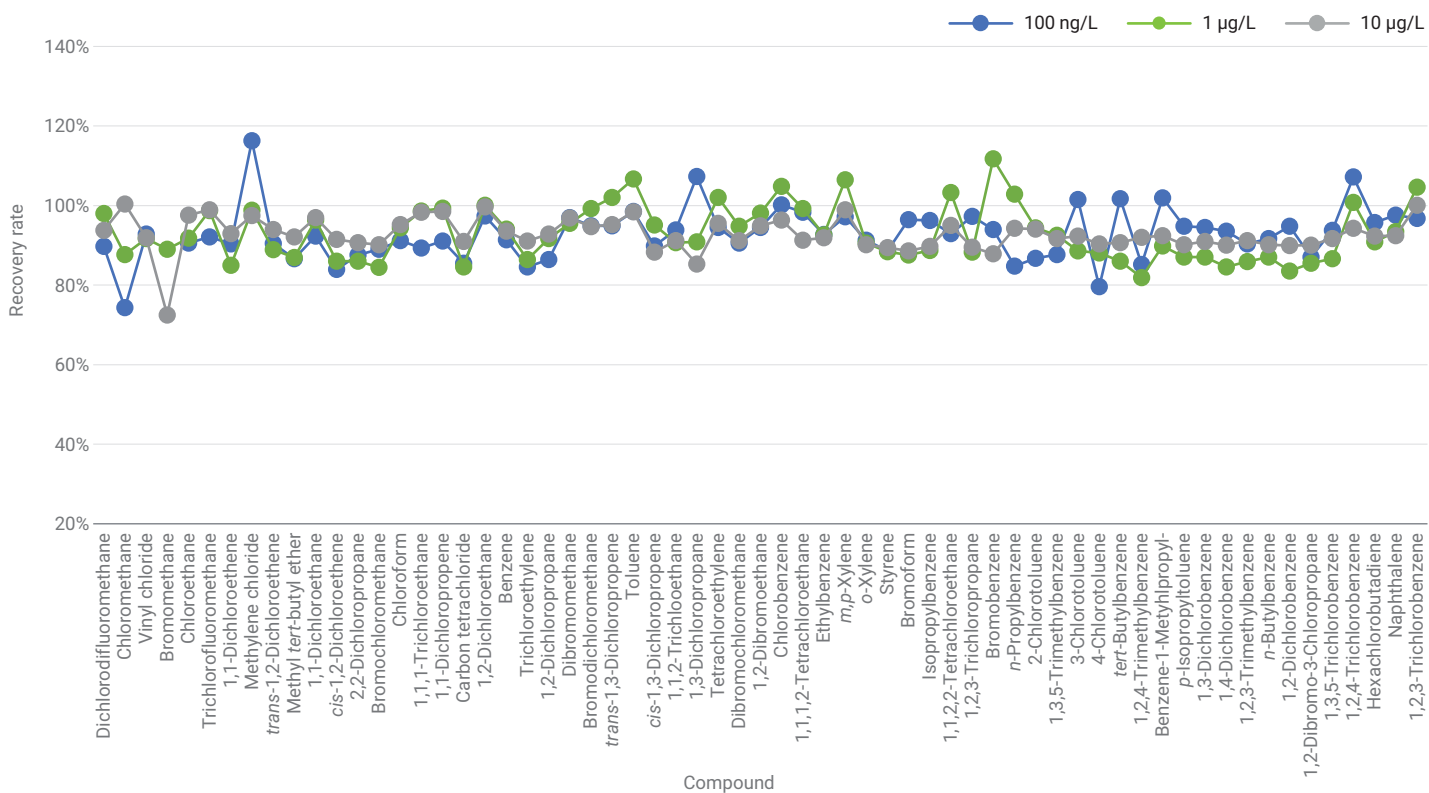
Figure 8. Recovery performance at three concentration levels: 100 ng/L (blue), 1 µg/L (green), and 10 µg/L (grey) using the SIM mode-based method. There was no recovery result for bromomethane at 100 ng/L.

LOQ obtained by scan mode with H_2 as the carrier gas was from 0.50 to 38.16 µg/L. The LOQ obtained by scan mode with He as the carrier gas ranged from 0.239 to 11.89 µg/L. The LOQs obtained with He as the carrier gas were better than those obtained with H_2 as the carrier gas. This is largely because, under the applied experimental conditions, the compound absolute response with the He carrier gas was higher and the background noise was lower, compared to that of the H_2 carrier gas. More details on the calculated LOQs are shown in Appendixes 1 to 3.

A real tap water sample was analyzed using the scan mode-based method with H_2 as carrier gas. The TIC is shown in Figure 9. The peak eluted at 2.71 minutes was chloroform, and quantitated as 8.97 µg/L. The peaks at 2.77, 2.91, 3.58 and 4.40 minutes came from IS standard. They were dibromofluromethane, 1,2-dichlorobenzene-d4, toluene-d8 and 4-bromofluorobenzene, respectively. Dibromofluromethane was not used as IS. It was included in the original IS

stock solution when it was purchased. The peak at 4.80 minutes was probably octene according to a NIST library search. Since this component was not contained in the original VOC calibration standard, no further effort was made to confirm its identity. However, this unexpected compound demonstrates one of the advantages of the MSD scan mode-based VOC analysis method: the identification of unknown compounds in the real sample can be made once their concentrations are higher than the MSD detection limit.
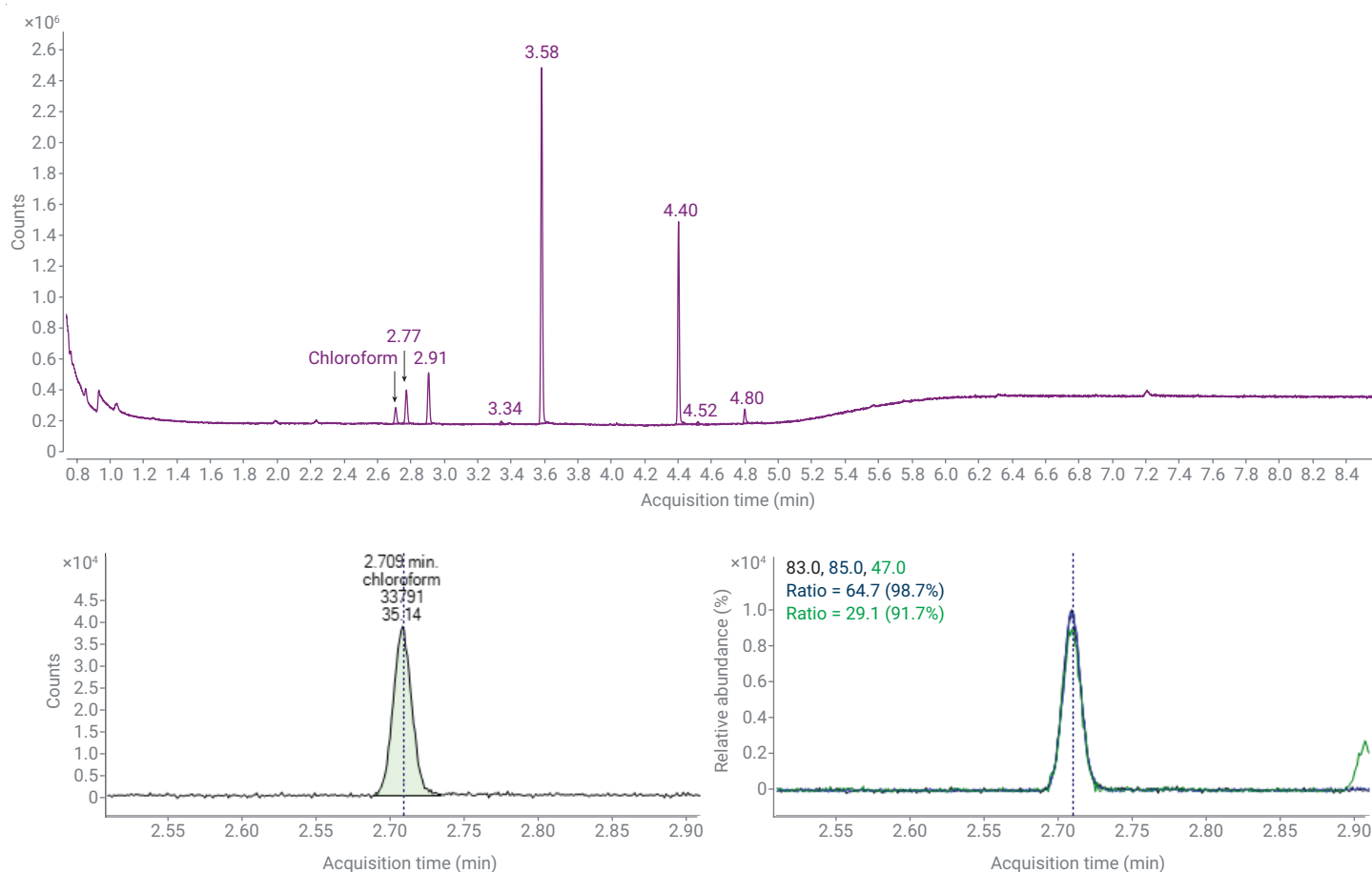

Figure 9. TIC of the tap water sample, with chloroform identified and quantified (using H_2 as the carrier gas).

Conclusion

This application note demonstrated fast VOC analysis of drinking water using the Agilent 8697 headspace sampler coupled with the Agilent Intuvo 9000 GC and 5977B GC/MSD system. The combined platform delivered good repeatability, which was demonstrated in the average response precision of 1.7% in SIM mode and 2.0% in scan mode for 64 VOCs. The linearity between 0.1 to 20 µg/L (SIM mode) and 2 to 200 µg/L (scan mode) were tested, with the average R^2 greater than 0.998. The method LOQ for SIM mode ranged from 0.033 to 1.51 µg/L, and from 0.50 to 38.16 µg/L for scan mode with H_2 as carrier gas, meeting the detection requirement for a headspace technique-based VOC analysis method. The GC cycle time for a single analysis was around 13 minutes (8.5 minutes for oven temperature program and 4 minutes for oven cooling). With such fast GC analysis and the sample overlapping capability of the Agilent 8697 headspace sampler, the lab throughput on real drinking water samples can be greatly improved.

References

1. 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**.

2. Gautschi, P.; Prest, H. Improved Volatiles Analysis Using Static Headspace, the Agilent 5977B GC/MSD, and a High-Efficiency Source, *Agilent Technologies application note*, publication number 5991-6539EN, **2016**.

Appendix

Table A1. Instrument linearity, LOQ, precision, and method recovery rate at applied operation conditions (SIM mode-based method with He as carrier gas).

Name	RT (min)	CF R^2	Response RSD%	LOQ (µg/kg)	Recovery Rate 100 ng/kg	1 µg/kg	10 µg/kg
Dichlorodifluoromethane	1.13	0.9996	1.2	0.156	89.7%	98.0%	93.8%
Chloromethane	1.264	0.9971 (0.2 to 20 µg/L)	1.4	0.391	74.3%	87.7%	100.4%
Vinyl Chloride	1.352	0.9946 (0.2 to 20 µg/L)	1.1	0.328	92.8%	91.7%	91.9%
Bromomethane	1.62	0.9994 (0.5 to 20 µg/L)	5.8	1.515	NA	89.0%	72.5%
Chloroethane	1.703	0.9992	1.3	0.475	90.6%	91.8%	97.6%
Trichlorofluoromethane	1.926	0.9996	0.4	0.052	92.1%	98.7%	98.9%
1,1-Dichloroethene	2.353	0.9989	1.2	0.077	90.4%	85.0%	92.9%
Methylene Chloride	2.7	0.9992	1.9	0.044	116.3%	98.8%	97.5%
trans-1,2-Dichloroethene[1]	2.885	0.9996 (0.2 to 20 µg/L)	1.4	0.242	90.5%	88.9%	94.0%
Methyl *tert*-Butyl Ether[1]	2.901	0.9997	1.4	0.226	86.6%	86.9%	92.1%
1,1-Dichloroethane	3.13	0.9994	0.6	0.057	92.3%	96.3%	97.0%
cis-1,2-Dichloroethene[2]	3.436	0.9996 (0.2 to 20 µg/L)	1.0	0.093	84.0%	86.0%	91.5%
2,2-Dichloropropane[2]	3.44	0.9998	3.3	0.212	87.6%	86.0%	90.7%
Bromochloromethane	3.553	0.9998	1	0.247	89.0%	84.5%	90.2%
Chloroform	3.59	0.9991	1.1	0.032	91.2%	94.4%	95.2%
1,1,1-Trichloroethane	3.685	0.9995	0.8	0.059	89.3%	98.6%	98.3%
1,1-Dichloropropene[3]	3.759	0.9993	2.7	0.218	91.1%	99.4%	98.5%
Carbon Tetrachloride[3]	3.766	0.9993	0.7	0.087	85.5%	84.6%	91.0%
1,2-Dichloroethane[4]	3.852	0.9994	1.4	0.066	97.4%	100.1%	99.7%
Benzene[4]	3.855	0.9998	2.4	0.066	91.4%	94.1%	93.6%
Trichloroethylene	4.128	0.9990	2.8	0.062	84.6%	86.4%	91.1%
1,2-Dichloropropane	4.22	0.9987	1.6	0.170	86.4%	91.7%	92.8%

Name	RT (min)	CF R^2	Response RSD%	LOQ (µg/kg)	Recovery Rate		
					100 ng/kg	1 µg/kg	10 µg/kg
Dibromomethane	4.267	0.9987	1.1	0.270	97.0%	95.5%	96.9%
Bromodichloromethane	4.325	0.9969	1.1	0.056	94.9%	99.2%	94.7%
trans-1,3-Dichloropropene	4.5	0.9992 (0.2 to 20 µg/L)	2.2	0.254	94.9%	102.0%	95.2%
Toluene	4.64	0.9996	2.9	0.039	98.5%	106.7%	98.4%
cis-1,3-Dichloropropene	4.71	0.9992 (0.2 to 20 µg/L)	2	0.426	89.8%	95.1%	88.3%
1,1,2-Trichlooethane	4.786	0.9983	1	0.145	93.9%	90.7%	91.2%
1,3-Dichloropropane[5]	4.854	0.9993	2.4	0.143	107.3%	90.9%	85.3%
Tetrachloroethylene[5]	4.857	0.9993	1.4	0.045	94.5%	102.0%	95.5%
Dibromochloromethane	4.944	0.9974	1	0.121	90.6%	94.8%	91.2%
1,2-Dibromoethane	4.999	0.9991	1.7	0.216	94.5%	98.1%	94.9%
Chlorobenzene	5.18	0.9994	2.6	0.054	100.2%	104.8%	96.4%
1,1,1,2-Tetrachloroethane[6]	5.205	0.9969	0.9	0.128	98.3%	99.2%	91.3%
Ethylbenzene[6]	5.212	0.9995	2.6	0.126	92.7%	92.6%	91.9%
m,p-Xylene[7]	5.25	0.9992	2.8	0.089	97.2%	106.5%	98.9%
o-Xylene[8]	5.404	0.9992	2.5	0.181	91.3%	90.6%	90.2%
Styrene[8]	5.406	0.9993	2.1	0.131	88.6%	88.4%	89.4%
Bromoform	5.488	0.9985	1	0.184	96.5%	87.6%	88.6%
Isopropylbenzene	5.537	0.9991	2.3	0.068	96.2%	88.7%	89.7%
1,1,2,2-Tetrachloroethane	5.634	0.9988 (0.2 to 20 µg/L)	5.4	0.293	92.9%	103.3%	95.0%
1,2,3-Trichloropropane[9]	5.662	0.9987 (0.2 to 20 µg/L)	2.8	0.328	97.3%	88.3%	89.5%
Bromobenzene[9]	5.67	0.9998	2.7	0.155	94.0%	111.7%	87.9%
n-Propylbenzene	5.69	0.9996	2.5	0.121	84.8%	102.9%	94.3%
2-Chlorotoluene	5.734	0.9982	3.9	0.167	86.7%	94.4%	94.1%
1,3,5-Trimethylbenzene[10]	5.749	0.9983	2.5	0.123	87.7%	92.5%	91.7%
3-Chlorotoluene[10]	5.75	0.9985	2.5	0.195	101.5%	88.6%	92.3%
4-Chlorotoluene	5.77	0.9976	4	0.209	79.6%	88.1%	90.4%
tert-Butylbenzene	5.879	0.9987	2	0.188	101.7%	86.0%	90.7%
1,2,4-Trimethylbenzene	5.892	0.9983	2.6	0.141	85.2%	81.9%	92.0%
Benzene-1-Metyhlpropyl-	5.96	0.9977	1.4	0.087	101.9%	89.8%	92.4%
p-Isopropyltoluene[11]	6.005	0.9969	2.0	0.173	94.8%	87.0%	90.1%
1,3-Dichlorobenzene[11]	6.012	0.9975	2.0	0.069	94.5%	87.1%	91.0%
1,4-Dichlorobenzene[12]	6.044	0.9976	2.1	0.086	93.6%	84.6%	90.0%
1,2,3-Trimethylbenzene[12]	6.053	0.9975	1.6	0.153	90.4%	85.9%	91.2%
n-Butylbenzene	6.152	0.9979	3.7	0.163	91.7%	87.0%	90.1%
1,2-Dichlorobenzene	6.181	0.9980	1.6	0.080	94.8%	83.5%	89.9%
1,2-Dibromo-3-Chloropropane	6.444	0.9992 (0.5 to 20 µg/L)	2.3	0.837	87.0%	85.5%	90.0%
1,3,5-Trichlorobenzene	6.52	0.9997	2.2	0.145	93.8%	86.6%	91.7%
1,2,4-Trichlorobenzene	6.739	0.9996	2	0.214	107.2%	100.8%	94.3%
Hexachlorobutadiene	6.793	0.9991	1.3	0.069	95.7%	90.9%	92.3%
Naphthalene	6.838	0.9995	2	0.149	97.6%	93.5%	92.4%
1,2,3-Trichlorobenzene	6.93	0.9993	1.5	0.232	96.8%	104.6%	100.1%

The compound with the same superscript coeluted.

Table A2. Instrument linearity, LOQ, precision, and method recovery rate at applied operation conditions (SCAN mode-based method with H_2 as carrier gas).

Name	RT (min)	CF R^2	Response RSD%	LOQ (µg/kg)	Recovery Rate 4 µg/kg	Recovery Rate 20 µg/kg	Recovery Rate 200 µg/kg
Dichlorodifluoromethane	0.770	0.9999	2.7	6.63	104.1%	107.4%	94.5%
Chloromethane	0.854	0.9996	2	4.38	93.2%	98.6%	96.8%
Vinyl Chloride	0.915	0.9992	2.5	5.21	112.8%	107.5%	92.5%
Bromomethane	1.089	0.9963 (10 to 200 µg/L)	6.5	34.60	NA	75.5%	62.6%
Chloroethane	1.144	0.9992	1.9	7.97	106.7%	101.1%	94.8%
Trichlorofluoromethane	1.292	0.9998	0.5	4.22	108.6%	105.9%	98.1%
1,1-Dichloroethene	1.598	0.9995	1.4	4.82	107.6%	102.7%	96.4%
Methylene Chloride	1.908	0.9997	1.2	2.81	101.3%	93.0%	89.8%
trans-1,2-Dichloroethene[1]	2.070	0.9995	1.3	4.33	100.3%	95.9%	92.9%
Methyl tert-Butyl Ether[1]	2.089	0.9996	3.5	4.25	95.9%	86.2%	92.5%
1,1-Dichloroethane	2.296	0.9997	1.4	3.41	99.4%	95.6%	94.6%
cis-1,2-Dichloroethene[2]	2.570	0.9997	7.2	9.71	102.0%	93.0%	92.7%
2,2-Dichloropropane[2]	2.570	0.9988	1.1	3.37	110.8%	98.6%	99.2%
Bromochloromethane	2.671	0.9994 (10 to 200 µg/L)	2.3	20.87	NA	91.7%	90.4%
Chloroform	2.706	0.9996	1.3	3.04	100.1%	93.4%	93.0%
1,1,1-Trichloroethane	2.784	0.9988	1.2	2.60	102.3%	100.2%	99.2%
1,1-Dichloropropene[3]	2.852	0.9993	1.8	3.79	105.1%	97.5%	98.1%
Carbon Tetrachloride[3]	2.852	0.9990	2.2	10.85	105.3%	99.6%	101.2%
1,2-Dichloroethane[4]	2.933	0.9994	1.5	1.64	107.6%	93.3%	89.0%
Benzene[4]	2.931	0.9997	1.3	2.78	99.5%	100.1%	91.7%
Trichloroethylene	3.166	0.9990	2.4	2.52	89.3%	81.4%	83.3%
1,2-Dichloropropane	3.244	0.9987 (4 to 200 µg/L)	1.2	4.29	89.9%	82.0%	85.2%
Dibromomethane	3.285	0.9995 (10 to 200 µg/L)	2.2	9.16	NA	83.2%	81.2%
Bromodichloromethane	3.337	0.9995	1.4	5.06	89.7%	81.6%	85.4%
trans-1,3-Dichloropropene	3.488	0.9991	1.7	5.23	86.3%	77.0%	79.4%
Toluene	3.602	0.9992	1.4	1.39	92.1%	92.1%	84.9%
cis-1,3-Dichloropropene	3.665	0.9991 (4 to 200 µg/L)	1.6	10.18	79.1%	75.8%	76.9%
1,1,2-Trichlooethane	3.726	0.9994 (4 to 200 µg/L)	1.8	6.98	85.9%	81.1%	82.9%
1,3-Dichloropropane[5]	3.779	0.9991	1.7	2.00	86.7%	79.0%	83.7%
Tetrachloroethylene[5]	3.780	0.9992	1.3	1.43	93.3%	88.5%	88.9%
Dibromochloromethane	3.854	0.9994 (10 to 200 µg/L)	1.7	15.67	NA	82.8%	83.5%
1,2-Dibromoethane	3.893	0.9995 (10 to 200 µg/L)	2.8	8.26	NA	80.1%	79.8%
Chlorobenzene	3.049	0.9996	1.6	0.50	88.8%	85.3%	84.2%
1,1,1,2-Tetrachloroethane[6]	4.071	0.9986	1.7	6.12	91.1%	81.1%	87.9%
Ethylbenzene[6]	4.077	0.9994	1.2	1.54	92.7%	92.0%	85.8%
m,p-Xylene[7]	4.113	0.9968	1	0.91	89.1%	95.0%	82.1%
o-Xylene[8]	4.236	0.9992	1.9	1.53	92.4%	83.2%	84.8%
Styrene[8]	4.240	0.9996	1.6	1.12	91.2%	90.3%	85.4%

Name	RT (min)	CF R^2	Response RSD%	LOQ (µg/kg)	Recovery Rate		
					4 µg/kg	20 µg/kg	200 µg/kg
Bromoform	4.301	0.9997 (10 to 200 µg/L)	2.4	12.00	NA	85.0%	80.5%
Isopropylbenzene	4.347	0.9996	1.5	0.72	94.4%	93.9%	87.8%
1,1,2,2-Tetrachloroethane	4.429	0.9986 (10 to 200 µg/L)	5.8	25.56	NA	108.0%	94.1%
1,2,3-Trichloropropane[9]	4.451	0.9988 (10 to 200 µg/L)	2.3	10.0	NA	87.4%	86.5%
Bromobenzene[9]	4.451	0.9991	1.6	8.35	98.7%	88.9%	90.0%
n-Propylbenzene	4.473	0.9995	1.2	1.10	98.2%	100.0%	90.5%
2-Chlorotoluene	4.505	0.9996	1.6	2.00	93.0%	91.8%	87.4%
1,3,5-Trimethylbenzene[10]	4.522	0.9997	1.8	1.02	98.8%	98.8%	91.0%
3-Chlorotoluene[10]	4.523	0.9982	3.6	1.96	91.0%	91.5%	87.9%
4-Chlorotoluene	4.537	0.9991	4.4	1.92	91.5%	95.8%	88.5%
tert-Butylbenzene	4.627	0.9995	1.7	2.33	102.6%	98.8%	95.0%
1,2,4-Trimethylbenzene	4.639	0.9998	1.4	1.16	98.0%	96.0%	90.1%
Benzene-1-Metyhlpropyl-	4.692	0.9998	1.8	0.89	101.8%	102.7%	93.7%
p-Isopropyltoluene[11]	4.733	0.9998	1.5	0.63	101.3%	97.9%	93.1%
1,3-Dichlorobenzene[11]	4.733	0.9995	1.7	0.94	92.7%	86.9%	87.4%
1,4-Dichlorobenzene[12]	4.761	0.9994	1.8	0.81	92.8%	85.4%	85.5%
1,2,3-Trimethylbenzene[12]	4.769	0.9996	1.9	1.14	96.9%	95.6%	90.1%
n-Butylbenzene	4.858	0.9997	1.3	1.48	97.5%	96.6%	90.2%
1,2-Dichlorobenzene	4.874	0.9995	1	0.78	94.8%	87.9%	87.2%
1,2-Dibromo-3-Chloropropane	5.103	0.9990 (10 to 200 µg/L)	1.8	38.16	NA	92.4%	84.0%
1,3,5-Trichlorobenzene	5.163	0.9982	1.1	0.96	89.6%	81.8%	85.6%
1,2,4-Trichlorobenzene	5.336	0.9986	0.8	1.07	87.6%	78.3%	84.3%
Hexachlorobutadiene	5.380	0.9957	1.8	1.03	104.1%	95.2%	98.4%
Naphthalene	5.410	0.9990	1.6	0.88	90.5%	88.0%	84.6%
1,2,3-Trichlorobenzene	5.478	0.9987	1.4	1.59	91.8%	80.4%	86.3%

The compound with the same superscript coeluted.

Table A3. Instrument linearity, LOQ and precision at applied operation conditions (SCAN mode-based method with He as carrier gas).

Name	RT (min)	CF R²	Response RSD%	LOQ (µg/kg)
Dichlorodifluoromethane	0.938	0.9991	4.3	0.733
Chloromethane	1.046	0.9996	2.6	2.332
Vinyl Chloride	1.122	0.9997	4.7	5.821
Bromomethane	1.335	0.9941 (4 to 200 µg/L)	4	11.891
Chloroethane	1.411	0.9998	3.4	4.777
Trichlorofluoromethane	1.593	0.9996	2.7	1.163
1,1-Dichloroethene	1.946	0.9958	1.8	2.092
Methylene Chloride	2.244	0.9997	1.6	3.174
trans-1,2-Dichloroethene	2.399	0.9972	3	1.860
Methyl tert-Butyl Ether	2.416	0.9784	1.9	1.537
1,1-Dichloroethane	2.606	0.9996	2.2	0.962
cis-1,2-Dichloroethene	2.863	0.9883	1.5	2.604
2,2-Dichloropropane	2.864	0.9969	2.1	3.231
Bromochloromethane	2.96	0.9992	2.5	5.000
Chloroform	2.991	0.9998	2	0.650
1,1,1-Trichloroethane	3.071	0.9993	2	0.616
1,1-Dichloropropene	3.136	0.9846	1	3.704
Carbon Tetrachloride	3.139	0.9995	1.5	1.392
1,2-Dichloroethane	3.213	0.9945	1.9	3.033
Benzene	3.213	0.9995	1.9	0.798
Trichloroethylene	3.442	0.9989	2	0.639
1,2-Dichloropropane	3.517	0.9986	1.7	2.000
Dibromoethane	3.559	0.9943	1.5	1.000
Bromodichloromethane	3.606	0.9934	1.5	0.517
trans-1,3-Dichloropropene	3.754	0.9984	1.1	3.535
Toluene	3.87	0.9959	2.1	0.558
cis-1,3-Dichloropropene	3.928	0.9985	1.9	4.697
1,1,2-Trichloroethane	3.987	0.9935	1.3	5.642
1,3-Dichloropropane	4.044	0.9987	1.7	2.709
Tetrachloroethylene	4.048	0.9980	2.4	0.239
Dibromochloromethane	4.125	0.9946	1.1	1.457
1,2-Dibromoethane	4.166	0.9966	1.4	2.857

Name	RT (min)	CF R²	Response RSD%	LOQ (µg/kg)
Chlorobenzene	4.317	0.9974	1.5	0.391
1,1,1,2-Tetrachloroethane	4.334	0.9958	2.4	0.460
Ethylbenzene	4.342	0.9699	1.8	1.258
m,p-Xylene	4.377	0.9624	2.1	0.792
o-ylene	4.502	0.9671	1.5	3.370
Styrene	4.503	0.9646	1.9	1.787
Bromoform	4.612	0.9944	1.3	4.138
Isopropylbenzene	4.683	0.9682	1.6	1.284
1,1,2,2-Tetrachloroethane	4.694	0.9526	4.5	4.434
1,2,3-Trichloropropane	4.713	0.9773	2.4	2.546
Bromobenzene	4.72	0.9981	3.3	1.602
n-Propylbenzene	4.736	0.9872	1.3	1.093
2-Chlorotoluene	4.775	0.9945	1.5	2.078
1,3,5-Trimethylbenzene	4.784	0.9760	2.9	1.683
3-Chlorotoluene	4.79	0.9925	3.2	1.749
4-Chlorotoluene	4.804	0.9951	3.5	2.058
tert-Butylbenzene	4.892	0.9873	2.5	3.213
1,2,4-Trimethylbenzene	4.904	0.9739	4.2	1.673
Benzene-1-Metyhlpropyl-	4.959	0.9888	2.1	1.204
p-Isopropyltoluene	4.995	0.9803	1.9	1.491
1,3-Dichlorobenzene	5.001	0.9959	2.1	0.784
1,4-Dichlorobenzene	5.027	0.9988	3	0.887
1,2,3-Trimethylbenzene	5.035	0.9844	2.4	1.336
n-Butylbenzene	5.117	0.9890	1.7	1.725
1,2-Dichlorobenzene	5.139	0.9980	2.3	0.927
1,2-Dibromo-3-Chloropropane	5.36	0.9896 (5 to 200 µg/L)	3.8	5.731
1,3,5-Trichlorobenzene	5.421	0.9959	5	0.345
1,2,4-Trichlorobenzene	5.603	0.9968	3.1	0.623
Hexachlorobutadiene	5.647	0.9806	1.9	0.462
Naphthalene	5.683	0.9871	1.3	2.180
1,2,3-Trichlorobenzene	5.758	0.9968	1.9	1.414

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