Application Note

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Analysis of 27 Halogenated Hydrocarbons and 11 Volatile Organic Compounds in Drinking Water

Using an Agilent 8697 headspace sampler and an Agilent 8860 GC system with ECD and FID

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Abstract

This application note describes the analysis of 27 halogenated hydrocarbons and 11 volatile organic compounds (VOCs) in drinking water using an Agilent 8697 headspace sampler coupled with an Agilent 8860 gas chromatography (GC) system. The targeted compounds were extracted in the headspace sampler and transferred to the 8860 GC for simultaneous separation on an Agilent J&W DB-Select 624 UI and an Agilent J&W DB-WAX UI column with corresponding detection by an electron capture detector (ECD) and a flame ionization detector (FID). Nitrogen was used as the carrier gas. A two-way splitter was applied to split the sample between the two analytical columns. The system performance in terms of repeatability, linearity, limit of quantitation (LOQ) and detection (LOD), and method recovery rate was evaluated. The response precisions of the 27 halogenated hydrocarbons by ECD were from 0.4 to 6.1%. The LODs were from 0.0001 to 0.30 µg/L. The response precisions of the 11 VOCs by FID were from 0.7 to 2.3%, and their LODs were from 0.085 to 1.96 µg/L. The recovery rate of all tested components ranged from 80 to 105%, which demonstrated the method effectiveness for sample extraction and analysis. The good linearity, with R^2 between 0.9974 and 0.9999 across the tested concentration range, guaranteed the quantitation accuracy of drinking water samples.

Introduction

Drinking water can be contaminated by chemicals, microbes, and radionuclides. Water quality varies from place to place but must meet the national or regional regulations. In China, the current drinking water quality regulation and measurement methods were published a decade ago.[1-2] With the advancements in contaminants research and analytical methods and the emergence of new pollutants in drinking water, the water quality regulation and analytical methods need to be revised accordingly. In March of 2022, the national standard GB 5749-2022[1] was officially released to replace the GB 5749-2006 version for drinking water quality regulation. New quality metrics were introduced and some existing key metrics were updated with more stringent regulation limits. GB5749-2022 will take effect on 1 April 2023.

GB/T 5750-202× is the analytical method assembly for measurement of those components regulated in GB 5749-2022. It was published for public comments in January of 2022 and is planned to be finalized by the end of 2022. In GB/T 5750.8-202× methods[2], headspace and gas chromatography techniques are recommended as one of several viable solutions for characterizing 27 halogenated hydrocarbons (halo-HCs) and 11 volatile organic compounds in the scope of the regulation. Method 4.3 in GB/T 5750.8-202× recommends that the halogenated hydrocarbons are separated on a 14% cyanopropylphenyl/86% dimethylpolysiloxane type column, with detection by an ECD due to the target compounds' high electron affinity.

Also, method 21.2 recommends that the 11 VOCs, mainly benzene and its derivatives, are separated on a WAX-type column and detected by an FID. With the above mentioned recommendations, an 8697 headspace sampler and 8860 GC system equipped with an FID, an ECD, and a two-way splitter was used to combine the analysis of halo-HCs and VOCs onto the same instrument platform.

In this work, the analysis of halo-HCs and VOCs were not run separately in two methods. The volatility of the 27 halo-HCs and 11 VOCs are similar, which makes the extraction of the two sets of compounds using the same extraction method possible. The extracted gas from the headspace sampler is transferred to the GC inlet and split equally to two analytical columns for separation and identification. Nitrogen was used as carrier gas for its safeness and economic benefits. The linearity, repeatability, recovery rate, LOD, and LOQ for the 36 compounds were evaluated to demonstrate the system's excellent performance for the target analysis.

Experimental

Stock solution

All chemicals and standards were purchased from Anpel Laboratory Technologies. Each purchased single component standard was weighed and mixed to form either a halo-HCs stock solution or a benzene derivatives (VOCs) stock solution. Sodium chloride (NaCl, analytical grade) was used to increase the method sensitivity due to the salting-out effect.

Calibration standards, recovery test, and real-world water sample preparation

The halo-HCs stock solution (or VOCs stock solution) was diluted and then used as working solution for calibration standard preparation.

The calibration standards were prepared as followed: 3.5 g NaCl was weighed and added to a 20 mL headspace vial, the salt was then dissolved with 10 mL deionized water. Aliquots of halo-HCs (or VOCs) working solutions were spiked into the salt solution quickly, then the vials were capped immediately and shaken to get a homogenous solution. The calibration standards were prepared at the concentrations shown in the Appendix in Tables 2 and 3.

The two sets of calibrants were used for method repeatability, LOD, and LOQ evaluation. Spiked tap water samples at different concentration levels were used for the recovery test.

Tap water (10 mL) and 3.5 g of salt were added to 20 mL sample vials for real-world sample analysis.

Instrumentation and analytical conditions

An Agilent 8697 headspace sampler and an Agilent 8860 GC equipped with an ECD and an FID was used for analysis. The instrument setup is shown in Figure 1. The headspace and GC conditions are shown in Table 1. Agilent OpenLab CDS, version 2.5 software was used for data acquisition and analysis.

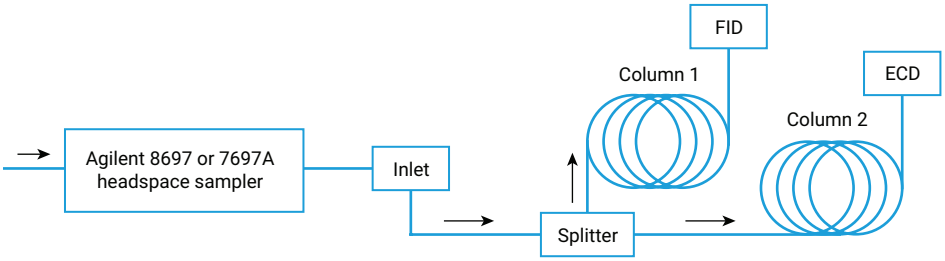

Figure 1. System configuration schematic for the analysis of halo-HCs and VOCs.

Table 1. Analytical conditions for the Agilent 8697 headspace sampler and the Agilent 8860 GC.

Agilent 8860 GC System Parameters	
Inlet Temperature	250 °C
Liner	Straight, deactivated, 2 mm id (p/n 5181-8818)
Carrier Gas	N_2
Column Flow	1.5 mL/min for oven program 1 2.0 mL/min for oven program 2
Split Ratio	6:1
Oven Program 1 (Simultaneous Analysis of Halo-HCs and VOCs)	40 °C (8 min), 10 °C/min to 90 °C (8 min), 8 °C/min to 115 °C, 25 °C/min to 240 °C (7 min)
Oven Program 2 (Analysis of VOCs Only)	40 °C, 5 °C/min to 45 °C (2.5 min), 15 °C/min to 90 °C (2 min), 20 °C/min to 150 °C (1 min)
Compact Splitter	p/n G3181-60500
Column 1	Agilent J&W DB-WAX UI, 30 m × 0.32 mm, 0.25 µm (p/n 123-7032UI)
Column 2	Agilent J&W DB-Select 624 UI, 30 m × 0.32 mm, 1.8 µm (p/n 123-0334UI)
ECD	260 °C
ECD Make Up Gas	N_2, 30 mL/min
FID	260 °C
FID Fuel Gas	H_2, 30 mL/min
FID Make Up	N_2, 25 mL/min
FID Oxidizer	Air, 400 mL/min
Agilent 8697 Headspace Sampler Parameters	
Loop Size	1 mL
Vial Pressurization Gas	N_2
HS Loop Temperature	70 °C
HS Oven Temperature	80 °C
HS Transfer Line Temperature	90 °C
Vial Equilibration Time	15 min
Vial Size	20 mL, PTFE/silicone septa (p/n 8010-0413)
Vial Shaking	Level 8, 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	2 psi
Loop Equilibration Time	0.1 min
Carrier Control Mode	GC carrier control
Vent After Extraction	On

Results and discussion

There are two GC oven programs developed in this analytical solution. Oven program 1 is intended for simultaneous analysis of halo-HC and VOCs, and takes approximately 30 minutes. If the 11 VOCs are the only target compounds, then oven program 2 can be used to increase the analysis speed by 50%. The oven program 1 was optimized and verified on two J&W DB-Select 624 UI columns from different batches. All 27 halo-HCs can be resolved well on a 6% cyanopropylphenyl with 94% dimethylpolysiloxane stationary phase under the applied conditions.

The chromatograms of 27 halo-HCs and 11 VOCs at calibration level 2 using oven program 1 are shown in Figures 2 and 3. The chromatogram of 11 VOCs obtained using oven program 2 is shown in Figure 4. Peak identification is shown in the Appendix Tables 4 and 5 according to their elution order.

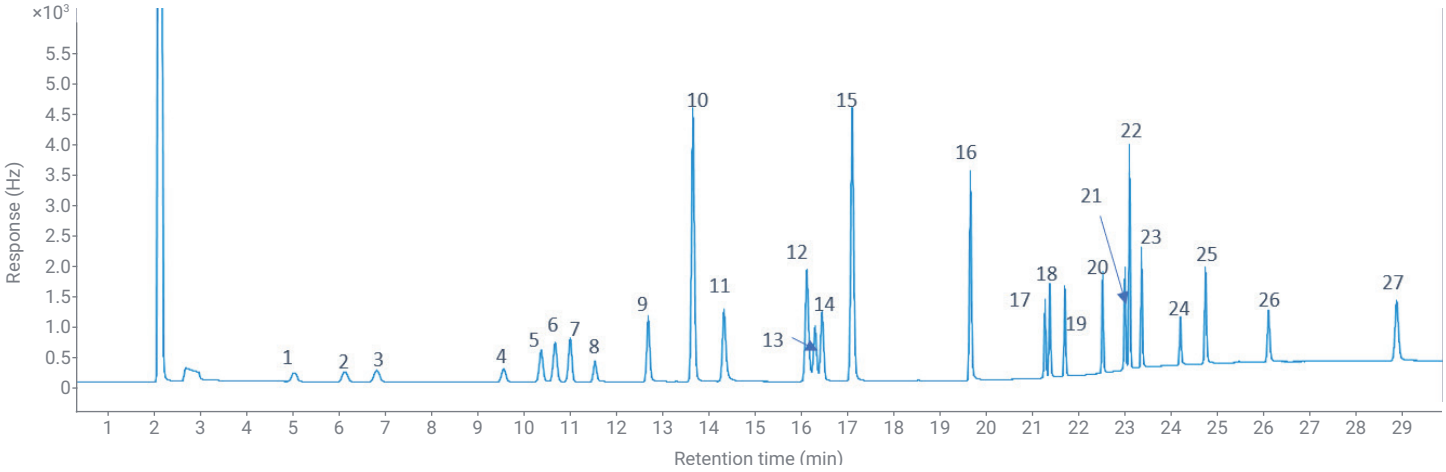

Figure 2. Chromatogram of 27 halogenated hydrocarbons (level 2) by ECD, obtained using oven program 1.

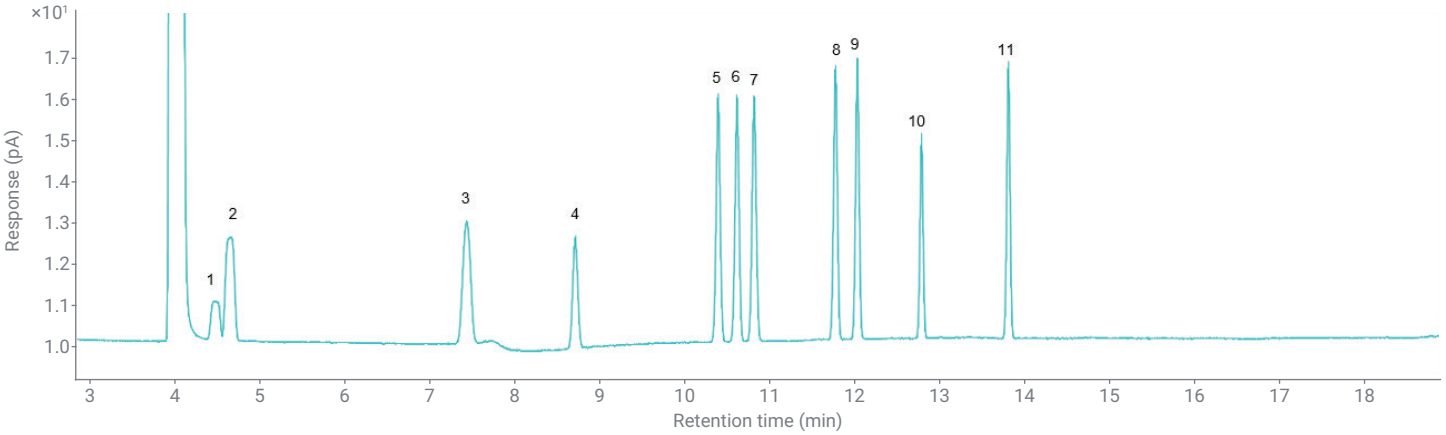

Figure 3. Chromatogram of 11 VOCs (mainly benzene and its derivatives, level 2) by FID, obtained using oven program 1.

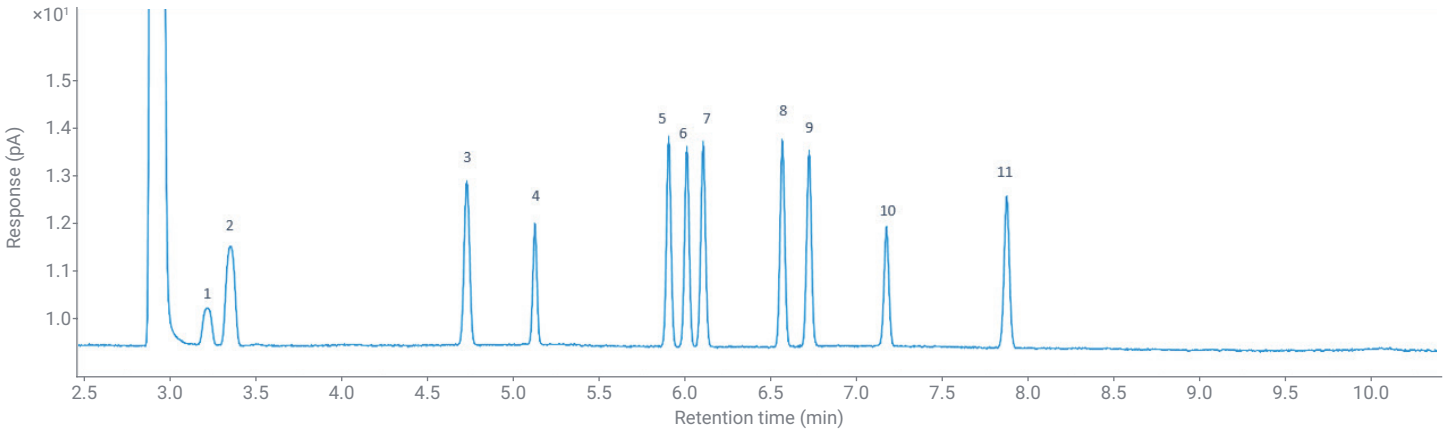

Figure 4. Chromatogram of 11 VOCs (mainly benzene and its derivatives, level 2) by FID, obtained using oven program 2.

In this work, the calibration solutions of halo-HCs and VOCs were prepared separately because the latter was also used to assess the effectiveness of oven program 2 for the analysis of the 11 VOCs only. The calibration curves of the two sets of compounds were not developed by analyzing their mixture in one headspace vial because the analyte concentration in the mixed calibrant would have been reduced. If all target compounds are prepared in one calibration solution initially, according to the concentration range required in methods 4.3 and 21.2, the two sets of calibration curves can be developed simultaneously on two analysis channels by analyzing the same calibrant.

The system response repeatability was evaluated at three concentration levels (L1, L3, and L5). Six replicates of each level were analyzed. The response %RSD of the 27 halo-HCs were in the range of 0.4 to 6.1%. The response precisions of the 11 VOCs were from 0.7 to 2.3%. This performance demonstrated excellent sampling and detection repeatability.

Method linearity was evaluated at six calibration levels as recommended in GB/T 5750.8-202× method 4.3 and method 21.2. The halo-HCs showed good linearity with the coefficients of determination (R^2) from 0.9974 to 0.9999. The 11 VOCs had R^2 values better than 0.9994. Linearity curves of four key regulated disinfection products, chloroform, chlorodibromomethane, dichlorobromomethane, and tribromomethane are shown with good R^2 values (>0.999) in Figure 5.

The method recovery was assessed with tap water spiked at three concentration levels (L1, L3, and L5). The recovery of halo-HCs was within 80.5 to 105% (Figure 6).

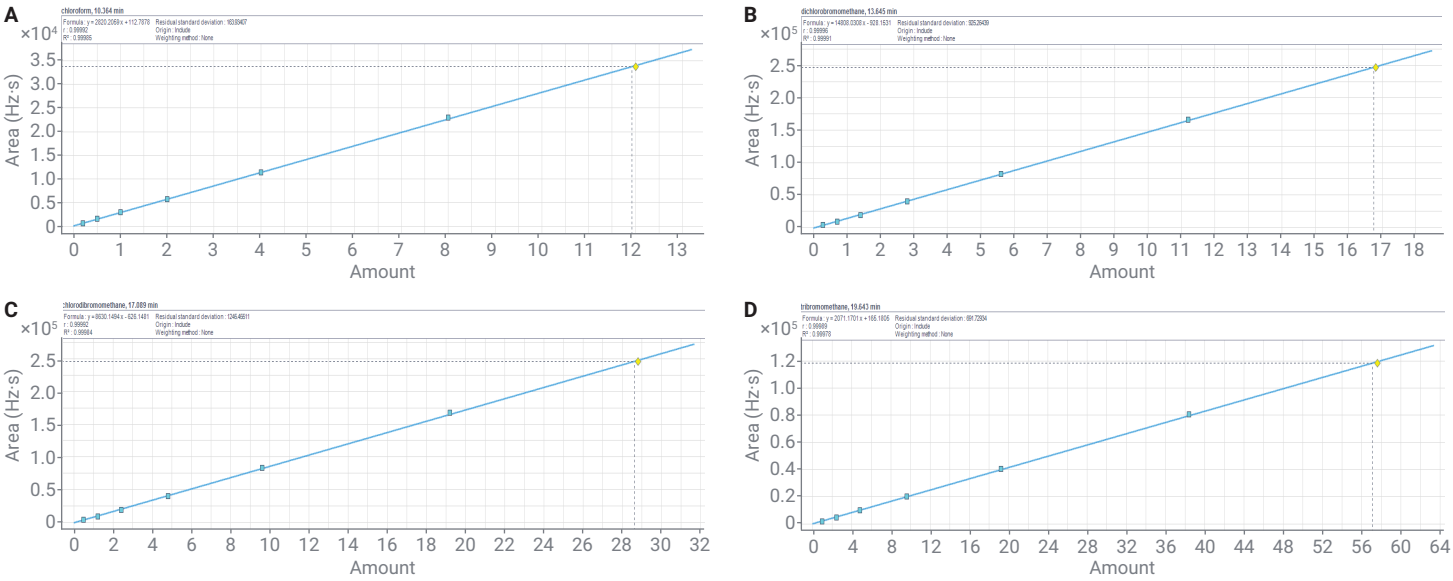

Figure 5. Calibration curves for four key compounds: (A) chloroform with R^2 0.9998; (B) dichlorobromomethane with R^2 0.9999; (C) chlorodibromomethane with R^2 0.9998; (D) tribromomethane with R^2 0.9997.

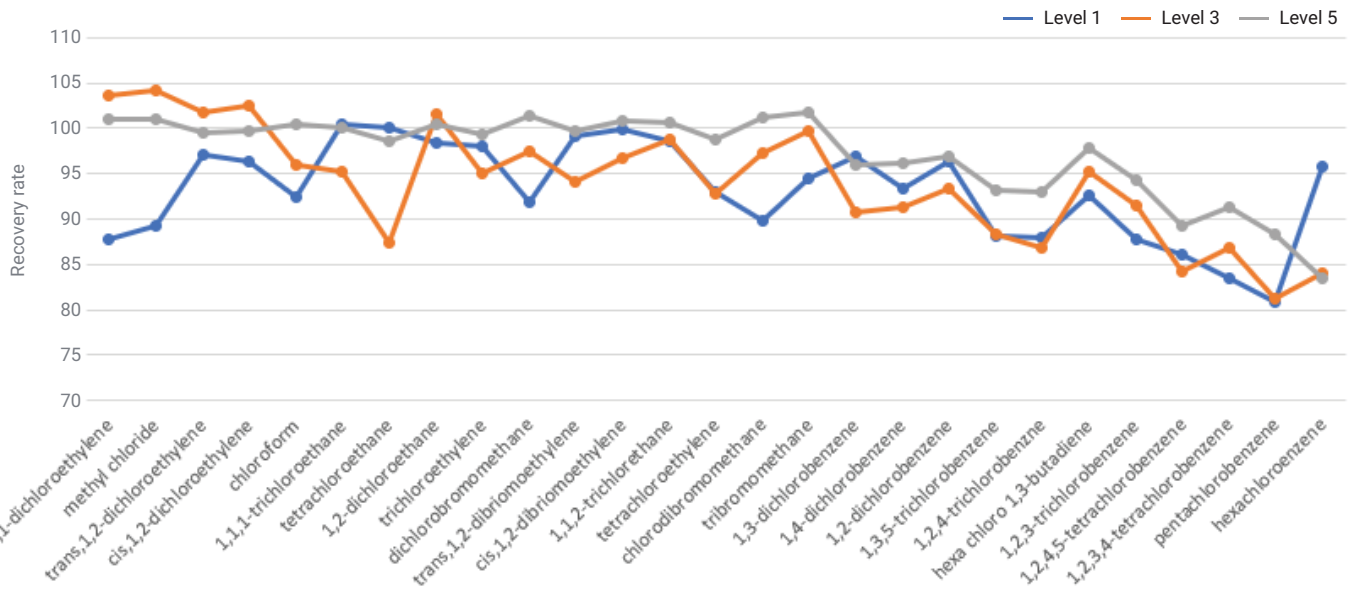

Figure 6. Recovery performance for 27 halogenated hydrocarbons at three calibration levels: L1 (blue), L3 (orange), and L5 (grey).

The recovery of VOCs was from 80.9 to 102% (Figure 7). The recovery rate results were comparable with the reference results in newly published GB/T 5750.8 methods.

The LOD and LOQ for the 36 target compounds were calculated at signal-to-noise ratio of 3:1 and 10:1 based on chromatograms of level 1 calibrants on the ECD and FID channels. The LOQ of halo-HCs ranged from 0.0004 to 1.03 µg/L (µg/L corresponding to µg/kg in a real water sample). The LOD of halo-HCs were from 0.0001 to 0.3091 µg/L. The LOQ and LOD of the 11 VOCs was from 0.28 to 6.52 µg/L and 0.085 to 1.96 µg/L.

The detailed test results, including linearity, LOD, LOQ, and repeatability are shown in Appendix Tables 4 and 5.

A tap water sample was analyzed, and the chromatogram is shown in Figure 8. The peak eluting at 10.364 minutes was chloroform and quantitated as 0.835 µg/L. The peaks at 13.647 and 17.092 minutes are identified by retention time as dichlorobromomethane (0.536 µg/L) and chlorodibromomethane (0.293 µg/L). The test results of the tap water show that the found compounds were detected below the regulation limits of 0.06 mg/L, 0.1 mg/L, and 0.06 mg/L respectively.

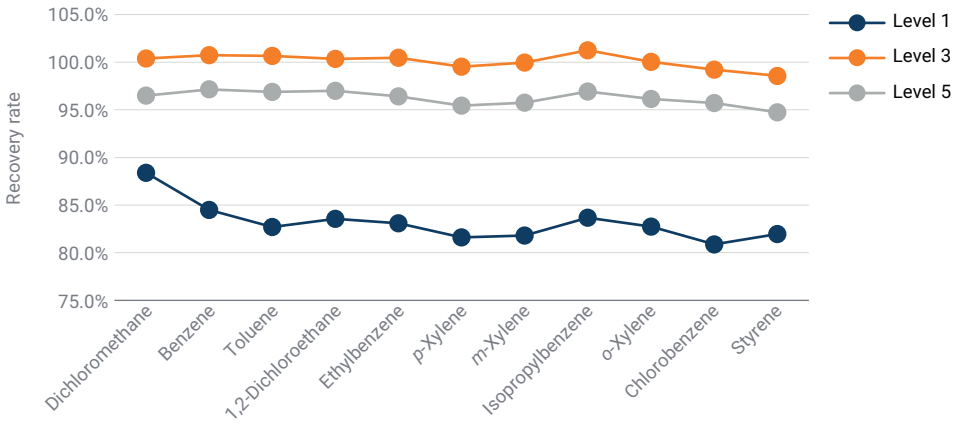

Figure 7. Recovery performance for 11 VOCs at three calibration concentration levels: L1 (blue), L3 (orange), and L5 (grey).

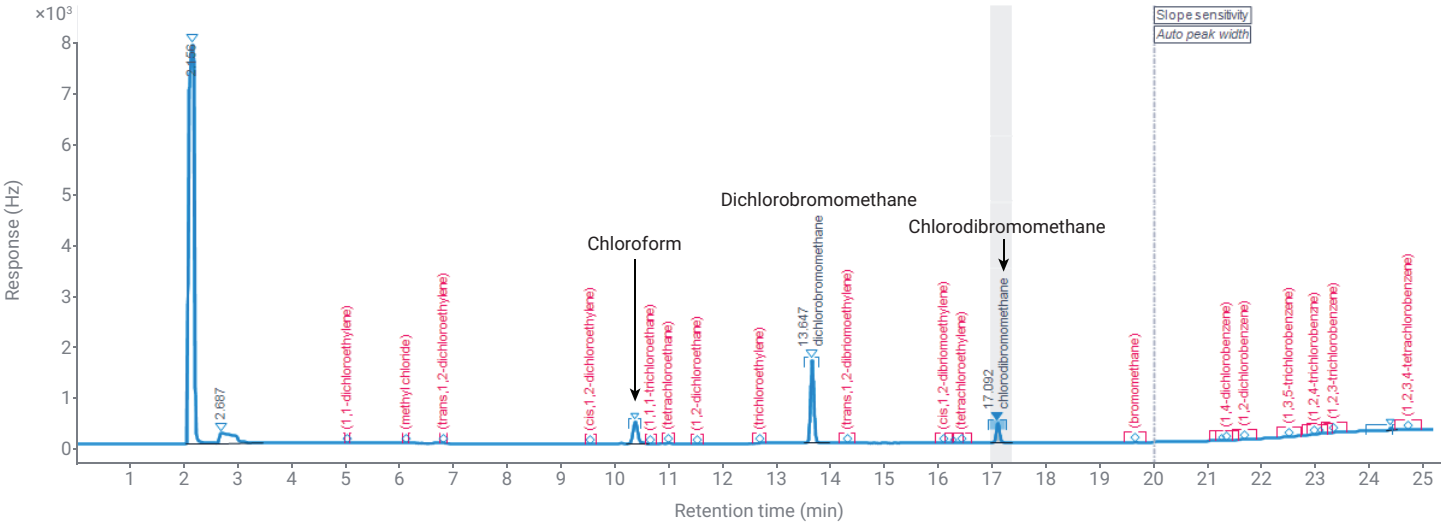

Figure 8. Chromatogram of the tap water sample on the ECD channel.

Conclusion

This application note demonstrated the analysis of 27 halogenated hydrocarbons and 11 VOCs in drinking water using an Agilent 8697 headspace sampler coupled with an Agilent 8860 GC/ECD/FID system. The combined platform delivered good repeatability, which was demonstrated with an average response precision of 1.7% on the ECD channel and 1.4% on the FID channel. The linearity was tested, and the average R^2 was greater than 0.999. The method LOQ for halo-HCs was from 0.0004 to 1.03 µg/L, and from 0.28 to 6.52 µg/L for the VOCs. The LODs for halo-HCs and VOCs were 0.0001 to 0.3091 µg/L and 0.085 to 1.96 µg/L respectively. These results met the regulation limits measurement requirement specified in GB 5749-2022, with method performance equal to or exceeding the reference performance shown in GB/T 5750.8-202× method 4.3 and 21.2.

References

1. GB 5749-2022, Standards for Drinking Water Quality.
2. GB/T 5750.8-202×, Standard Examination Methods for Drinking Water—Part 8: Organic indices.
3. Zhang, Y. Determination of Halogenated Hydrocarbons, Benzene, and Derivatives in Drinking Water with the Agilent 8697 Headspace Sampler and Agilent 8890 GC System. *Agilent Technologies application note*, publication number 5994-5238EN, **2022**.

Appendix

Table 2. Linearity range for 27 halogenated hydrocarbons.

Compounds	Working Solution (mg/L)	Calibrants (µg/L)					
		L1	L2	L3	L4	L5	L6
1,1-Dichloroethylene	4.84	2.420	4.840	9.680	19.360	38.720	58.080
Dichloromethane	35.52	17.760	35.520	71.040	142.080	284.160	426.240
trans-1,2-Dichloroethylene	48.96	24.480	48.960	97.920	195.840	391.680	587.520
cis-1,2-Dichloroethylene	71.2	35.600	71.200	142.400	284.800	569.600	854.400
Chloroform	0.904	0.452	0.904	1.808	3.616	7.232	10.848
1,1,1-Trichloroethane	0.416	0.208	0.416	0.832	1.664	3.328	4.992
Carbon Tetrachloride	0.1272	0.064	0.127	0.254	0.509	1.018	1.526
1,2-Dichloroethane	53.76	26.880	53.760	107.520	215.040	430.080	645.120
Trichloroethylene	1.008	0.504	1.008	2.016	4.032	8.064	12.096
Dichlorobromomethane	1.208	0.604	1.208	2.416	4.832	9.664	14.496
trans-1,2-Dibromoethylene/ *cis*-1,2-Dibromoethylene	3.632	1.816	3.632	7.264	14.528	29.056	43.584
1,1,2-Trichloroethane	0.276	0.138	0.276	0.552	1.104	2.208	3.312
Tetrachloroethylene	14.08	7.040	14.080	28.160	56.320	112.640	168.960
Chlorodibromomethane	2.256	1.128	2.256	4.512	9.024	18.048	27.072
Tribromomethane	4.512	2.256	4.512	9.024	18.048	36.096	54.144
1,3-Dichlorobenzene	12.16	6.080	12.160	24.320	48.640	97.280	145.920
1,4-Dichlorobenzene	25.68	12.840	25.680	51.360	102.720	205.440	308.160
1,2-Dichlorobenzene	14.96	7.480	14.960	29.920	59.840	119.680	179.520
1,3,5-Trichlorobenzene	1.584	0.792	1.584	3.168	6.336	12.672	19.008
1,2,4-Trichlorobenzene	2.36	1.180	2.360	4.720	9.440	18.880	28.320
Hexachlorobutadiene	0.2144	0.107	0.214	0.429	0.858	1.715	2.573
1,2,3-Trichlorobenzene	1.384	0.692	1.384	2.768	5.536	11.072	16.608
1,2,4,5-Tetrachlorobenzene	0.896	0.448	0.896	1.792	3.584	7.168	10.752
1,2,3,4-Tetrachlorobenzene	0.824	0.412	0.824	1.648	3.296	6.592	9.888
Pentachlorobenzene	0.3912	0.196	0.391	0.782	1.565	3.130	4.694
Hexachlorobenzene	0.5928	0.296	0.593	1.186	2.371	4.742	7.114

Table 3. Linearity range for 11 VOCs.

Compounds	Working Solution (mg/L)	Calibrants (µg/L)					
		L1	L2	L3	L4	L5	L6
Dichloromethane	40	20	40	80	160	240	320
Benzene	10	5	10	20	40	60	80
Toluene	10	5	10	20	40	60	80
1,2-Dichloroethane	40	20	40	80	160	240	320
Ethylbenzene	10	5	10	20	40	60	80
p-Xylene	10	5	10	20	40	60	80
m-Xylene	10	5	10	20	40	60	80
Isopropylbenzene	10	5	10	20	40	60	80
o-Xylene	10	5	10	20	40	60	80
Chlorobenzene	10	5	10	20	40	60	80
Styrene	10	5	10	20	40	60	80

Table 4. Test results of 27 halo-HCs, including linearity, LOD, LOQ, and repeatability.

Peak No.	Name	RT (min)	CF R^2	LOD (µg/kg)	LOQ (µg/kg)	Repeatability (%RSD)		
						Level 1	Level 3	Level 5
1	1,1-Dichloroethylene	5.032	0.99897	0.0350	0.1166	0.596	0.917	0.434
2	Methyl chloride	6.124	0.99879	0.1119	0.3730	0.638	0.831	0.454
3	*trans*-1,2-Dichloroethylene	6.813	0.99921	0.2574	0.8580	1.08	1.241	0.782
4	*cis*-1,2-Dichloroethylene	9.553	0.99941	0.3091	1.0302	0.727	0.932	0.458
5	Chloroform	10.361	0.99985	0.0017	0.0056	0.849	1.031	0.644
6	1,1,1-Trichloroethane	10.663	0.99989	0.0008	0.0028	0.912	0.828	0.772
7	Tetrachloroethane	10.989	0.99864	0.0004	0.0014	1.125	1.164	0.701
8	1,2-Dichloroethane	11.526	0.99959	0.1971	0.6571	0.714	0.803	0.511
9	Trichloroethylene	12.675	0.99987	0.0010	0.0035	0.971	1.174	0.543
10	Dichlorobromomethane	13.642	0.99991	0.0005	0.0018	0.776	1.119	0.993
11	*trans*-1,2-Dibromoethylene	14.315	0.99983	0.0019	0.0063	1.068	1.206	0.427
12	*cis*-1,2-Dibromoethylene	16.105	0.99991	0.0012	0.0040	0.817	0.994	0.881
13	1,1,2-Trichloroethane	16.281	0.99987	0.0150	0.0499	0.656	0.959	0.912
14	Tetrachloroethylene	16.434	0.99984	0.0004	0.0014	1.133	1.279	0.741
15	Chlorodibromomethane	17.085	0.99984	0.0010	0.0032	0.772	1.195	0.879
16	Tribromomethane	19.641	0.99978	0.0016	0.0055	0.753	0.877	0.891
17	1,3-Dichlorobenzene	21.255	0.99972	0.0116	0.0388	1.804	1.77	1.018
18	1,4-Dichlorobenzene	21.356	0.99964	0.0197	0.0656	1.772	1.957	1.138
19	1,2-Dichlorobenzene	21.681	0.99987	0.0109	0.0365	1.299	1.607	0.609
20	1,3,5-Trichlorobenzene	22.498	0.99909	0.0011	0.0035	3.349	2.969	2.333
21	1,2,4-Trichlorobenzene	22.981	0.99918	0.0016	0.0055	4.099	2.564	1.682
22	Hexachloro-1,3-butadiene	23.078	0.99974	0.0001	0.0004	1.79	2.7	1.659
23	1,2,3-Trichlorobenzene	23.34	0.9996	0.0010	0.0032	2.232	2.953	1.359
24	1,2,4,5-Tetrachlorobenzene	24.178	0.99816	0.0012	0.0040	6.031	2.509	3.065
25	1,2,3,4-Tetrachlorobenzene	24.721	0.99903	0.0006	0.0021	2.929	3.388	2.362
26	Pentachlorobenzene	26.085	0.99845	0.0004	0.0015	4.977	3.32	2.636
27	Hexachlorobenzene	28.855	0.99744	0.0007	0.0023	3.739	5.128	5.123

Table 5. Test results for 11 VOCs, including linearity, LOD, LOQ, and repeatability.

Peak No.	Name	RT (min)	CF R^2	LOD (µg/kg)	LOQ (µg/kg)	Repeatability (%RSD)		
						Level 1	Level 3	Level 5
1	Dichloromethane	3.227	0.99985	1.96	6.52	1.417	1.5	1.433
2	Benzene	3.36	0.99974	0.18	0.59	1.467	1.596	0.686
3	Toluene	4.736	0.99959	0.11	0.36	1.249	1.849	0.696
4	1,2-Dichloroethane	5.131	0.99966	0.58	1.93	1.667	1.459	0.691
5	Ethylbenzene	5.912	0.99957	0.09	0.29	1.297	1.969	0.742
6	*p*-Xylene	6.019	0.99945	0.09	0.29	1.501	2.019	0.888
7	*m*-Xylene	6.113	0.99944	0.09	0.29	1.513	1.928	0.826
8	Isopropylbenzene	6.573	0.99948	0.09	0.28	1.463	2.31	0.683
9	*o*-Xylene	6.727	0.99953	0.09	0.30	1.851	2.17	0.787
10	Chlorobenzene	7.177	0.99956	0.14	0.48	1.759	1.654	0.785
11	Styrene	7.877	0.99963	0.12	0.39	1.939	1.843	0.893

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Printed in the USA, November 9, 2022
5994-5492EN