Application Note

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Determination of Volatile Organic Compounds in Water by Purge and Trap Gas Chromatography/Mass Spectrometry

Using the Chinese Ministry of Environmental Protection method HJ 639-2012

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Abstract

This application note highlights the determination of 57 volatile organic compounds (VOCs) in water using an Agilent Intuvo 9000 GC, an Agilent 5977B GC/MSD, and a Teledyne Tekmar Atomx XYZ purge and trap sample preparation system. Great performance was achieved with linearity across the expected range of concentrations and repeatability through eight injections. The limit of detection (LOD) and limit of quantitation (LOQ) were researched in both scan and selected ion monitoring (SIM) modes.

Introduction

The detection of VOCs is important in ensuring high water quality. Typically, headspace (HS) or purge and trap (P&T) coupled with GC or GC/MS is used for the analysis of VOCs in water. P&T technology is generally more sensitive than HS injection for VOC sample introduction, which is also known as dynamic headspace sampling. Theoretically, almost all the samples are purged out of the matrix and into the chromatographic system with P&T technology. Thus, the P&T sampler has been widely welcomed and used in many laboratories for VOC analysis for higher sensitivity. HJ 639-2012 is a P&T GC/MS method from the Chinese Ministry of Environmental Protection, which is used for the determination of VOCs in water.[1]

This application note demonstrates that an Intuvo 9000 GC combined with a 5977B GC/MSD with a P&T sampler can easily achieve the performance specifications for VOCs in method HJ 639-2012. The calibration curves determined for those target compounds were found to be within the method requirements. The correlation coefficients were also well above 0.9989. The area % RSD was studied for each compound in scan mode and was determined to be 0.9 to 7.6%. The LOD was ≤1.6 µg/L in scan mode and ≤0.33 µg/L in SIM mode.

Experimental

The P&T GC/MS system used for these experiments is described in Table 1.

Sample preparation

A stock solution of 57 VOCs and three surrogates at a concentration of 100 µg/mL was prepared in methanol. Some intermediate stock solutions were prepared for scan and SIM modes, respectively.

Calibration standard preparation is critical for successful VOC analysis. Calibration solutions from 5 to 200 µg/L for scan mode and 1 to 40 µg/L for SIM mode were prepared. Calibrants were prepared by the P&T device automatically using the manually prepared intermediate stock solutions.

Table 1. Instrument conditions, method type: water. TekLink method for the P&T system with 5 mL purge vessel using trap number 9.

Parameter	Value
Teledyne Tekmar Atomx XYZ P&T Sample Preparation System	
Standby	
Valve Oven Temperature	140 °C
Transfer Line Temperature	140 °C
Sample Mount Temperature	90 °C
Water Heater Temperature	90 °C
Sample Cup Temperature	20 °C
Soil Valve Temperature	100 °C
Standby Flow	10 mL/min
Purge Ready Temperature	40 °C
Purge	
Presweep Time	0.25 min
Prime Sample Fill Volume	3 mL
Sample Volume	5 mL
Sweep Sample Time	0.25 min
Sweep Sample Flow	100 mL/min
Purge Time	11 min
Purge Flow	40 mL/min
Purge Temperature	20 °C
MCS Purge Temperature	20 °C
Dry Purge Time	1 min
Dry Purge Flow	100 mL/min
Dry Purge Temperature	20 °C

Parameter	Value
Desorb	
Water Needle Rinse Volume	7 mL
Sweep Needle Time	0.25 min
Desorb Preheat Temperature	245 °C
Desorb Time	2 min
Drain Flow	300 mL/min
Desorb Temperature	250 °C
GC Start Signal	Begin desorb
Bake	
Number Of Water Bake Rinses	1
Water Bake Rinse Volume	7 mL
Bake Rinse Sweep Time	0.25 min
Bake Rinse Sweep Flow	100 mL/min
Bake Rinse Drain Time	0.4 min
Bake Time	2 min
Bake Flow	200 mL/min
Bake Temperature	280 °C
MCS Bake Temperature	180 °C

Parameter	Value
Agilent Intuvo 9000 GC	
Inlet	220 °C, split 30:1
Liner	Agilent Ultra Inert inlet liner, straight, 2 mm id (p/n 5190-6168)
Column	Agilent J&W DB-624 UI, 30 m × 0.25 mm, 1.4 µm (p/n 122-1334UI-INT)
Carrier	Helium, 1 mL/min, constant flow
Guard Chip	Track oven
Bus Temperature	220 °C
Oven	35 °C (2 min), then 5 °C/min to 120 °C, then 10 °C/min to 220 °C (2 min)
Transfer Line Temperature	250 °C
Agilent 5977B GC/MSD	
Parameter	Value
Ionization Type	EI
Source Temperature	230 °C
Quad Temperature	150 °C
Drawout Plate	6 mm
Tune File	BFB_Atune.u
Acquisition Type	Scan or SIM
Solvent Delay	2 min
Gain Factor	1

An internal standard mixture of fluorobenzene and 1,4-dichlorobenzene-d_4 was diluted with methanol to a concentration of 25 µg/mL. The internal standard was added into each 5 mL sample automatically by P&T.

Results and discussion

Full scan data acquisition (scan) and selected ion monitoring (SIM) are both introduced and accepted by method HJ 639-2012. For unknown samples with high concentration, scan mode can be used for qualitative and quantitative analysis. However, SIM mode uses a defined compound list with known quantitation and qualifier ions. SIM mode typically results in a sensitivity increase compared to scan mode. In this application, data were collected in both scan mode and SIM mode. Figure 1 shows a typical chromatogram of the 57 target compounds plus two internal standards and three surrogate standards at a concentration of 10 µg/L with SIM mode.

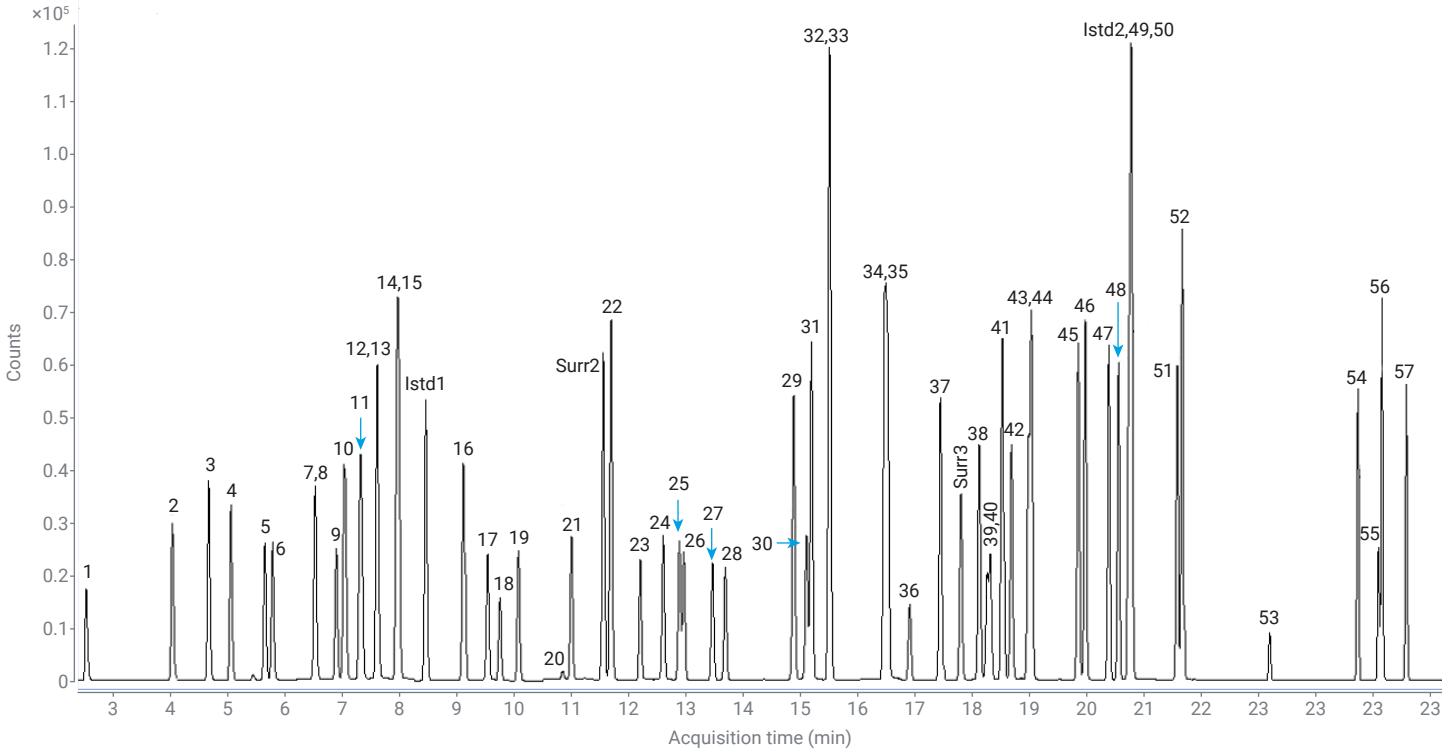

Figure 1. SIM total ion chromatogram of the 57 target VOCs (10 µg/L).

The system was calibrated at five levels in scan mode: 5, 25, 50, 100, and 200 µg/L. The system was also calibrated at another five levels in SIM mode: 1, 5, 10, 20, and 40 µg/L. Each calibration level contained 57 compounds plus two internal standards and three surrogate standards. Linearity across the range studied gave R^2 values of 0.9989 or greater for all compounds with both acquisition modes, as shown in Table 2. Repeatability (n = 8) was tested at 5 µg/L and 100 µg/L levels in scan mode. As Table 3 shows, the area % RSD was 0.9 to 7.6%. Table 3 also gives the results of the LOD and LOQ study for 57 compounds in scan mode and SIM mode. For scan mode, the LOD and LOQ study was performed at 5 µg/L with eight replicate analyses. All LODs are below 1.6 µg/L. For SIM mode, the LOD and LOQ study was performed at 1 µg/L with eight replicate analyses. All LODs are below 0.33 µg/L while most compounds produce LODs below 0.2 µg/L.

Table 2. R^2 values for 57 VOCs in calibration standards for both scan and SIM modes, including two internal standards (ISTD) and three surrogate standards (SURR).

	Name	RT (min)	*m/z*	R^2	
				Scan	SIM
ISTD 1	Fluorobenzene	8.472	96		
1	Vinyl chloride	2.547	62	0.9998	0.9999
2	1,1-Dichloroethene	4.045	96	0.9998	0.9998
3	Methylene chloride	4.682	84	0.9999	0.9996
4	*trans*-1,2-Dichloroethene	5.068	96	0.9999	0.9998
5	1,1-Dichloroethane	5.666	63	0.9998	0.9997
6	2-Chloro-1,3-butadiene	5.804	53	0.9998	0.9999
7	2,2-Dichloropropane	6.54	77	0.9995	0.9991
8	*cis*-1,2-Dichloroethane	6.55	95.9	0.9999	0.9999
9	Bromochloromethane	6.923	128	1.0000	0.9997
10	Chloroform	7.058	83	0.9999	0.9997
SURR 1	Dibromofluoromethane	7.319	111	1.0000	0.9999
11	1,1,1-Trichloroethane	7.351	97	0.9998	0.9998
12	Carbon tetrachloride	7.624	116.9	0.9997	0.9999
13	1,1-Dichloropropene	7.627	75	0.9998	0.9999
14	Benzene	7.974	78	0.9998	0.9998
15	1,2-Dichloroethane	8.013	62	0.9989	0.9996
16	Trichloroethylene	9.145	132	0.9999	0.9993
17	1,2-Dichloropropane	9.556	63	0.9999	0.9999
18	Dibromomethane	9.772	174	0.9999	0.9999
19	Bromodichloromethane	10.1	83	1.0000	0.9999
20	1-Chloro-2,3-epoxypropane	10.865	57	0.9997	0.9998
21	*cis*-1,3-Dichloropropene	11.029	75	1.0000	0.9997
SURR 2	Toluene-d_8	11.572	98	0.9999	0.9998
22	Toluene	11.708	91	0.9998	0.9998
23	*trans*-1,3-Dichloropropene	12.235	75	1.0000	0.9997
24	1,1,2-Trichloroethane	12.624	96.9	1.0000	0.9999
25	Tetrachloroethylene	12.904	166	0.9999	0.9999
26	1,3-Dichloropropane	12.987	76	1.0000	0.9999
27	Dibromochloromethane	13.476	129	0.9999	0.9998
28	1,2-Dibromoethane	13.695	107	0.9999	0.9999
ISTD 2	1,4-Dichlorobenzene	20.729	152		
29	Chlorobenzene	14.904	112	0.9996	0.9998
30	1,1,1,2-Tetrachloroethane	15.122	130.9	0.9998	0.9997
31	Ethylbenzene	15.212	91	0.9992	0.9999
32, 33	*m*-Xylene, *p*-Xylene	15.514	91	0.9993	0.9996
34	*o*-Xylene	16.489	91.1	0.9995	0.9999
35	Styrene	16.537	104	0.9997	0.9999
36	Bromoform	16.92	173	0.9998	0.9998
37	Isopropylbenzene	17.466	105	0.9993	0.9999
SURR 3	4-Bromofluorobenzene	17.813	174	0.9997	0.9999
38	Bromobenzene	18.138	156	0.9998	0.9999
39	1,1,2,2-Tetrachloroethane	18.276	83	0.9999	0.9993
40	1,2,3-Trichloropropane	18.334	75	0.9998	0.9996
41	*n*-Propylbenzene	18.543	91	0.9992	0.9999
42	2-Chlorotoluene	18.694	91	0.9996	0.9999
43	4-Chlorotoluene	18.994	91	0.9997	0.9999
44	1,3,5-Trimethylbenzene	19.048	105	0.9995	0.9998
45	*tert*-Butylbenzene	19.862	119	0.9996	0.9997
46	1,2,4-Trimethylbenzene	19.987	105	0.9996	0.9998
47	*sec*-Butylbenzene	20.402	105	0.9993	0.9999
48	1,3-Dichlorobenzene	20.572	146	0.9998	0.9999
49	*p*-Isopropyltoluene	20.775	119	0.9996	0.9999
50	1,4-Dichlorobenzene	20.788	146	0.9999	0.9999
51	1,2-Dichlorobenzene	21.598	146	0.9998	1.0000
52	*n*-Butylbenzene	21.685	91	0.9995	0.9998
53	1,2-Dibromo-3-chloropropane	23.206	157	0.9990	0.9993
54	1,2,4-Trichlorobenzene	24.749	182	0.9997	0.9997
55	Hexachlorobutadiene	25.103	225	0.9999	0.9999
56	Naphthalene	25.164	128	0.9998	0.9995
57	1,2,3-Trichlorobenzene	25.588	179.9	0.9997	0.9999

Table 3. RSD, LOD, and LOQ for VOCs.

Name	Scan				SIM	
	Area % RSD					
	5 µg/L	100 µg/L	LOD	LOQ	LOD	LOQ
Vinyl chloride	3.4	3.9	0.85	2.85	0.11	0.36
1,1-Dichloroethene	3.1	3.8	0.83	2.78	0.11	0.35
Methylene chloride	1.7	2.3	0.81	2.70	0.06	0.21
trans-1,2-Dichloroethene	2.7	3.6	0.90	3.01	0.10	0.35
1,1-Dichloroethane	2.6	2.8	0.81	2.71	0.08	0.25
2-Chloro-1,3-butadiene	3.2	3.7	0.47	1.56	0.10	0.32
2,2-Dichloropropane	1.7	2.9	0.77	2.57	0.33	1.10
cis-1,2-Dichloroethane	7.6	6.6	1.60	5.33	0.07	0.24
Bromochloromethane	1.4	2.4	0.83	2.78	0.05	0.16
Chloroform	2.3	2.8	0.95	3.15	0.07	0.24
Dibromofluoromethane	2.2	2.5	0.89	2.97	0.07	0.23
1,1,1-Trichloroethane	2.6	3.5	0.81	2.72	0.10	0.32
Carbon tetrachloride	2.7	3.8	0.86	2.88	0.10	0.34
1,1-Dichloropropene	3.5	3.5	0.87	2.90	0.10	0.33
Benzene	2.5	2.9	0.82	2.75	0.08	0.28
1,2-Dichloroethane	1.3	1.6	0.85	2.82	0.04	0.15
Trichloroethylene	3	4.5	0.63	2.11	0.08	0.27
1,2-Dichloropropane	1.8	2.3	0.79	2.62	0.06	0.20
Dibromomethane	2.4	2.5	0.95	3.15	0.04	0.12
Bromodichloromethane	2	2	0.92	3.05	0.06	0.19
1-Chloro-2,3-epoxypropane	4.2	4.9	1.20	3.99	0.08	0.27
cis-1,3-Dichloropropene	1.9	1.1	0.93	3.11	0.07	0.24
Toluene-d_8	2.4	2.9	0.85	2.84	0.08	0.28
Toluene	1.9	3	0.83	2.76	0.08	0.27
trans-1,3-Dichloropropene	2.7	1	1.03	3.44	0.07	0.23
1,1,2-Trichloroethane	1.7	2	0.87	2.91	0.04	0.14
Tetrachloroethylene	2.4	3.4	0.83	2.76	0.09	0.30
1,3-Dichloropropane	0.9	1.9	0.83	2.76	0.04	0.13
Dibromochloromethane	1.5	2.1	0.91	3.03	0.04	0.14
1,2-Dibromoethane	1.3	2.5	0.87	2.90	0.03	0.11

Name	Scan				SIM	
	Area % RSD					
	5 µg/L	100 µg/L	LOD	LOQ	LOD	LOQ
Chlorobenzene	2.5	2.5	0.71	2.37	0.15	0.49
1,1,1,2-Tetrachloroethane	3.3	2.3	0.80	2.66	0.13	0.42
Ethylbenzene	2.4	3	0.75	2.50	0.16	0.53
m-Xylene, *p*-Xylene	3.2	3.2	0.88	2.94	0.16	0.53
o-Xylene	2.5	2.6	0.76	2.52	0.15	0.50
Styrene	1.8	2.1	0.74	2.48	0.17	0.55
Bromoform	2.7	2.5	0.87	2.89	0.13	0.45
Isopropylbenzene	2.9	3.1	0.80	2.68	0.16	0.54
4-Bromofluorobenzene	5.6	2.4	1.11	3.69	0.17	0.56
Bromobenzene	2.2	1.9	0.72	2.40	0.16	0.52
1,1,2,2-Tetrachloroethane	3.9	4.9	0.96	3.18	0.26	0.87
1,2,3-Trichloropropane	4.3	3.4	0.87	2.89	0.14	0.45
n-Propylbenzene	2.7	3.1	0.81	2.69	0.19	0.64
2-Chlorotoluene	2.9	2.7	0.79	2.62	0.17	0.57
4-Chlorotoluene	4.6	2.6	0.60	2.01	0.19	0.62
1,3,5-Trimethylbenzene	3	2.7	0.84	2.79	0.18	0.59
tert-Butylbenzene	2.5	3.1	0.69	2.29	0.16	0.52
1,2,4-Trimethylbenzene	2.8	2.6	0.83	2.75	0.18	0.59
sec-Butylbenzene	3.3	3.1	0.90	3.01	0.20	0.67
1,3-Dichlorobenzene	2.9	2.3	0.88	2.93	0.18	0.61
p-Isopropyltoluene	3.5	2.9	0.91	3.02	0.21	0.70
1,4-Dichlorobenzene	3	2.2	0.86	2.85	0.18	0.60
1,2-Dichlorobenzene	1.9	1.9	0.78	2.59	0.16	0.54
n-Butylbenzene	5.3	3	1.16	3.88	0.27	0.91
1,2-Dibromo-3-chloropropane	2.7	5.4	0.89	2.95	0.09	0.32
1,2,4-Trichlorobenzene	5.1	2	1.15	3.85	0.22	0.72
Hexachlorobutadiene	5.7	2.9	1.19	3.96	0.23	0.78
Naphthalene	3.5	2.9	0.99	3.30	0.18	0.59
1,2,3-Trichlorobenzene	4.8	1.8	1.11	3.71	0.19	0.64

Conclusion

This application note demonstrates the reliable capability of the Agilent Intuvo 9000 GC, the Agilent 5977B GC/MSD, and the Teledyne Tekmar Atomx XYZ P&T sample preparation system to process VOCs in water. Both scan and SIM modes achieve excellent results and meet the requirements specified in method HJ 639-2012.

Reference

1. Water quality – Determination of Volatile Organic Compounds – Purge and Trap/Gas Chromatography-Mass Spectrometer. Chinese Ministry of Environmental Protection, method HJ 639-2012.

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