SHIMADZU

WP 257

Analysis of Volatile Organic Compounds in Water Using Dynamic Headspace-GCMS in Accordance with US EPA Method 8260D

Elvi Horiyanto, Elgin Guo Wei Ting, Chun Kiang Chua, Cynthia Melanie Lahey
Shimadzu (Asia Pacific) Pte. Ltd., Singapore

INTRODUCTION

The US EPA defines volatile organic compounds (VOCs) as highly evaporative substances that can contaminate underground water through improper waste disposal, posing health risks such as cancer and nervous system damage. US EPA developed Method 8260D, using purge and trap with a single quadrupole GCMS, to quantify these VOCs to safeguard public health and the environment.[1] Our study introduces an alternative method employing a dynamic headspace autosampler with a cold trap, coupled to a single quadrupole GCMS system (**Fig. 1**), which concentrates VOCs for heightened sensitivity during analysis and yielding comparable results to the traditional method.

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

EXPERIMENTAL

2.1. Instrumental, Analytical Conditions & Software

The analysis was performed on GCMS-QP2020 NX with HS-20 NX (Trap Model) (Shimadzu Corporation, Japan), as shown in **Fig. 1**, while the details of the analytical conditions 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, as well as ***Peakintelligence™ for GCMS*** that incorporates Shimadzu AI-powered integrator that provides highly accurate peak integration at a fraction of the time.

Table 1 Analytical conditions for the analysis of VOCs using dynamic HS-GCMS

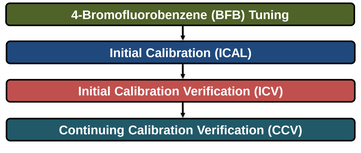
Headspace Parameters		**Gas Chromatograph Parameters**	
HS Mode	Trap	Injection Mode	Split (5.0)
HS Oven Temp.	60 °C	Carrier Gas	Helium
Sample & Transfer Line Temp.	150 °C	Flow Control Mode	Linear Velocity
Pressurizing Gas Pressure	57.0 kPa	Linear Velocity	36.2 cm/s
Equilibrating Time	30.0 min	Column Temp. Program	35 °C (5 min) 11 °C/min to 60 °C 20 °C/min to 220 °C (5 min)
Load Time	0.30 min		
Injection Time	20.0 min		
Trap Cooling Temp.	-10 °C	**Mass Spectrometer Parameters**	
Trap Desorption Temp.	250 °C	Ion Source & Interface Temp.	230 °C & 220 °C
Multi Injection Count	10	Acquisition Mode	SIM

2.2. Standards Preparation

- VOC standard, internal standard (IS) and surrogate mixtures were purchased from Restek Corporation. 65 out of 76 VOCs were selected as target analytes in this study.
- Initial calibration (ICAL) solutions were prepared at 0.5, 1, 2, 5, 10 to 20 ng/mL, and 5 ng/mL for IS and surrogates.
- Initial calibration verification (ICV) was performed by using a standard from the same manufacturer, but of a different batch from that of the ICAL.
- Continuing calibration verification (CCV) standard was prepared at the same concentration as ICAL mid-point level (5 ng/mL).

RESULTS

In accordance with US EPA method 8260D, the QC procedures were performed prior to analysis of sample but not limited to the following:



3.1. Instrument Performance Check – BFB Tuning

Result of BFB tuning is tabulated in **Table 2**.

Table 2 BFB relative abundance results

m/z	Suggested Criteria	BFB Relative Abundance (%)	Result Status
95	50-200 % of *m/z* 174	139.8	Pass
96	5-9 % of *m/z* 95	6.4	Pass
173	<2 % of *m/z* 174	0.9	Pass
174	50-200 % of *m/z* 95	71.5	Pass
175	5-9 % of *m/z* 174	6.7	Pass
176	95-105 % of *m/z* 174	97.7	Pass
177	5-10 % of *m/z* 176	6.1	Pass

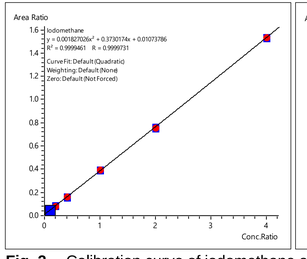
3.2. ICAL, ICV and CCV

The criteria and results of ICAL, ICV and CCV are shown in **Table 3**:

- 6-point ICAL was built with quadratic regression calibration model. 64 out of the 65 target VOCs passed ICAL criteria. Example of calibration curves are displayed in **Fig. 2**.
- 61 out of the 65 target VOCs passed ICV criteria.
- 59 out of the 65 target VOCs passed CCV criteria.

Table 3 R and R^2 values in ICAL, ICV recovery, CCV accuracy, S/N at LLOQ, and calculated MDL at 5 and 10 ng/mL of target VOCs

No	Compounds \ 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	0.00
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



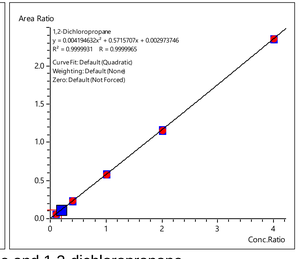


Fig. 2 Calibration curve of iodomethane and 1,2-dichloropropane

- ICAL 4 which was the mid-ICAL with a concentration of 5 ng/mL, was taken as a reference for the retention time, ion ratio and IS response check within the analysis.
- Method blanks (MB) were analyzed before and after ICAL acquisition to ensure negligible contamination from the environment and carryover in the system. No significant peak was detected in MB.

3.3. Lower Limit of Quantitation (LLOQ)

The LLOQ of the 59 target analytes were determined to be 0.5 ng/mL with S/N of more than 10 (see **Table 3**). The standard recalculated concentration of all target analytes were within 50 % of the true value, ranging from 0.36 - 0.65 ng/mL.

3.4. Method Detection Limit (MDL)

The calculated MDL of each VOC at 0.5 ng/mL and 1.0 ng/mL are shown in **Table 3**.[2]

CONCLUSION

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

Reference

1) US EPA Method 8260D, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, February 2017.
2) Definition and Procedure for the Determination of the Method Detection Limit. Fed. Regist. 1984. 49 (209), Appendix B to Part 136.