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Application News

HS-20 NX (Trap Model) Headspace Autosampler
GCMS-QP2020 NX Single Quadrupole Gas Chromatograph Mass Spectrometer

Analysis of Volatile Organic Compounds (VOCs) in Water Using Trap-Headspace-GCMS in Accordance with US EPA Method 8260D Criteria

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User Benefits

- Using trap-headspace-GCMS as an alternative technique to purge-and-trap with GCMS in accordance with US EPA Method 8260D criteria for the analysis of VOCs in water matrix.
- Capability of analyzing volatile organic compounds (VOCs) at very low limit of quantitation, as low as 0.5 ng/mL.

■ Introduction

According to United States Environmental Protection Agency (US EPA), volatiles organic compounds (VOCs) are defined as compounds with high vapor pressure that can easily evaporate into gases. Improper dumping of waste or industrial leachates contaminates underground water. This contaminated water exposes humans to VOCs in their daily lives. Each VOC poses different exposure risk based on its individual constituents. To protect human health and the environment, the US EPA developed Method 8260D[1)] to identify and quantify VOCs in water using single quadrupole GCMS.

Purge-and-trap is a common sampling technique for this application. However, in this study, Shimadzu's Trap-Headspace system is utilized as an alternative sampling technique and is evaluated against EPA 8260D criteria. VOCs sampled from the headspace are concentrated in a trap before being injected into the GC, providing high sensitivity in the analysis. The headspace system, HS-20 NX (Trap Model), also features heated and inert sample lines with a short transfer line to suppress analytes adsorption. In this application news, the HS-20 NX (Trap Model) is coupled with Shimadzu GCMS-QP2020 NX (Fig. 1) to achieve high sensitivity in VOCs in water analysis.

Fig. 1 HS-20 NX (Trap Model) Coupled with GCMS-QP2020 NX

■ Experimental

Instrumental and Analytical Conditions

A headspace autosampler system, HS-20 NX (Trap model) (Shimadzu Corporation, Japan) and a single quadrupole GCMS system, GCMS-QP2020 NX (Shimadzu Corporation, Japan) were employed in this work. The details of the system and analytical conditions for the dynamic headspace and GC-MS/MS method are shown in Table 1. Data were acquired using *LabSolutions™ GCMS* while processing was done in *LabSolutions Insight™* enhanced with *Environmental Option* that allows the implementation of QC procedures in accordance with US EPA method.

Table 1. Analysis Conditions

Instrumentation	
GCMS system	GCMS-QP2020 NX
Auto sampler	HS-20 NX (Trap Model)
Column	SH-I-624Sil MS* (30 m x 0.25 mm x 1.40 µm)
Headspace Parameters	
HS Mode	Trap
HS Oven Temp.	60 °C
Sample Line Temp.	150 °C
Transfer Line Temp.	150 °C
Pressurizing Gas Pressure	57.0 kPa
Equilibrating Time	30.0 min
Load Time	0.30 min
Injection Time	20.0 min
Trap Cooling Temp.	-10 °C
Trap Desorption Temp	250 °C
Multi Injection Count	10
Gas Chromatograph Parameters	
Injection Mode	Split mode (Split Ratio: 5.0)
Carrier Gas	Helium
Flow Control Mode	Linear velocity (36.2 cm/s)
Column Temperature Program	35 °C (5 min) → 11 °C/min to 60 °C → 20 °C/min to 220 °C (5 min)
Mass Spectrometer Parameters	
Ion Source Temperature	230 °C
Interface Temperature	220 °C
Acquisition Mode	SIM

*P/N: 221-75962-30

Preparation of 4-Bromofluorobenzene (BFB) Standard for MS Tuning

BFB standard with 99.5% purity (P/N N-10809) were purchase from Chem Service, Inc. A 1-ppm BFB working standard was prepared in methanol. A 50-ppb BFB solution was prepared by diluting the working standard in a 100 mL volumetric flask with ultrapure water. 1 mL of the final BFB solution was transferred to headspace vial for analysis.

BFB tuning was performed following this application news: *The Guide to BFB Tuning for Analysis of Volatiles Organic Compounds*, AN No. SSI-GCMS-1405.[2)]

Preparation of VOC Calibration Standards

8260 MegaMix® Calibration Mix (#30475) containing 76 VOCs, 8260 Internal Standard Mix (#30074) and 4 internal standards (IS) were purchased from Restek Corporation. 65 out of 76 VOCs were selected as target VOCs for this study. First, calibration stock solutions were prepared in a cold environment using vials with the Mininert® valve system to minimize VOC loss. The eVol® syringes were used to dilute MegaMix with pre-chilled methanol to final concentrations of 1, 2, 4, 10, 20 and 40 ng/mL,

with 10 ng/mL for IS, ensuring accuracy. Subsequently, initial calibration (ICAL) solutions for headspace injection were prepared by diluting the calibration stock solutions in 100 ml volumetric flasks with ultrapure water. The ICAL concentrations prepared were 0.5, 1, 2, 5, 10, and 20 ng/mL, and 5 ng/mL of IS. 1 mL of the prepared ICAL solutions were transferred into headspace vials for analysis. These steps were performed in a cold environment.

Initial calibration verification (ICV) was prepared using a standard from the same manufacturer but of a different batch from that of the ICAL, at the same concentration as ICAL midpoint level (5 ng/mL). Continuous calibration verification (CCV) standard was prepared using the same standard as ICAL, at the same concentration as ICAL midpoint level (5 ng/mL).

Preparation of Unknown Samples

Two unknown samples were analyzed in this study as described in Table 2.

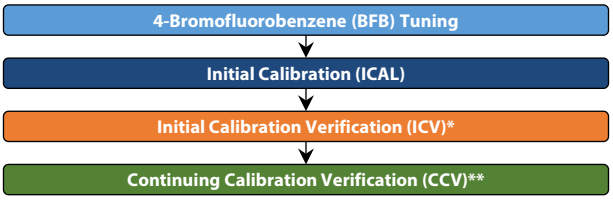
Table 2. Samples Analyzed in This Study

No.	Sample	Sample Name	Description
1	Tap water	TW	Fresh tap water
2	Chilled Tap Water	CTW	Tap water which was placed overnight in a refrigerator used to store GC chemical standards

1 mL of these unknown samples was transferred into headspace vials for analysis.

■ Results & Discussion

In accordance with US EPA Method 8260D, QC procedures were performed prior to the analysis of unknown samples. Below are the list of QC procedures performed.



*After each ICAL and prior to analyzing unknown samples
**Once every 12 hours

Instrumental Performance Check – BFB Tuning

In addition to a standard instrument autotune, the US EPA requires another tuning using BFB, a VOC tuning compound, which is required to meet a set of suggested criteria[3] as described in EPA 8260D method (Table 3). The result of BFB tuning obtained in this experiment was "PASS" for all criteria (Table 3), which indicate that the instrument met all the suggested criteria.

Table 3. BFB Tuning Suggested Criteria and Result

m/z over *m/z*	Relative Abundance	BFB Tuning Result Obtained	Criteria Check
95 / 174	50 – 200 %	139.8	Pass
96 / 95	5 – 9 %	6.4	Pass
173 / 174	<2%	0.9	Pass
174 / 95	50 – 200 %	71.5	Pass
175 / 174	5 – 9 %	6.7	Pass
176 / 174	95 – 105 %	97.7	Pass
177 / 176	5 – 10 %	6.1	Pass

Target VOCs Chromatogram

The scan total ion chromatogram (TIC) of the high-concentration mixture of 8260 MegaMix Calibration Mix with 4 internal standards (IS) is shown in Fig. 2. All target VOCs and IS were detected and identified.

Method Blanks

Method Blanks, which were prepared by transferring 1 mL of blank ultrapure water into headspace vial, were analyzed before and after ICAL acquisition to ensure negligible contamination from the environment and carryover in the system. No significant peaks were detected in Method Blanks.

ICAL, ICV, and CCV

The suggested criteria and experimental results of ICAL, ICV and CCV are shown in Table 4. 6-point ICAL calibration curves were constructed using a quadratic regression calibration model. The calibration curves of some target VOCs are displayed in Fig. 3.

ICAL 4 which was the midpoint of each ICAL with a concentration of 5 ng/mL, was used as a reference for the retention time, ion ratio and IS response check within the analysis.

The standard samples analysis results processed by the *LabSolutions Insight* with *Environmental Option* showed that:

- 64 out of the 65 target VOCs passed ICAL criteria (98%)
- 61 out of the 65 target VOCs passed ICV criteria (94%)
- 59 out of the 65 target VOCs passed CCV criteria (89%)

Overall, 58 out of 65 target VOCs passes all ICAL, ICV and CCV criteria. Further studies are required to investigate the reasons some of these target VOCs did not pass the suggested criteria. Nevertheless, EPA 8260D requires only >90% of target analytes meet ICAL criteria and >80% meet CCV criteria before analyzing sample, this result allowed us to use the ICAL calibration curves to be used for quantitative analysis of the unknown samples.

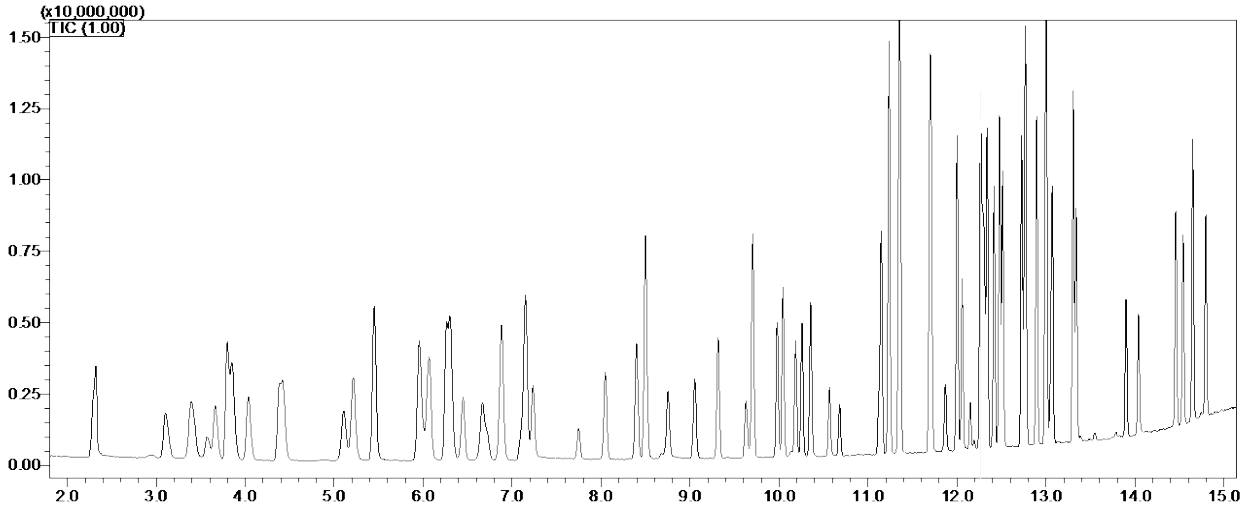


Fig. 2. Total Ion Chromatogram the High Concentration Mixture of 8260 MegaMix Calibration Mix (76 components) with 8260 Internal Standard Mix (4 components).

Table 4. R and R^2 Values in ICAL, ICV Recovery, CCV Accuracy, S/N at LLOQ, and Calculated MDL at 5 and 10 ng/mL for the Target VOCs

ID No	Criteria	ICAL		ICV	CCV	LLOQ	Calculated MDL (ng/mL)	
		R	R^2	Accuracy (%)	Accuracy (%)	S/N at 0.5 ng/mL	at 0.5 ng/mL	at 1.0 ng/mL
		> 0.995	> 0.99	70 - 130 %	80 - 120 %	> 10	Nil	Nil
1	Ethyl ether	0.99992	0.99984	115	99	13.7	0.07	0.55
2	1,1-Dichloroethene	0.99990	0.99980	110	100	56.6	0.05	0.45
3	CFC-113	0.99912	0.99825	136	101	14.2	0.11	0.54
4	Iodomethane	0.99997	0.99995	112	97	73.1	0.04	0.45
5	Carbon disulfide	0.99990	0.99979	103	94	83.0	0.06	0.46
6	Allyl chloride	0.99997	0.99994	104	93	15.9	0.08	0.41
7	Methylene chloride	0.99999	0.99997	118	103	39.7	0.10	0.77
8	2-Propenenitrile	0.99970	0.99940	121	102	12.2	0.18	0.65
9	trans-1,2-Dichloroethene	0.99998	0.99995	106	98	64.3	0.06	0.48
10	1,1-Dichloroethane	0.99998	0.99997	111	97	84.6	0.07	0.62
11	Chloroprene	0.99995	0.99989	128	104	25.8	0.12	0.74
12	2,2-Dichloropropane	0.99994	0.99989	192	174	13.6	0.80	1.26
13	cis-1,2-Dichloroethene	0.99998	0.99996	239	235	22.7	1.14	2.13
14	Bromochloromethane	0.98998	0.98005	96	92	29.2	0.42	0.69
15	Trichloromethane	0.99997	0.99994	109	103	79.6	0.81	0.92
16	1,1,1-Trichloroethane	0.99995	0.99991	107	107	20.3	0.38	0.57
17	Carbon Tetrachloride	0.99998	0.99995	117	113	29.1	0.15	0.50
18	1,1-Dichloropropene	0.99999	0.99998	104	101	37.5	0.04	0.40
19	Benzene	0.99997	0.99993	105	102	207.6	0.03	0.04
20	1,2-Dichloroethane	0.99993	0.99986	113	105	60.5	0.04	0.07
21	Trichloroethene	0.99998	0.99996	107	118	133.5	0.05	0.11
22	1,2-Dichloropropane	1.00000	0.99999	109	103	29.2	0.04	0.04
23	Dibromomethane	0.99996	0.99993	108	104	70.7	0.07	0.25
24	Methyl methacrylate	0.99992	0.99983	93	100	31.9	0.07	0.13
25	Bromodichloromethane	0.99999	0.99999	111	107	53.2	0.08	0.29
26	cis-1,3-Dichloropropene	0.99998	0.99997	112	98	43.0	0.06	0.24
27	Toluene	0.99996	0.99993	105	103	248.5	0.10	0.24
28	trans-1,3-Dichloropropene	0.99998	0.99995	109	92	35.0	0.04	0.18
29	Ethyl methacrylate	0.99997	0.99994	156	103	42.8	0.08	0.22
30	1,1,2-Trichloroethane	0.99999	0.99998	114	103	20.7	0.06	0.29
31	Tetrachloroethene	0.99996	0.99993	111	118	209.8	0.07	0.06
32	1,3-Dichloropropane	0.99998	0.99996	109	104	12.4	0.06	0.25
33	Dibromochloromethane	0.99999	0.99997	117	112	81.1	0.05	0.23
34	1,2-Dibromoethane	0.99997	0.99993	110	103	133.6	0.06	0.22
35	Chlorobenzene	0.99999	0.99998	105	102	156.6	0.01	0.02
36	1,1,1,2-Tetrachloroethane	0.99999	0.99998	110	110	46.7	0.04	0.15
37	Ethylbenzene	0.99997	0.99994	100	102	156.7	0.02	0.05
38	m,p-Xylene	0.99998	0.99996	100	101	221.5	0.02	0.09
39	o-Xylene	1.00000	1.00000	100	103	179.1	0.02	0.06
40	Styrene	1.00000	1.00000	104	99	397.9	0.02	0.08
41	Tribromomethane	0.99998	0.99996	116	111	43.1	0.06	0.17
42	Isopropylbenzene	0.99990	0.99980	97	105	237.3	0.30	0.74
43	cis-1,4-Dichloro-2-butene	0.99999	0.99997	126	80	26.0	0.45	0.47
44	1,1,2,2-Tetrachloroethane	0.99999	0.99998	113	80	43.9	0.19	0.65
45	Bromobenzene	0.99996	0.99992	106	104	167.3	0.10	0.32
46	trans-1,4-Dichloro-2-butene	0.99997	0.99993	110	72	25.5	0.21	0.46
47	1,2,3-Trichloropropane	0.99999	0.99997	111	104	16.5	0.20	0.86
48	Propylbenzene	0.99990	0.99980	104	105	261.1	0.03	0.14
49	Chlorotoluene	0.99991	0.99981	105	105	156.9	0.05	0.25
50	1,3,5-Trimethylbenzene	0.99988	0.99977	103	105	86.8	0.02	0.15
51	1-Chloro-4-methylbenzene	0.99994	0.99988	104	102	167.6	0.14	0.25
52	t-Butylbenzene	0.99998	0.99997	127	105	75.1	0.04	0.23
53	Pentachloroethane	0.99948	0.99895	99	16	23.2	0.32	0.21
54	1,2,4-Trimethylbenzene	0.99995	0.99990	104	102	39.8	0.69	1.24
55	sec-Butylbenzene	0.99993	0.99987	105	106	29.9	0.02	0.14
56	1,3-Dichlorobenzene	0.99997	0.99995	107	102	386.8	0.02	0.07
57	4-Isopropyltoluene	0.99992	0.99985	102	104	94.2	0.08	0.20
58	1,4-Dichlorobenzene	0.99997	0.99995	105	102	400.1	0.01	0.02
59	n-Butylbenzene	0.99995	0.99991	99	105	10.7	0.06	0.16
60	1,2-Dichlorobenzene	0.99999	0.99998	107	104	275.8	0.03	0.07
61	1,2-Dibromo-3-chloropropane	0.99998	0.99995	120	109	60.3	0.24	0.78
62	1,2,4-Trichlorobenzene	1.00000	0.99999	101	97	68.9	0.05	0.10
63	Hexachloro-1,3-butadiene	0.99996	0.99993	102	104	79.4	0.14	0.44
64	Naphthalene	0.99999	0.99997	112	105	392.6	0.07	0.22
65	1,2,3-Trichlorobenzene	1.00000	0.99999	104	101	65.5	0.05	0.12

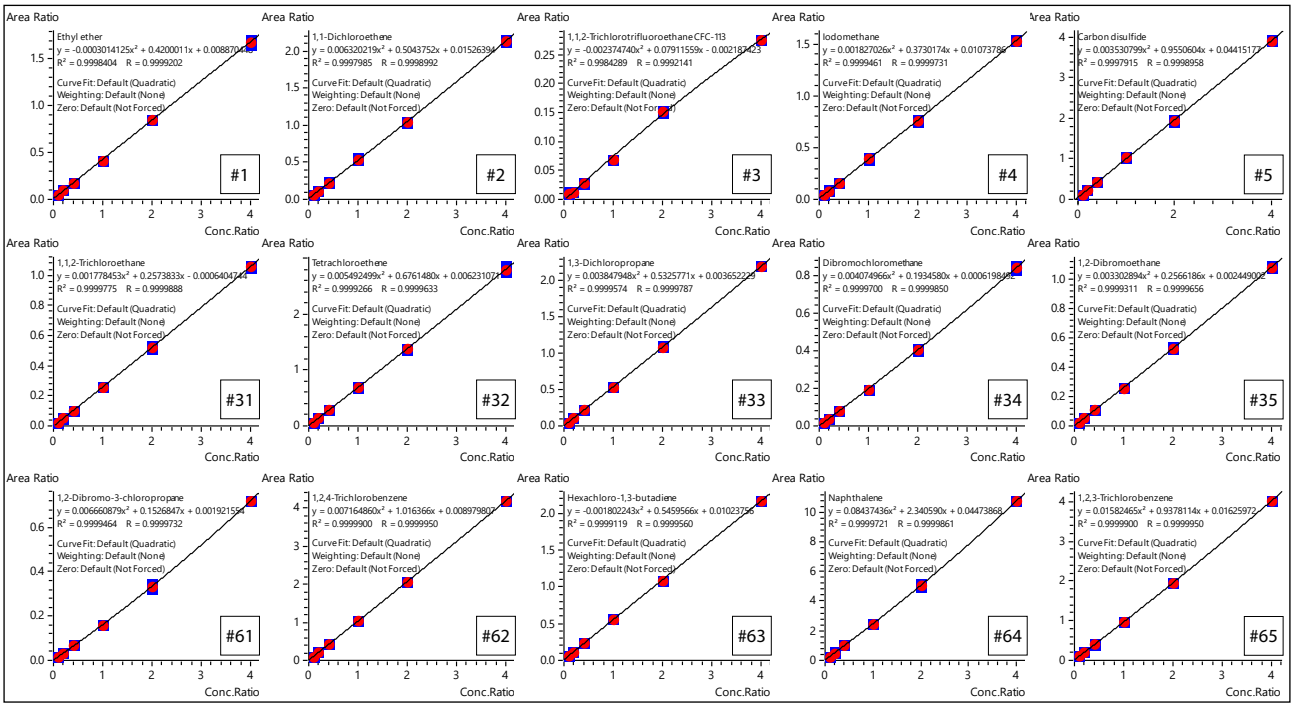


Fig. 3. Calibration Curve of (#1) Ethyl ether, (#2) 1,1-Dichloroethene, (#3) CFC-113, (#4) Iodomethane, (#5) Carbon disulfide, (#31) Tetrachloroethene, (#32) 1,3-Dichloropropane, (#33) Dibromochloromethane, (#34) 1,2-Dibromoethane, (#35) Chlorobenzene, (#61) 1,2-Dibromo-3-chloropropane, (#62) 1,2,4-Trichlorobenzene, (#63) Hexachloro-1,3-butadiene, (#64) Naphthalene, and (#65) 1,2,3-Trichlorobenzene.

Lower Limit of Quantitation (LLOQ)

The LLOQ of the 58 target analytes that passed all criteria, including the ICAL, ICV and CCV criteria, was determined to be 0.5 ng/mL with S/N of more than 10 (Table 4). The recalculated concentration of all target VOCs at LLOQ were within 50 % of the true value, ranging from 0.36 to 0.65 ng/mL.

Method Detection Limit (MDL)

The MDL was calculated based on the MDL procedure outlined in 40 CFR 136 Appendix B published by US EPA[4]. The calculated MDL of each target VOC at 0.5 ng/mL and 1.0 ng/mL is tabulated in Table 4.

Quantitation of Unknown Samples

The concentrations of the target VOCs in unknown samples was determined using the same technique. Table 5 shows concentration of the detected target VOCs in both Tap Water (TP) and Chilled Tap Water (CTW) samples.

■Conclusion

The analysis results unequivocally validate the concept of using trap-headspace system as a viable pretreatment method for further exploration and application for the US EPA Method 8260D.

Table 5. Concentration of the Detected Target VOCs in TW Repetitive #1 & #2 and CTW Repetitive #1 & #2.

ID No.	Compound Names	Concentration (ppb)			
		TW#1	TW#2	CTW#1	CTW#2
7	Methylene chloride	-	-	19.81	21.70
15	Trichloromethane	19.03	18.84	7.11	7.06
17	Carbon Tetrachloride	0.51	0.56	<LOQ*	<LOQ*
24	Methyl methacrylate	-	-	<LOQ*	<LOQ*
25	Bromodichloromethane	5.46	5.40	2.48	2.47
27	Toluene	-	-	12.03	11.50
33	Dibromochloromethane	1.87	1.86	1.26	1.29
41	Tribromomethane	<LOQ*	<LOQ*	<LOQ*	<LOQ*
57	4-Isopropyltoluene	-	-	<LOQ*	<LOQ*

*<LOQ = Detected below LOQ

■References

1) US EPA Method 8260D, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, February 2017.
2) Shimadzu Guide to BFB Tuning for Analysis of Volatile Organic Compounds, Application News No. SSI-GCMS-1405.
3) US EPA Method 524.4, Measurement of Purgeable Organic Compounds in Water by Gas Chromatography /Mass Spectrometry Using Nitrogen Purge Gas, May 2013.
4) Definition and Procedure for the Determination of the Method Detection Limit. Fed. Regist. 1984. 49 (209), Appendix B to Part 136.

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