

Determination of Halogenated Hydrocarbons, Benzene, and Derivatives in Drinking Water with the Agilent 8697 Headspace Sampler and Agilent 8890 GC System

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Abstract

This application note demonstrates the validation of method GB/T 5750.8-2022 for the analysis of halogenated hydrocarbons and benzene and its derivatives in drinking water using the Agilent 8697 headspace sampler and Agilent 8890 GC system. The whole system provided excellent performance with high sensitivity and stability. The correlation coefficient (R^2) was found to be 0.999 or better for most compounds. The area RSD was 0.53 to 5.49%. The method detection limit (MDL) was 0.001 to 0.63 $\mu\text{g/L}$ for all compounds, and the recovery was 75.5 to 129.1%.

Introduction

To ensure the quality and safety of drinking water, the government of China has recently issued relevant national standards. GB/T 5749-2022¹ is a new standard specifying the regular and expanded indices and limited values for drinking water quality, while GB/T 5750.8-2022² provides procedures for the measurement of organic compounds in drinking water. Both the headspace/gas chromatograph (HS/GC) method and the purge and trap/gas chromatograph mass selective detector (P&T/GCMSD) method are demonstrated in GB/T 5750.8-2022 for volatile organic compound (VOC) analysis. More analytes, higher sensitivity, and greater qualitative capability can be achieved by the P&T/GCMSD system. However, the HS/GC configuration can also provide a reliable and more economical solution for VOC determination. Besides a universal P&T/GCMSD method for simultaneous analysis of multiple types of VOCs, GB/T 5750.8-2022 also recommends two separate HS/GC methods for halogenated hydrocarbons and benzene and its derivatives. A headspace/gas chromatograph/electron capture detector (HS/GC/ECD) system equipped with a mid-polarity column is designed for halogenated hydrocarbon analysis, while a headspace/gas chromatograph/flame ionization detector (HS/GC/FID) system coupled with a high-polarity column is used for determination of benzene and its derivatives. The HS/GC methods provide routine workflows for many labs that pursue ease-of-operation and detection of target compounds.

This application note demonstrates the performance of the Agilent 8697 headspace sampler coupled with the Agilent 8890 GC for delivering accurate and reliable solutions for halogenated hydrocarbons and VOCs in

drinking water. One of the target groups contained 27 halogenated hydrocarbons, and the other contained 11 VOCs consisting of one benzene and eight of its derivatives, and two halogenated hydrocarbons. This system can easily achieve the performance specification for the relevant compounds detailed in GB/T 5749-2022 and GB/T 5750.8-2022.

Experimental

Chemicals and reagents

The single standards of benzene and its derivatives and halogenated hydrocarbons were purchased from ANPEL Laboratory Technologies (Shanghai) Inc.

Solutions and standards

The mixed standard stock solutions were prepared by adding defined amounts of each single standard compound in methanol. 3.7 g sodium chloride and 10 mL ultrapure water were added into each headspace vial to form saturated solutions for calibration standards preparation. The concentrations of each compound at different levels (L) are shown in Appendixes A and B.

Instrument conditions

An Agilent 8697 headspace sampler coupled with an Agilent 8890 GC/FID/ECD was used to analyze two groups of compounds in drinking water. Halogenated hydrocarbon compounds were separated using the Agilent J&W DB-624 Ultra Inert GC column, 30 m × 0.25 mm, 1.4 μm, and detected by ECD, while an Agilent J&W DB-WAX GC column, 30 m × 0.32 mm, 0.25 μm, and FID was used for the separation and detection of 11 VOCs. The two groups of compounds were tested separately. Agilent OpenLab CDS 2.5 software was used for data acquisition and analysis. The instrument conditions are shown in Tables 1 to 4.

Table 1. Agilent 8697 headspace sampler operating conditions for the 27 halogenated hydrocarbons analysis.

Parameter	Value
Loop Size	1 mL
Pressurization Gas	Nitrogen
Oven Temperature	70 °C
Loop Temperature	80 °C
Transfer Line Temperature	90 °C
Vial Equilibration Time	15 min
Injection Duration	0.5 min
Vial Size	20 mL
Fill Pressure	15 psi
Loop Final Pressure	2 psi
Vial Shaking	Level 8

Table 2. GC method conditions for the 27 halogenated hydrocarbons analysis.

Parameter	Value
GC System	Agilent 8890 GC/ECD
Inlet	Split/splitless 250 °C; split ratio 10:1 Agilent inlet liner: straight, deactivated, 2 mm id (p/n 5181-8818)
Column	Agilent J&W DB-624 Ultra Inert column, 30 m × 0.25 mm, 1.4 μm (p/n 122-1334UI)
Carrier	Nitrogen, 1.5 mL/min, constant flow
Oven	40 °C (8 min), then 10 °C/min to 100 °C, then 25 °C/min to 230 °C (10 min)
ECD	250 °C; make up gas (N ₂): 30 mL/min

Table 3. Agilent 8697 headspace sampler operating conditions for the 11 VOCs analysis.

Parameter	Value
Loop Size	1 mL
Pressurization Gas	Nitrogen
Oven Temperature	60 °C
Loop Temperature	70 °C
Transfer Line Temperature	80 °C
Vial Equilibration Time	15 min
Injection Duration	0.5 min
Vial Size	20 mL
Fill Pressure	15 psi
Loop Final Pressure	2 psi
Vial Shaking	Level 8

Table 4. GC method conditions for the 11 VOCs analysis.

Parameter	Value
Inlet	Split/splitless 220 °C, split ratio 10:1 Agilent inlet liner: straight, deactivated, 2 mm id (p/n 5181-8818)
Column	Agilent DB-WAX, 30 m × 0.32 mm, 0.25 μm (p/n 123-7032)
Carrier	Nitrogen, 2 mL/min, constant flow
Oven	40 °C, then 5 °C/min to 45 °C (2.5 min), then 15 °C/min to 90 °C (2 min), then 15 °C/min to 150 °C
FID	250 °C, hydrogen: 30 mL/min, air: 300 mL/min, make up gas (nitrogen): 25 mL/min

Results and discussion

Analysis of 27 halogenated hydrocarbons

Columns

A mid-polarity column is recommended in GB/T 5750.8 method 4.3 for the 27 halogenated hydrocarbons analysis, with an Rtx-1701 column (14% cyanopropyl/phenyl, 86% polydimethylsiloxane, 30 m × 0.25 mm, 0.25 μm) as an example. For the first test, we used the recommended Rtx-1701 column and oven temperature and found two pairs of coeluted compounds (dichloromethane and *trans*-1,2-dichloroethylene; 1,1,1-trichloroethane and carbon tetrachloride), as shown in Figure 1A. This can lead to peak identification problems and also quantitative difficulties. In our next test, we used a DB-1701 (30 m × 0.25 mm, 0.25 μm) column, which has a theoretically equivalent performance to the recommended column.

Figure 1B shows that there was no improvement in separation for the two pairs of compounds. Then, a DB-1701 column (30 m × 0.25 mm, 1 μm) with a thicker film was chosen to improve resolution. As Figure 1C demonstrates, the separation of dichloromethane and *trans*-1,2-dichloroethylene was significantly improved, but the baseline separation was still not achieved. There was no resolution improvement of 1,1,1-trichloroethane and carbon tetrachloride. A different

oven temperature program was also applied, and baseline separation was still a problem. Finally, to achieve a good resolution for all 27 compounds, an Agilent DB-624 (30 m × 0.25 mm, 1.4 μm) column was used with optimized oven temperature program. Figure 1D shows excellent separation of all 27 compounds using a DB-624 column. Therefore, all performance results in this study were generated using an Agilent J&W DB-624 Ultra Inert column.

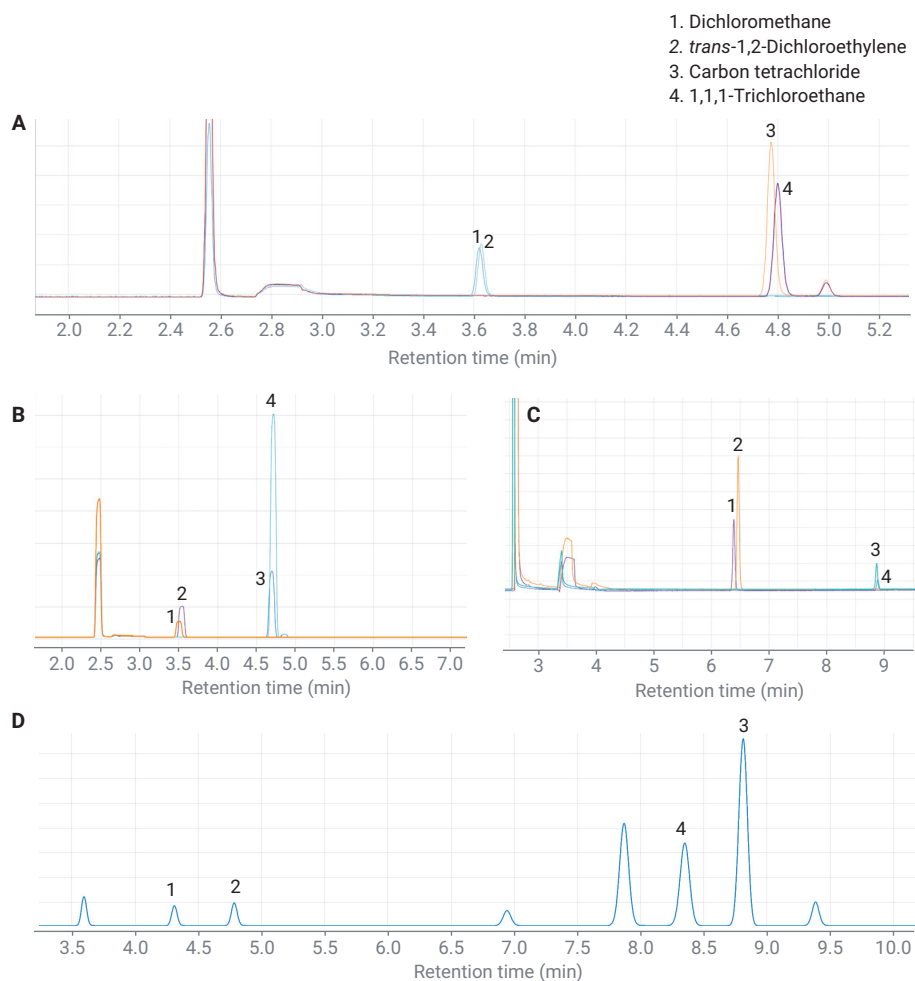


Figure 1. GC/ECD chromatograms of two pairs of coeluted compounds on (A) a Restek Rtx-1701 (30 m × 0.25 mm, 0.25 μm) column; (B) an Agilent DB-1701 (30 m × 0.25 mm, 0.25 μm) column, and (C) an Agilent DB-1701 (30 m × 0.25 mm, 1 μm) column. (D) The chromatograms of four compounds standard mixture on an Agilent DB-624 (30 m × 0.25 mm, 1.4 μm) column.

Chromatogram

Figure 2 shows the chromatogram of the 27 target compounds at level 3 concentration. Most of method parameters refer to GB/T 5750.8 recommendation except for column type and optimized oven temperature. Great resolution and peak shape were obtained for all the compounds, especially for the early-eluted peaks. Good peak shape and resolution are the premise of accurate quantification.

Linearity, repeatability, method detection limit, and recovery results

Table 3 shows the results of the 27 halogenated hydrocarbons. According to GB/T 5750.8-2022, the linearity range of each compound varies, as shown in Appendix A. Linearity across the range studied gave R^2 values of greater than 0.999 for all the compounds except 1,2,4,5-tetrachlorobenzene and pentachlorobenzene, which had R^2 values greater than 0.998.

Repeatability was evaluated by seven replicates at low and high concentrations of calibration standard (levels 2 and 5). Table 3 and Figure 3 illustrate that the area RSD is between 0.57 and 5.49%, which meets the requirements of the GB/T 5750.8-2022 method. The repeatability of late-eluted compounds,

which have relatively high boiling points, showed relatively high area RSD results.

A concentration of level 1 standard solution was used to test MDL based on signal-to-noise ratio (SNR) calculation. The MDL values are listed in Table 3, ranging from 0.001 to 0.345 $\mu\text{g/L}$, which meet the specifications of the GB/T 5750.8-2022 method.

Method recoveries were also verified. Standards containing the 27 halogenated hydrocarbons were spiked into tap water at the concentration levels 2 and 5. Three parallel spiking samples at each level were analyzed. The recovery data are listed in Table 3 and Figure 4, illustrating that the recovery results ranged from 75.5 to 129.1%.

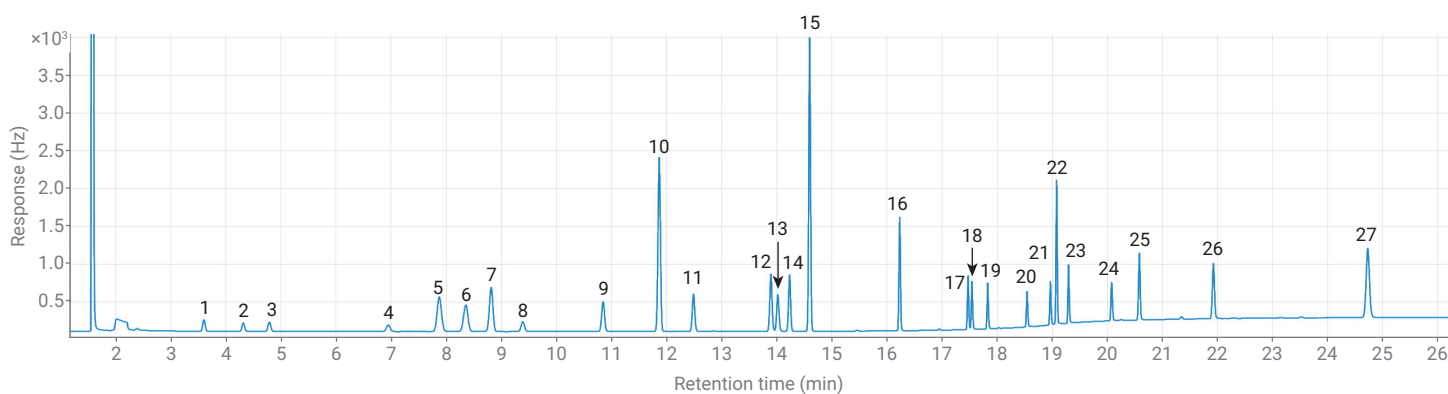


Figure 2. GC/ECD chromatogram of the 27 target compounds at level 3 concentration: (1) 1,1-dichloroethylene, (2) dichloromethane, (3) *trans*-1,2-dichloroethylene, (4) *cis*-1,2-dichloroethylene, (5) chloroform, (6) 1,1,1-trichloroethane, (7) carbon tetrachloride, (8) 1,2-dichloroethane, (9) trichloroethylene, (10) dichlorobromomethane, (11) *trans*-1,2-dibromoethylene, (12) *cis*-1,2-dibromoethylene, (13) 1,1,2-trichloroethane, (14) tetrachloroethylene, (15) chlorodibromomethane, (16) tribromomethane, (17) 1,3-dichlorobenzene, (18) 1,4-dichlorobenzene, (19) 1,2-dichlorobenzene, (20) 1,3,5-trichlorobenzene, (21) 1,2,4-trichlorobenzene, (22) hexachlorobutadiene, (23) 1,2,3-trichlorobenzene, (24) 1,2,4,5-tetrachlorobenzene, (25) 1,2,3,4-tetrachlorobenzene, (26) pentachlorobenzene, (27) hexachlorobenzene.

Table 5. R² values, area RSD, MDL, and recovery percentages for 27 halogenated hydrocarbons.

Number	Compound	Retention Time (min)	R ²	Area RSD (%) (n = 7)		Average Recovery (%) (n = 3)		MDL (µg/L)
				Low (L2)	High (L5)	Low (L2)	High (L5)	
1	1,1-Dichloroethylene	3.593	0.9997	1.12	0.71	92.40	98.13	0.014
2	Dichloromethane	4.309	0.9996	1.14	1.47	78.60	100.67	0.134
3	<i>trans</i> -1,2-Dichloroethylene	4.784	0.9998	1.15	0.95	102.06	100.48	0.173
4	<i>cis</i> -1,2-Dichloroethylene	6.942	0.9993	0.72	1.43	78.80	101.45	0.345
5	Chloroform	7.866	0.9998	1.24	1.59	78.83	92.29	0.003
6	1,1,1-Trichloroethane	8.346	0.9998	1.36	2.15	112.00	94.23	0.001
7	Carbon tetrachloride	8.808	0.999	1.83	3.27	129.07	90.93	0.001
8	1,2-Dichloroethane	9.383	0.9997	0.87	0.57	81.27	99.71	0.231
9	Trichloroethylene	10.841	0.9998	1.28	1.33	109.44	94.50	0.002
10	Dichlorobromomethane	11.859	0.9998	1.78	2.71	78.59	94.97	0.001
11	<i>trans</i> -1,2-Dibromoethylene	12.481	0.9998	1.21	1.62	112.47	94.78	0.002
12	<i>cis</i> -1,2-Dibromoethylene	13.886	0.9998	1.2	1.2	106.20	95.90	0.001
13	1,1,2-Trichloroethane	14.012	0.9998	1.21	1.48	103.06	95.94	0.013
14	Tetrachloroethylene	14.225	0.9997	1.69	2.06	114.56	92.13	0.001
15	Chlorodibromomethane	14.59	0.9998	1.75	2.87	75.46	94.33	0.001
16	Tribromomethane	16.224	0.9997	1.33	2.72	80.02	94.80	0.002
17	1,3-Dichlorobenzene	17.465	0.9998	1.57	1.27	112.11	92.52	0.009
18	1,4-Dichlorobenzene	17.535	0.9998	1.71	1.34	109.91	92.25	0.020
19	1,2-Dichlorobenzene	17.821	0.9998	1.51	1.19	107.79	93.87	0.010
20	1,3,5-Trichlorobenzene	18.536	0.9998	1.98	2.12	103.04	91.60	0.002
21	1,2,4-Trichlorobenzene	18.959	0.9996	1.88	2.51	111.86	91.28	0.002
22	Hexachlorobutadiene	19.072	0.9998	1.87	2.69	108.59	91.84	0.001
23	1,2,3-Trichlorobenzene	19.288	0.9997	2.25	1.86	110.61	92.38	0.001
24	1,2,4,5-Tetrachlorobenzene	20.071	0.9987	3.39	4.92	119.68	91.35	0.002
25	1,2,3,4-Tetrachlorobenzene	20.572	0.9991	2.69	3.79	121.39	91.98	0.001
26	Pentachlorobenzene	21.917	0.9982	2.91	5.49	124.05	90.47	0.001
27	Hexachlorobenzene	24.721	0.9994	3.3	4.41	107.95	87.09	0.001

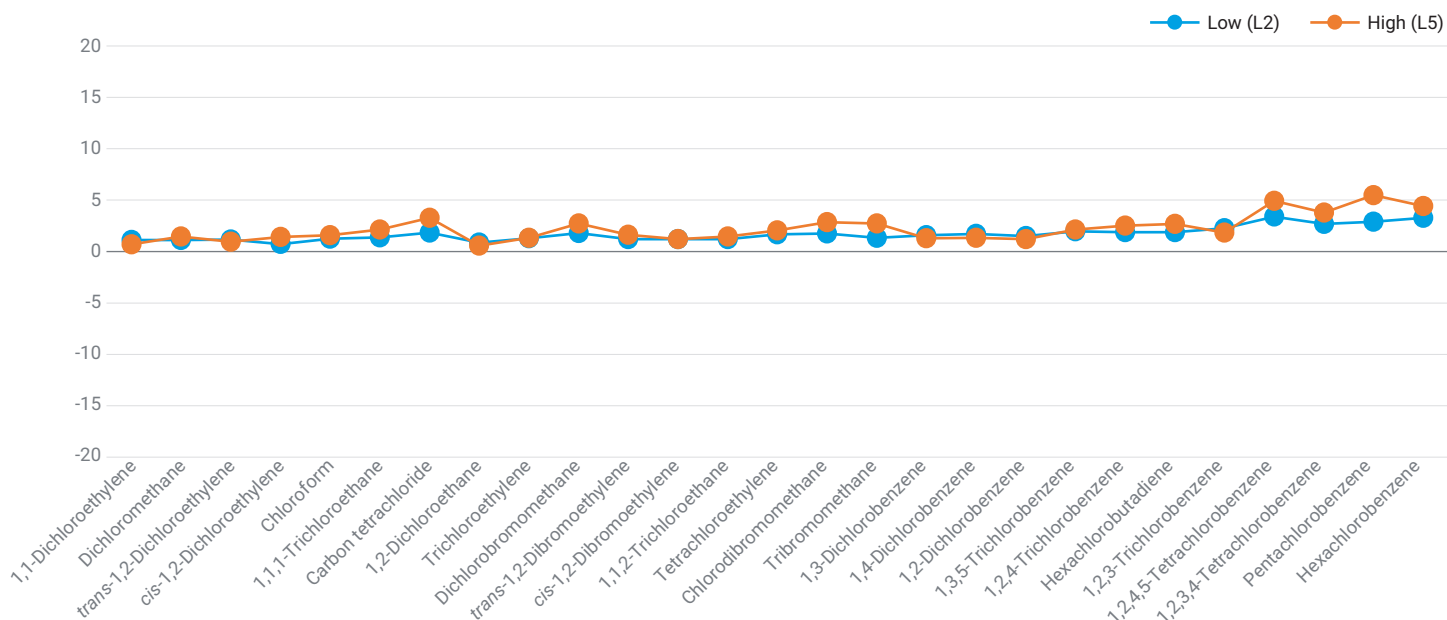


Figure 3. Area repeatability results of the 27 target compounds.

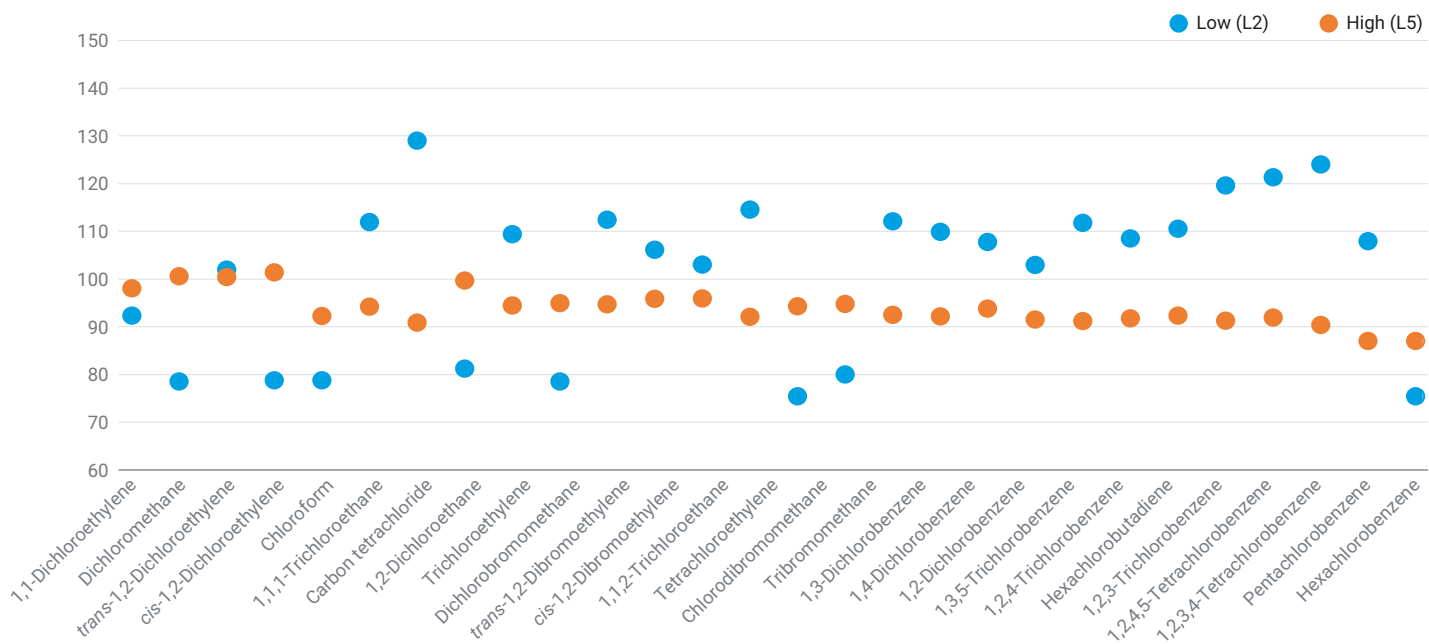


Figure 4. Recovery results of the 27 target compounds.

Analysis of 11 volatile organic compounds

Chromatogram

GB/T 5750.8-2022 method 21.2 details an HS/GC/FID method for VOC analysis. Our analysis contained 11 VOCs consisting of 1 benzene and 8 of its derivatives, and 2 halogenated hydrocarbons (dichloromethane and 1,2-dichloroethane). Figure 5 shows an example chromatogram acquired by the HS/GC/FID system. The DB-WAX column was used for separation. Excellent resolution and peak shape were obtained for all the compounds.

Linearity, repeatability, method detection limit, and recovery results

The 11 VOCs were well separated on this configuration. Excellent area repeatability was achieved with the area RSD below 1.7% for all compounds (Table 4 and Figure 6). Calibration coefficients for each component were above 0.9994.

A low concentration of standard solution (2 µg/L benzene for example) was used for MDL calculation. For

all compounds, the MDLs were 0.05 to 0.63 µg/L, as shown in Table 4, which meets the specifications of the GB/T 5750.8-2022 method.

Method recoveries were measured with the standards containing 11 VOCs spiked into tap water at the concentration of low, middle, and high levels. Table 6 and Figure 7 show excellent recovery results, which ranged from 91.46 to 106.61%.

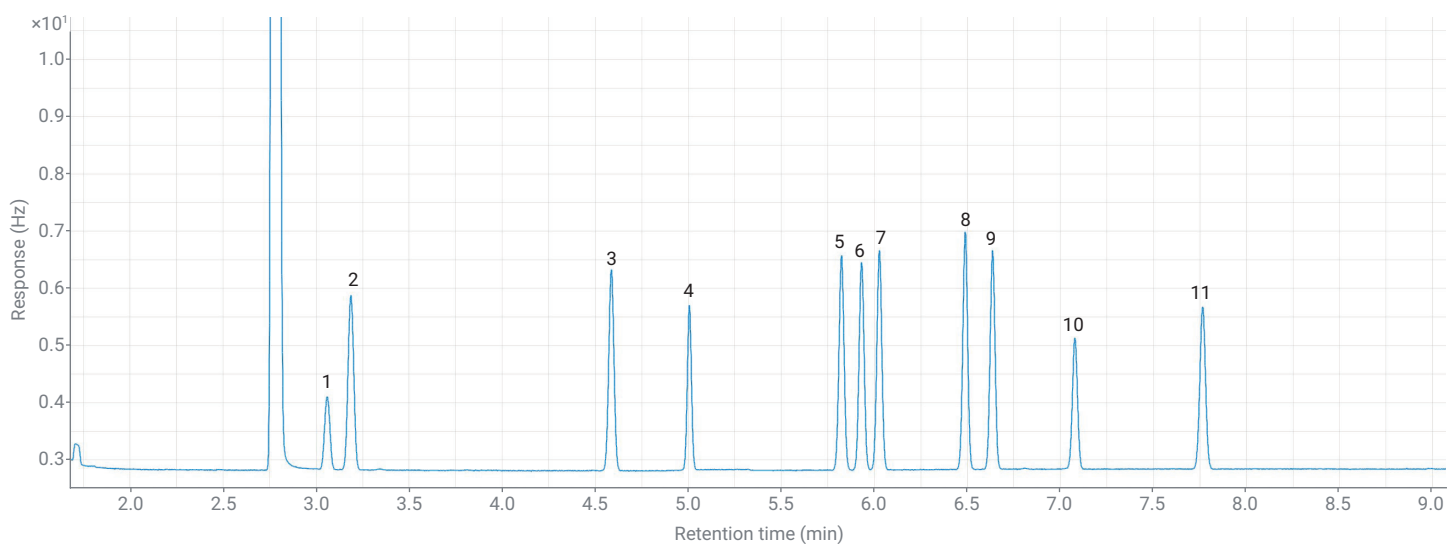


Figure 5. GC/FID chromatogram of 11 VOCs at concentration level 2: (1) dichloromethane, (2) benzene, (3) toluene, (4) 1,2-dichloroethane, (5) ethylbenzene, (6) *p*-xylene, (7) *m*-xylene, (8) cumene, (9) *o*-xylene, (10) chlorobenzene, (11) styrene.

Table 6. R² values, area RSD, MDL, and recovery percentages for 11 VOCs.

Number	Compound	Linearity Range (µg/L)	R ²	MDL (µg/L)	Area RSD (%) (n = 7)			Average Recovery (%) (n = 3)		
					L1	L3	L6	L1	L3	L6
1	Dichloromethane	20 to 320	0.9997	0.63	0.63	0.71	0.73	102.15	97.53	94.80
2	Benzene	5 to 80	0.9997	0.07	0.76	0.76	0.92	103.64	99.38	95.41
3	Toluene	5 to 80	0.9996	0.06	0.58	0.77	1.10	103.33	98.60	94.48
4	1,2-Dichloroethane	20 to 320	0.9997	0.29	0.53	0.67	0.64	100.83	97.58	94.72
5	Ethylbenzene	5 to 80	0.9995	0.06	1.25	0.89	1.25	103.60	97.56	93.69
6	<i>p</i> -Xylene	5 to 80	0.9995	0.05	1.00	0.95	1.69	102.16	96.09	92.45
7	<i>m</i> -Xylene	5 to 80	0.9995	0.05	1.05	0.90	1.40	103.43	96.76	93.05
8	Cumene	5 to 80	0.9994	0.05	1.03	1.20	1.04	106.61	97.67	94.30
9	<i>o</i> -Xylene	5 to 80	0.9995	0.05	1.07	0.85	1.21	102.84	97.11	93.36
10	Chlorobenzene	5 to 80	0.9995	0.09	1.58	0.78	1.48	98.82	96.43	92.63
11	Styrene	5 to 80	0.9995	0.07	0.78	0.96	1.63	99.11	95.12	91.46

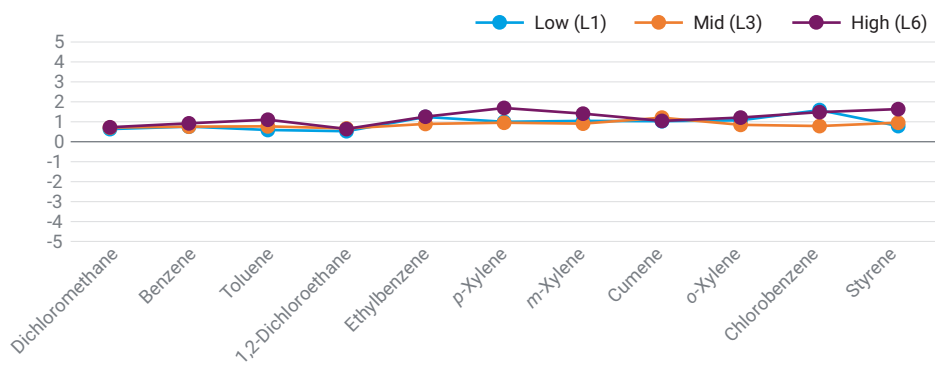


Figure 6. Area repeatability results of the 11 VOCs.

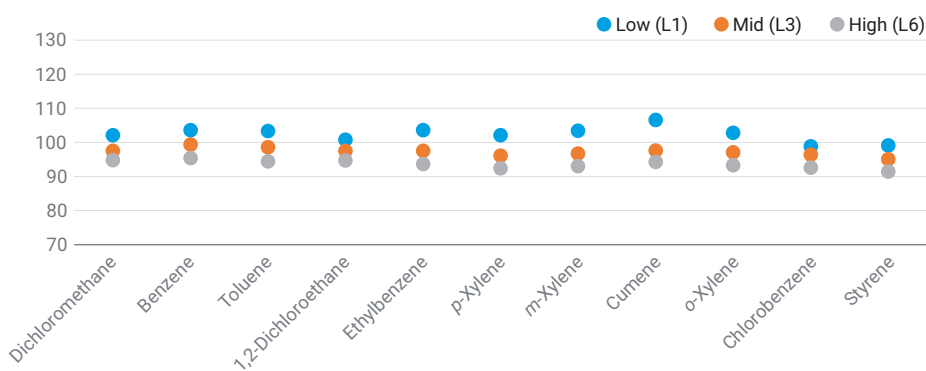


Figure 7. Recovery results of the 11 VOCs.

Conclusion

The Agilent 8697 headspace sampler coupled with an Agilent 8890 GC/FID/ECD system demonstrates outstanding performance for the analysis of both halogenated hydrocarbons and benzene and its derivatives in drinking water and meets requirements specified in GB/T 5750.8-2022 method. The whole system provides excellent peak shape, resolution, repeatability, and recovery results.

References

1. State Administration for Market Regulation; Standardization Administration of the People's Republic of China. *Standards for drinking water quality*. GB/T 5749-2022.
2. General Administration of Quality Supervision, Inspection, and Quarantine; Standardization Administration of the People's Republic of China. *Standard examination methods for drinking water – organic parameters*. GB/T 5750.8-2022.

Appendix

Appendix A

Table 7. The concentration of each halogenated hydrocarbon in the different levels analyzed.

Name	L1 (µg/L)	L2 (µg/L)	L3 (µg/L)	L4 (µg/L)	L5 (µg/L)	L6 (µg/L)	L7 (µg/L)
1,1-Dichloroethylene	1.094	2.188	4.375	8.750	17.50	35.0	70.0
Dichloromethane	7.813	15.625	31.250	62.500	125.00	250.0	500.0
<i>trans</i> -1,2-Dichloroethylene	10.938	21.875	43.750	87.500	175.00	350.0	700.0
<i>cis</i> -1,2-Dichloroethylene	15.625	31.250	62.500	125.000	250.00	500.0	1000.0
Chloroform	0.625	1.250	2.500	5.000	10.00	20.0	40.0
1,1,1-Trichloroethane	0.156	0.313	0.625	1.250	2.50	5.0	10.0
Carbon tetrachloride	0.078	0.156	0.313	0.625	1.25	2.5	5.0
1,2-Dichloroethane	15.625	31.250	62.500	125.000	250.00	500.0	1000.0
Trichloroethylene	0.234	0.469	0.938	1.875	3.75	7.5	15.0
Dichlorobromomethane	0.391	0.781	1.563	3.125	6.25	12.5	25.0
<i>trans</i> -1,2-Dibromoethylene	0.391	0.781	1.563	3.125	6.25	12.5	25.0
<i>cis</i> -1,2-Dibromoethylene	0.391	0.781	1.563	3.125	6.25	12.5	25.0
1,1,2-Trichloroethane	3.125	6.250	12.500	25.000	50.00	100.0	200.0
Tetrachloroethylene	0.078	0.156	0.313	0.625	1.25	2.5	5.0
Chlorodibromomethane	0.781	1.563	3.125	6.250	12.50	25.0	50.0
Tribromomethane	0.938	1.875	3.750	7.500	15.00	30.0	60.0
1,3-Dichlorobenzene	3.125	6.250	12.500	25.000	50.00	100.0	200.0
1,4-Dichlorobenzene	6.250	12.500	25.000	50.000	100.00	200.0	400.0
1,2-Dichlorobenzene	3.125	6.250	12.500	25.000	50.00	100.0	200.0
1,3,5-Trichlorobenzene	0.313	0.625	1.250	2.500	5.00	10.0	20.0
1,2,4-Trichlorobenzene	0.469	0.938	1.875	3.750	7.50	15.0	30.0
Hexachlorobutadiene	0.078	0.156	0.313	0.625	1.25	2.5	5.0
1,2,3-Trichlorobenzene	0.313	0.625	1.250	2.500	5.00	10.0	20.0
1,2,4,5-Tetrachlorobenzene	0.313	0.625	1.250	2.500	5.00	10.0	20.0
1,2,3,4-Tetrachlorobenzene	0.234	0.469	0.938	1.875	3.75	7.5	15.0
Pentachlorobenzene	0.156	0.313	0.625	1.250	2.50	5.0	10.0
Hexachlorobenzene	0.234	0.469	0.938	1.875	3.75	7.5	15.0

Appendix B

Table 8. The concentration of 11 VOCs in the different levels analyzed.

Name	L1 (µg/L)	L2 (µg/L)	L3 (µg/L)	L4 (µg/L)	L5 (µg/L)	L6 (µg/L)
Dichloromethane	20	40	80	160	240	320
Benzene	5	10	20	40	60	80
Toluene	5	10	20	40	60	80
1,2-Dichloroethane	20	40	80	160	240	320
Ethylbenzene	5	10	20	40	60	80
<i>p</i> -Xylene	5	10	20	40	60	80
<i>m</i> -Xylene	5	10	20	40	60	80
Cumene	5	10	20	40	60	80

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