

Application News

No. AD-0086

HS-20 GCMS-QP2010 Ultra

Determination of Volatile Organic Compounds in Drinking Water by EPA Method with Static Headspace GC-MS

□ Introduction

Determination of Volatile Organic Compounds (VOCs) has been well established by the Environmental Protection Agency (EPA) to monitor VOCs pollutant in drinking water. The EPA method 524.3 uses purge and trap with gas chromatography - mass spectrometry to extract and analyze VOCs quantitatively in drinking water.

Headspace is considered as an alternative to extract the VOCs from drinking water. In a previous study, the dynamic headspace has proven to be able to extract VOCs and meets the EPA 524.3 quality control requirement. Details of analysis conditions and results were described in the Shimadzu Application News (No. AD-0073, 2014). In this report, we describe the results of a further study of analysis of VOCs in drinking water using static headspace method.

It is known that static headspace is relatively less efficient in extraction of VOCs compared to dynamic headspace. To compensate this drawback, Selected Ion Monitoring (SIM) mode of GCMS was used in data acquisition. The results of this study show that static headspace coupling with GC-MS operated in SIM mode for VOCs analysis meet all of the requirements, the Initial Demonstration of Capability (IDC) and Ongoing Quality Control specified in EPA 524.3.

□ Experimental

1) Preparation of Initial Tuning Standard Solutions

The EPA 524.3 method requires to perform MS tune with 4-bromofluorobenzene (BFB), which is also one of the surrogate analytes in this analysis. The surrogate standard solution was diluted to 8 µg/mL, 25 µL of which is then spiked into a 100 mL of pure water. The headspace vial was filled with 10 mL of the final diluted (5 µg/L) tuning solution.

2) Preparation of Standard Samples

A series of calibration standard samples of seven levels, ranging from 2 to 160 µg/mL was prepared in methanol from stock solutions obtained from commercial supplier. Concurrently, internal standards and surrogate standards of 8 µg/mL were prepared in methanol. Seven volumetric flasks of 100 mL were prepared. Each volumetric flask was filled with reagent water containing 0.625 g/L of ascorbic acid and 5 g/L of maleic acid. Calibration standard and internal standard were spiked separately at 25 µL into the volumetric flask. Reagent water was added to top up the volumetric flasks to 100 mL.

The final concentrations of the standard solutions were in the range from 0.5 to 40 µg/L. Headspace vials were then filled with the standard samples prepared and crimped to tightness.

3) Preparation of Field Sample

Tap water was used as the field sample in this study. The field sample was dechlorinated with ascorbic acid solution at pH 2.0. Ascorbic acid (0.625 g) and maleic acid (5.00 g) were weighed and added respectively into a 1L volumetric flask. A volume of 400 mL of field sample was added to the volumetric flask to dissolve the solid preservatives. After that, additional field sample was added to the gauge line of the volumetric flasks. Headspace vials were filled with 10 mL of dechlorinated field samples and immediately crimped to tightness.

4) Instrument and Analytical Conditions

Table 1: Headspace and GC-MS analytical conditions

HS-20	
Mode	Loop
Oven Temp.	60 °C
Sample Line Temp.	120 °C
Shaking Level	5
Equilibrating Time	20 min
Pressurizing Time	1 min
Injection Time	2 min
Sample Volume	10 mL
GC	
Carrier Gas	He
Flow Control Mode	Linear Velocity
Linear Velocity	31.3 mL/min
Purge Flow	3 mL/min
Split Ratio	10
Column	Rtx-VMS 60 m x 0.25 mm x 1.4 µm
Column Oven Temp.	45 °C(4.5 min), 12 °C/min →100 °C, 25 °C/min → 240 °C (5.32 min)
MS	
Ion Source Temp.	200 °C
Interface Temp.	200 °C
Ionization Mode	Electron impact (EI)
Ionization Voltage	70 eV
Solvent cut Time	1.5 min
Acquisition Mode	Selected Ion Monitoring (SIM) Quantitation ions were selected based on the recommendation in EPA 524.3 method

Results and Discussion

A: Tuning of Mass Spectrometer with BFB

The mass abundance of 4-bromofluorobenzene (BFB) was monitored by the QA/QC function in the GCMSsolution. The BFB mass spectrum mass abundance criteria must be achieved prior to analysis. The detailed criteria and results of tuning with BFB are shown in Table 2.

Table 2: BFB tuning criteria and result specified by EPA 524.3 method

m/z	Spectrum Check Criteria	Result	Status
95	Base Peak, 100% Relative Abundance	100.0	Pass
96	5 to 9% of mass 95	7.52	Pass
173	<2% of mass 174	0	Pass
174	>50% of mass 95	50.42	Pass
175	5 to 9% of mass 174	6.94	Pass
176	>95% but <105% of mass 174	95.07	Pass
177	5 to 10% of mass 176	6.09	Pass

B: Initial Demonstration of Capability (IDC)

The EPA 524.3 IDC requires demonstration of low system background, carryover test, precision, accuracy, minimum reporting level and quality control sample.

1) System Background and Carryover Test

A blank reagent water was analyzed prior to the analysis and after the injection of the highest calibration standard (40 µg/L). None of the target compounds was detected in both reagent water analyses.

2) Precision and Accuracy

Seven replicate standard samples were prepared at 1 µg/L in reagent water to demonstrate the precision and accuracy of headspace technique in the extraction of volatile organic compounds from drinking water. According to the EPA 524.3 IDC, the %RSD of concentration must be below 20% and mean recovery must be within ±20% of the true value. The experimental data showed that the HS-20 is capable to extract all the VOCs with %RSD less than 6.82% and the recovery in reagent water within the range of 80% to 120%. The %RSD of concentration and recovery for all the target analytes are tabulated in Table 3. Figure 1 shows the results of replicate injections of trichlorobenzene, which average was used to calculate the analysis accuracy.

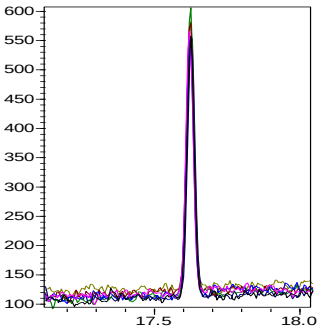


Figure 1: Overlay chromatograms of seven replicate injections of 1,2,3-trichlorobenzene standard at 1 µg/L

3) Detection Limits of Mixed Standards

Method detection limits (MDLs) of 76 compounds were determined from the results of seven replicates control sample of mixed standards each at 0.1 ug/L. The standard derivations (s) and MDL of the compounds were calculated by the GCMSsolution QA/QC function from the chromatograms of these samples. The equation of MDL calculation is shown as below: The MDL results of all the compounds are shown in Table 3.

$$MDL = s \times t_{(n-1, 1-\alpha=0.99)}$$

s: standard deviation of concentration from seven replicated data
t: t data in t-distribution (degree of freedom 6, confidence interval of 99%)

C: Ongoing Quality Control

The ongoing quality control describes the requirements that must be strictly followed when analysing field samples. Before analysing field samples, the calibration curves established are required to perform continuing calibration check (CCC) and monitored on the validity of the calibration curves.

1) Calibration Curves

Seven standard samples were prepared with concentration ranging from 0.5 to 40 µg/L. Each standard sample was spiked with equal amount of internal standards and surrogate standards. A chromatogram of a mixed standard sample is shown in Figure 2, which consists of all the compounds, including 76 target analytes, 3 internal standards and 3 surrogate. Figures 3 (a, b and c) show a few selected calibration curves: the most volatile and the least volatile compound respectively. All the target compounds exhibited good linearity with correlative regression more than 0.9974.

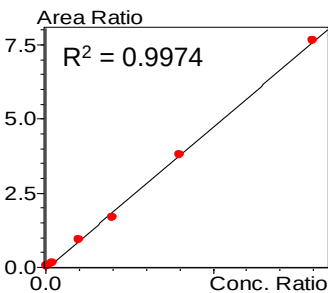


Figure 3a: Calibration curve of Difluorochloromethane (most volatile compound)

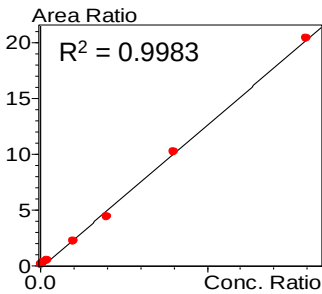


Figure 3b: Calibration curve of Styrene (mid range volatile compound)

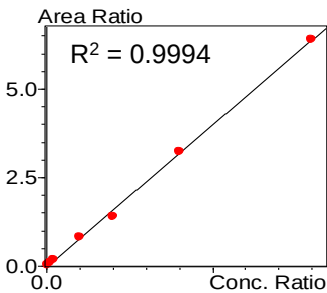


Figure 3c: Calibration curve of 1,2,3-trichlorobenzene (least volatile compound)

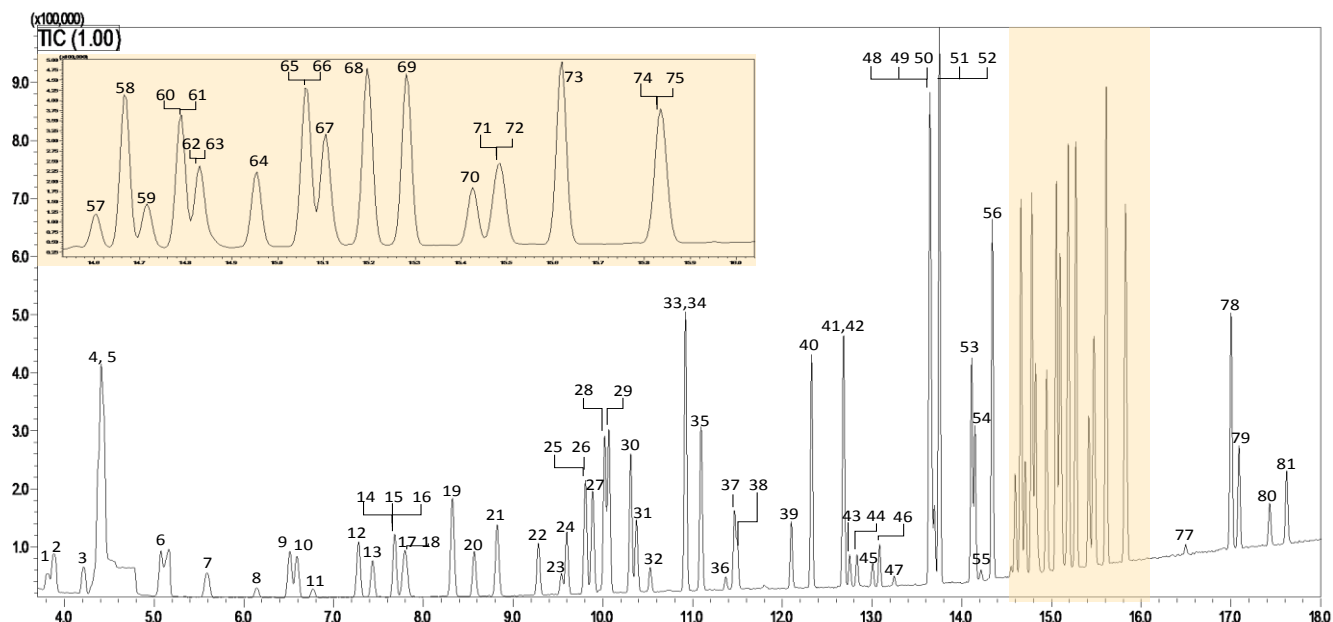


Figure 2: TIC of all compounds required by EPA 524.3, including 76 targets, 3 internal standards (No. 34, 49 and 71) and 3 surrogate standards (No. 16, 57 and 75)

Table 3: Summary of correlation regression of calibration curve (0.5~40 µg/L), method detection limit (MDL), repeatability and recovery in reagent water (n=7) at 1 µg/L for all analytes specified in EPA 524.3

ID	Compound	Correlative Regression (R ²)	Method Detection Limit (µg/L)	Repeatability (n=7), RSD (%)	Recovery % (n=7)
1	Dichlorodifluoromethane	0.9974	0.075	3.78	102
2	Chlorodifluoromethane	0.9992	0.051	3.02	80
3	Chloromethane	0.9994	0.075	1.62	86
4	Vinyl Chloride	0.9998	0.037	2.67	100
5	1,3-Butadiene	0.9996	0.054	3.56	100
6	Bromomethane	0.9995	0.096	2.27	85
7	Trichlorofluoromethane	0.9995	0.080	2.17	109
8	Diethyl ether	0.9998	0.076	4.83	99
9	1,1-Dichloroethene	0.9997	0.174	3.45	119
10	Carbon Disulfide	0.9998	0.129	1.64	101
11	Methyl Iodide	0.9997	0.157	1.69	110
12	Allyl Chloride	0.9995	0.201	2.39	86
13	Methylene Chloride	0.9995	0.211	6.82	85
14	trans-1,2-Dichloroethene	0.9997	0.458	6.15	80
15	Methyl Acetate	0.9995	0.195	2.81	99
16	Methyl-t-Butyl Ether (MtBE)-d3	Surrogate Standard			
17	Methyl-t-Butyl Ether (MtBE)	0.9995	0.196	5.38	102
18	t-Butyl Alcohol (TBA)	0.9987	0.362	6.56	120
19	Diisopropyl Ether (DIPE)	0.9996	0.184	2.18	101
20	1,1- dichloroethane	0.9995	0.154	1.20	84
21	t-Butyl Ethyl Ether (ETBE)	0.9995	0.063	2.81	103
22	cis-1,2-dichloroethene	0.9994	0.068	2.87	95
23	Bromochloromethane	0.9994	0.173	2.82	97
24	Chloroform	0.9995	0.056	1.51	86
25	Carbon Tetrachloride	0.9995	0.182	1.44	99
26	Tetrahydrofuran	0.9992	0.653	6.35	81
27	1,1,1-Trichloroethene	0.9995	0.042	1.01	100
28	1,1-Dichloropropene	0.9994	0.069	1.62	106
29	1-Chlorobutane	0.9994	0.058	1.38	99
30	Benzene	0.9993	0.060	1.97	81
31	t-Amyl Methyl Ether (TAME)	0.9995	0.110	3.64	105
32	1,2-Dichloroethane	0.9995	0.093	3.78	83
33	Trichloroethene	0.9992	0.063	1.46	118
34	1,4-Difluorobenzene	Internal Standard			
35	t-Amyl Ethyl Ether (TAEE)	0.9992	0.060	2.38	107
36	Dibromomethane	0.9995	0.094	2.85	94
37	1,2-Dichloropropane	0.9994	0.051	2.60	96
38	Bromodichloromethane	0.9995	0.098	2.59	97
39	cis-1,3-Dichloropropene	0.9995	0.055	2.82	94

ID	Compound	Correlative Regression (R ²)	Method Detection Limit (µg/L)	Repeatability, RSD% (n=7)	Recovery % (n=7)
40	Toluene	0.9991	0.048	1.80	96
41	trans-1,3-Dichloropropene	0.9995	0.078	4.25	103
42	Tetrachloroethene	0.9993	0.060	3.41	115
43	Ethyl Methacrylate	0.9995	0.071	1.67	115
44	1,1,2-Trichloropropane	0.9996	0.055	5.16	94
45	Dibromochloromethane	0.9996	0.084	1.88	112
46	1,3-Dichloropropane	0.9994	0.134	4.71	98
47	1,2-Dibromoethane	0.9995	0.081	5.52	101
48	Ethylbenzene	0.9994	0.016	0.87	102
49	Chlorobenzene-d5	Internal Standard			
50	Chlorobenzene	0.9994	0.015	0.56	108
51	1,1,1,2-Tetrachloroethane	0.9994	0.131	4.17	111
52	m-Xylene, p-Xylene	0.9969	0.017	1.08	104
53	o-Xylene	0.9994	0.017	0.67	105
54	Styrene	0.9992	0.035	0.61	115
55	Bromoform	0.9994	0.167	3.51	114
56	Isopropylbenzene	0.9991	0.017	1.33	119
57	4-Bromofluorobenzene	Surrogate Standard			
58	n-propylbenzene	0.9977	0.032	3.10	102
59	Bromobenzene	0.9993	0.105	3.20	114
60	1,1,2,2-Tetrachloroethane	0.9994	0.080	4.52	104
61	1,3,5-Trimethylbenzene	0.9991	0.028	1.06	116
62	2-Chlorotoluene	0.9994	0.049	2.00	99
63	1,2,3-Trichloropropane	0.9995	0.259	3.40	97
64	4-Chlorotoluene	0.9994	0.030	1.13	89
65	t-Butylbenzene	0.9991	0.053	1.76	113
66	1,2,4-Trimethylbenzene	0.9993	0.029	1.02	99
67	Pentachloroethane	0.9995	0.087	2.69	116
68	sec-Butylbenzene	0.9985	0.021	1.99	97
69	4-Isopropyltoluene	0.9992	0.025	1.81	105
70	1,3-Dichlorobenzene	0.9993	0.038	0.55	110
71	1,4-Dichlorobenzene-d4	Internal Standard			
72	1,4-Dichlorobenzene	0.9992	0.026	1.03	109
73	n-Butylbenzene	0.9988	0.023	2.54	81
74	Hexachloroethane	0.9989	0.064	3.97	103
75	1,2-Dichlorobenzene-d4	Surrogate Standard			
76	1,2-Dichlorobenzene	0.9990	0.027	1.03	119
77	1,2-Dibromo-3-chloropropane	0.9995	0.396	5.46	97
78	Hexachlorobutadiene	0.9991	0.051	4.22	102
79	1,2,4-Trichlorobenzene	0.9994	0.097	2.54	100
80	Naphthalene	0.9994	0.063	3.74	96
81	1,2,3-Trichlorobenzene	0.9994	0.214	2.58	104

2) Continuing Calibration Check

Continuing Calibration Checks (CCC) of standard solutions were prepared and performed with mixed standards of 5 µg/L. The CCC standard solutions were analyzed at the beginning, after every tenth field samples and at the end of a batch. The GCMSsolution with EPA optional software allows tabulation of CCC recovery along with the standard calibration curves. The CCC recoveries throughout the analysis were in the range of 71% to 123%, which was valid with the EPA requirement of ±30%.

3) Internal Standards

Responses of internal standards in field samples were monitored by comparing the internal standards peak areas with the most recent CCC standard solutions. The peak areas of internal standards in 10 field samples were quantitated and compared with the most recent CCC standard solutions by the GCMSsolution QA/QC function. The deviation of the internal standard peak areas, ranged

from 80% to 117%, was within the EPA requirement of less than 30%.

4) Surrogate Analytes

Three surrogate analytes namely, methyl-t-butyl ether-*d*₃, 4-bromofluorobenzene and 1,2-dichlorobenzene-*d*₄, as specified in EPA 524.3, were chosen to monitor the recovery of headspace extraction. All the field samples were spiked with 5 µg/L of surrogate analytes. The surrogate recovery of all the field samples was in the range of 71% to 121%, which fulfilled the requirement of 70% to 130% specified by EPA 524.3 method.

5) Field Sample Analysis

Concentration of VOCs in field sample, which was tap water, was determined by using headspace-GCMS. The analysis was replicated for 10 times. Concentration of all the VOCs in 10 field samples is tabulated on Table 4. %RSD of 10 field samples is in the range from 0.96% to 13.2%.

Table 4: Summary of VOCs concentration, deviation of the internal standard area from the most recent Continuous Calibration Check (CCC) standard solutions and the recoveries of surrogate analytes in 10 field samples

ID 97	Compound	Deviation of ISTD peak area from the most recent CCC	Surrogate Recoveries, % (n=10)	Concentration (µg/L)	Repeatability, RSD% (n=10)
1	Dichlorodifluoromethane			N.D.	--
2	Chlorodifluoromethane			N.D.	--
3	Chloromethane			N.D.	--
4	Vinyl Chloride			N.D.	--
5	1,3-Butadiene			N.D.	--
6	Bromomethane			N.D.	--
7	Trichlorofluoromethane			N.D.	--
8	Diethyl ether			N.D.	--
9	1,1-Dichloroethene			N.D.	--
10	Carbon Disulfide			N.D.	--
11	Methyl Iodide			N.D.	--
12	Allyl Chloride			N.D.	--
13	Methylene Chloride			1.22	13.2
14	trans-1,2-Dichloroethene			N.D.	--
15	Methyl Acetate			N.D.	--
16	Methyl-t-Butyl Ether (MtBE)-d3		122	Surrogate Standard	
17	Methyl-t-Butyl Ether (MtBE)			1.15	4.43
18	t-Butyl Alcohol (TBA)			N.D.	--
19	Diisopropyl Ether (DIPE)			N.D.	--
20	1,1- dichloroethane			N.D.	--
21	t-Butyl Ethyl Ether (ETBE)			N.D.	--
22	cis-1,2-dichloroethene			N.D.	--
23	Bromochloromethane			N.D.	--
24	Chloroform			6.21	2.89
25	Carbon Tetrachloride			N.D.	--
26	Tetrahydrofuran			N.D.	--
27	1,1,1-Trichloroethene			N.D.	--
28	1,1-Dichloropropene			N.D.	--
29	1-Chlorobutane			N.D.	--
30	Benzene			1.1	2.42
31	t-Amyl Methyl Ether (TAME)			N.D.	--
32	1,2-Dichloroethane			N.D.	--
33	Trichloroethene			N.D.	--
34	1,4-Difluorobenzene	95	Internal Standard		
35	t-Amyl Ethyl Ether (TAEE)			N.D.	--
36	Dibromomethane			N.D.	--
37	1,2-Dichloropropane			N.D.	--
38	Bromodichloromethane			3.26	3.82
39	cis-1,3-Dichloropropene			N.D.	--
40	Toluene			1.1	9.36
41	trans-1,3-Dichloropropene			N.D.	--
42	Tetrachloroethene			N.D.	--
43	Ethyl Methacrylate			N.D.	--
44	1,1,2-Trichloropropane			N.D.	--
45	Dibromochloromethane			1.8	8.28
46	1,3-Dichloropropane			N.D.	--
47	1,2-Dibromoethane			N.D.	--
48	Ethylbenzene			0.58	2.32
49	Chlorobenzene-d5	105	Internal Standard		
50	Chlorobenzene			N.D.	--
51	1,1,1,2-Tetrachloroethane			N.D.	--
52	m-Xylene, p-Xylene			0.98	0.96
53	o-Xylene			0.78	1.91
54	Styrene			0.86	3.07
55	Bromoform			N.D.	--
56	Isopropylbenzene			N.D.	--
57	4-Bromofluorobenzene		97	Surrogate Standard	
58	n-propylbenzene			N.D.	--
59	Bromobenzene			N.D.	--
60	1,1,2,2-Tetrachloroethane			N.D.	--

ID	Compound	Deviation of ISTD peak area with the most recent CCC	Surrogate Recoveries, % (n=10)	Concentration (µg/L)	Repeatability, RSD% (n=10)
61	1,3,5-Trimethylbenzene	98		N.D.	--
62	2-Chlorotoluene			N.D.	--
63	1,2,3-Trichloropropane			N.D.	--
64	4-Chlorotoluene			N.D.	--
65	t-Butylbenzene			N.D.	--
66	1,2,4-Trimethylbenzene			N.D.	--
67	Pentachloroethane			N.D.	--
68	sec-Butylbenzene			N.D.	--
69	4-Isopropyltoluene			1.82	3.15
70	1,3-Dichlorobenzene			N.D.	--
71	1,4-Dichlorobenzene-d4	71		Internal Standard	
72	1,4-Dichlorobenzene			N.D.	--
73	n-Butylbenzene			N.D.	--
74	Hexachloroethane			N.D.	--
75	1,2-Dichlorobenzene-d4			Surrogate Standard	
76	1,2-Dichlorobenzene			N.D.	--
77	1,2-Dibromo-3-chloropropane			N.D.	--
78	Hexachlorobutadiene			N.D.	--
79	1,2,4-Trichlorobenzene			N.D.	--
80	Naphthalene			N.D.	--
81	1,2,3-Trichlorobenzene			N.D.	--

* N.D. indicates no detection of the respective target compounds in the field samples

□ Conclusions

The analysis results of static headspace with Selective Ion Monitoring complied to the EPA 524.3 Initial Demonstration of Capability (IDC) and Ongoing Quality Control requirements. This shows that the HS-20 Loop with GCMS-QP2010 *Ultra* is capable as an alternative in the analysis of EPA 524.3.

□ References

1. B. Prakash, A.D. Zaffiro, M. Zimmerman, D. J. Munch and B.V. Pepich, EPA Document # EPA 815-B-009, Version 1.0, June 2009
2. Shimadzu Application News, AD-0073