GC-MS
APPLICATION NOTES

Determination of volatile organic compounds in water

GC-MS

GBC

Introduction

Volatile Organic Compounds (VOCs) in the sample were purged by high purity helium (or nitrogen) and then adsorbed in the collection tube. Then, the collection tube is heated and backflushed with high purity helium. The desorbed components were separated by a gas chromatograph and were detected by a mass spectrometer. The internal standard was determined by comparing the retention time of the target compound and the standard mass spectrum or characteristic ions.

Experimental

Instrumentation and reagents

A GBC Aludra GC-MS equipped with an OI 4760 purge and trap concentrator was used for this experiment. Reagents utilized were 56 VOCs standard solutions, two internal standards, three substitute standard solutions, methanol (chromatographically pure), and purified water.

Experimental instrument conditions

Experimental purge and trap conditions

Sample Temperature: Room temperature

Purge time: 11 min

Purge gas flow: 35 mL/min

Trap: Trap-10

Desorption temperature: 190℃

Desorption time: 2 min

Baking temperature: 210℃

Baking time: 10 min

Transmission line temperature: 130℃

Six-way valve box temperature: 130℃

Water processor temperature: purge state 110℃

Desorption state: 0℃

Baking state: 240℃

Experimental GC conditions

Column: VF-624 ms (30 m × 0.25 mm 1.4 μm) quartz capillary column

Carrier gas: high purity helium

Column pressure: 55 Kpa

Split injection, split ratio: 25:1

Inlet: 220℃

Interface: 230℃

Column box: Hold at 35℃ for 3 min, increase 5℃/min to 200℃ and hold 2 min.

Experimental MS conditions

Ion source: EI source

Electron energy: 70 eV

Ion source temperature: 200℃

Interface temperature: 230℃

Solvent delay: 2 min

Scan mode: full scan qualitative

Scan range: 45~270 u

SIM scan quantification, SIM scan segment setting see Table 1.

Order	Time Period/min	Monitored Ions
1	2.0-3.3	62,64
2	3.3-6.3	49,53,61,63,65,83,84,86,88,96,98
3	6.3-9.3	47,49,51,61,62,64,70,75,77,78,79,83,85,96,97,98,99, 110,111,113,117,119,121,128,130,192
4	9.3-11.3	41,63,76,83,85,93,95,129,130,132,172,174
5	11.3-15.3	41,57,75,76,77,78,83,91,92,97,98,99,100,107,109, 110,127,129,131,164,166,188
6	15.3-17.3	77,91,106,112,114,117,131,133
7	17.3-21.0	75,77,78,83,85,91,95,103,104,105,106,110,120,126, 131,156,158,171,173,174,175,176
8	21.0-25.0	91,92,105,111,115,119,120,134,146,148,150,152
9	25.0-27.1	75,155,157
10	27.1-35.0	128,180,182,184,190,223,225,227,260

Table 1: VOC SIM scanning segmentation settings

Results

Standard spectrum

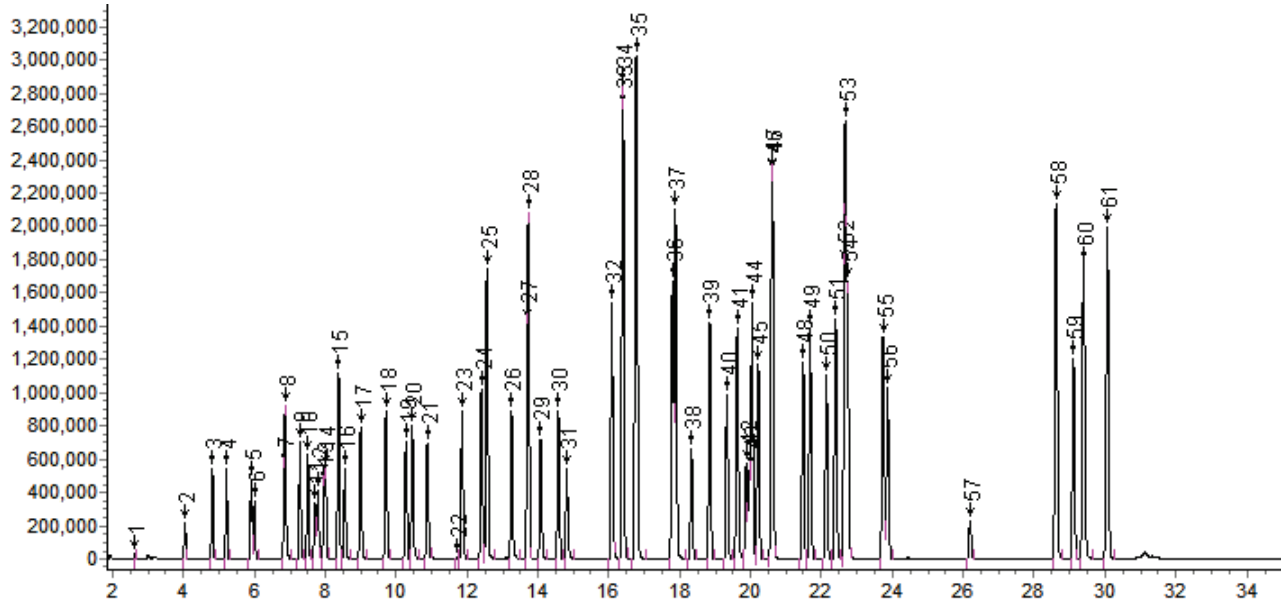

Figure 1: TIC for 61 VOCs (20 ppb)

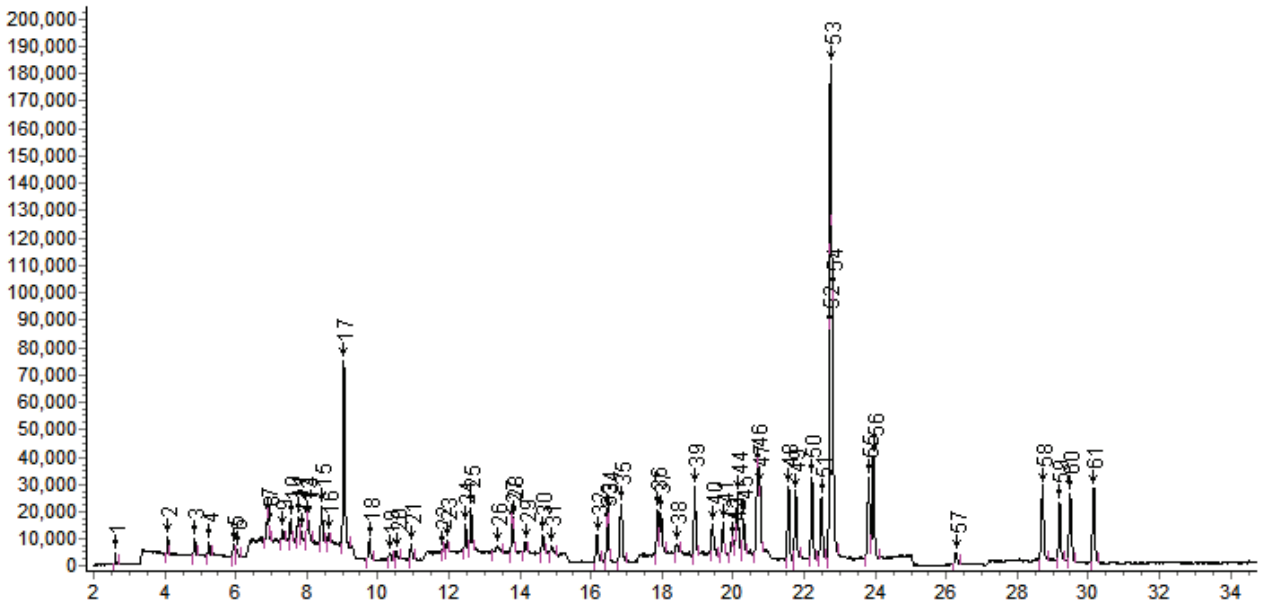

Figure 2: TIC for 61 VOCs (1 ppb)

No.	Compound	Retention Time	CAS Number	Characteristic Ion	Molecular Formula
1	Chloroethylene	2.59	75-01-4	62,64	C2H3Cl
2	1,1-Dichloroethylene	4.07	75-35-4	61,96,98	C2H2Cl2
3	Dichloromethane	4.83	75-09-2	84,49,86	CH2Cl2
4	*trans*-1,2-Dichloroethylene	5.24	156-60-5	61,96,98	C2H2Cl2
5	1,1-Dichloroethane	5.94	75-34-3	63,65,83	C2H4Cl2
6	2-Butynyl chloride	6.04	3355-17-7	53,88	C4H5Cl
7	2,2-Dichloropropane	6.87	594-20-7	77,79,97	C3H6Cl2
8	*cis*-1,2-dichloroethylene	6.91	156-59-2	61,96,98	C2H2Cl2
9	Bromochloromethane	7.33	74-97-5	130,128,49	CH2BrCl
10	Chloroform	7.54	67-66-3	83,85,47	CHCl3
11	1,1,1-Trichloroethane	7.76	71-55-6	97,99,61	C2H3Cl3
12	Dibromofluoromethane (Substitute)	7.83	1868-53-7	111,113,192	CHBr2F
13	Carbon tetrachloride	7.99	56-23-5	117,119,121	CCl4
14	1,3-Dichloropropene	8.05	542-75-6	75,110,77	C3H4Cl2
15	Benzene	8.42	71-43-2	78,51	C6H6
16	1,2-Dichloroethane	8.60	107-06-2	62,64,98	C2H4Cl2
17	Fluorobenzene (Internal Standard 1)	9.05	462-06-6	96,70	C6H5F
18	Trichloroethylene	9.77	79-01-6	130,132,95	C2HCl3
19	1,2-Dichloropropane	10.34	78-87-5	63,41,76	C3H6Cl2
20	Dibromomethane	10.52	74-95-3	174,93,172	CH2Br2
21	Bromodichloromethane	10.94	75-27-4	83,85,129	CHBrCl2
22	Epichlorohydrin	11.85	106-89-8	57,49	C9H14O4

No.	Compound	Retention Time	CAS Number	Characteristic Ion	Molecular Formula
23	*cis*-1,3-Dichloropropene	11.94	10061-01-5	75,55,110	C3H4Cl2
24	Toluene-d_8 (Substitute)	12.48	2037-26-5	98,100	C7D8
25	Methylbenzene	12.63	108-88-3	91,92	C7H8
26	*trans*-1,3-Dichloropropene	13.35	10061-02-6	75,77,110	C3H4Cl2
27	1,1,2-Trichloroethane	13.76	79-00-5	97,83,99	C2H3Cl3
28	Tetrachloroethylene	13.82	127-18-4	166,164,129	C2Cl4
29	1,3-Dichloropropane	14.16	142-28-9	76,78,41	C3H6Cl2
30	Dibromochloromethane	14.65	124-48-1	129,127,131	CHBr2Cl
31	1,2-Dibromoethane	14.90	106-93-4	107,109,188	C2H4Br2
32	Chlorobenzene	16.17	108-90-7	112,77,114	C6H5Cl
33	1,1,1,2-Tetrachloroethane	16.44	630-20-6	131,133,117	C2H2Cl4
34	Ethylbenzene	16.48	100-41-4	91,106	C8H10
35	*p*-Xylene	16.84	106-42-3	91,106	C8H10
36	*o*-Xylene	17.87	95-47-6	91,106	C8H10
37	Styrene	17.97	100-42-5	104,103,78	C8H8
38	Bromoform	18.41	75-25-2	173,171,175	CHBr3
39	Cumene	18.92	98-82-8	105,120	C9H12
40	1-Bromo-4-fluorobenzene (Substitute)	19.42	460-00-4	174,176,95	C6H4BrF
41	Bromobenzene	19.71	108-86-1	156,77,158	C6H5Br
42	1,1,2,2-Tetrachloroethane	19.95	79-34-5	83,85,131	C2H2Cl4
43	1,2,3-Trichloropropane	20.06	96-18-4	75,110,77	C3H5Cl3
44	Propylbenzene	20.12	103-65-1	91,120	C9H12
45	2-Chlorotoluene	20.28	95-49-8	91,126	C7H7Cl
46	4-Chlorotoluene	20.67	106-43-4	91,126	C7H7Cl
47	1,3,5-Trimethylbenzene	20.70	108-67-8	105,120	C9H12
48	*tert*-Butylbenzene	21.55	98-06-6	119,91,134	C10H14
49	1,2,4-Trimethylbenzene	21.75	95-63-6	105,120	C9H12
50	*sec*-Butylbenzene	22.21	135-98-8	105,134,91	C10H14
51	1,3-Dichlorobenzene	22.48	541-73-1	146,148,111	C6H4Cl2
52	*p*-Cymene	22.71	99-87-6	119,134,91	C10H14
53	1,4-Dichlorobenzene-d_4 (Internal Standard 2)	22.74	3855-82-1	152,115,150	C6H4Cl2
54	1,4-Dichlorobenzene	22.80	106-46-7	146,148,111	C6H4Cl2
55	1,2-Dichlorobenzene	23.82	95-50-1	146,148,111	C6H4Cl2
56	Butylbenzene	23.94	104-51-8	91,134	C10H14
57	1,2-Dibromo-3-chloropropane	26.27	96-12-8	157,155,75	C3H5Br2Cl

No.	Compound	Retention Time	CAS Number	Characteristic Ion	Molecular Formula
58	1,2,4-Trichlorobenzene	28.70	120-82-1	180,182,184	C6H3Cl3
59	Hexachlorobutadiene	29.18	87-68-3	225,227,223	C4Cl6
60	Naphthalene	29.48	91-20-3	128	C10H8
61	1,2,3-Trichlorobenzene	30.14	87-61-6	180,182,184	C6H3Cl3

Table 2: Information about various components for VOCs

Sample preparation and drawing the standard curve

Preparation of 56 VOCs mixed standard intermediate solutions

Accurately transfer 25 µL of 2000 µg/mL standard solution into 10 mL volumetric flask, dilute with methanol to scale, and shake well to obtain 5 µg/mL standard intermediate solution.

Preparation of 3 substitute solutions

Accurately transfer 25 µL 2000 µg/mL standard solution into a 10 mL volumetric flask, dilute with methanol to scale, and shake well to obtain 5 µg/mL substitute standard intermediate solution.

Preparation of 2 internal standard solutions

Accurately transfer 10 µL of 2000 µg/mL internal standard solution into 1.6 mL of methanol and shake well to obtain 12.5 µg/mL internal standard intermediate solution.

Transfer 1, 2, 4, 6, 8, 10, 20 µL of 5 µg/mL VOCs standard intermediate solutions and substitute intermediate solutions directly into the gas-tight syringes, each containing 5 mL of pure water. Add 4 µL of 12.5 µg /mL of internal standard intermediate solution. The concentrations of the target compound and the substitutes were 1, 2, 4, 6, 8, 10, and 20 ng/mL, and the concentration of the internal standard was 10 ng/mL. Then, inject these solutions into the purge and trap, starting from low concentrations to high concentrations following the above instrument conditions. Draw the standard curve. The curve equations are shown in Table 3.

No.	Compound	Retention Time	Quantitative Ion	Linear Equation	Correlation
1	Chloroethylene	2.59	62	Y = 0.330716 X +0.014106	0.99835
2	1,1-Dichloroethylene	4.07	61	Y = 0.405587 X -0.006823	0.99849
3	Dichloromethane	4.83	84	Y = 0.405861 X -0.011485	0.99802
4	trans-1,2-Dichloroethylene	5.24	61	Y = 0.416907 X -0.023461	0.99935
5	1,1-Dichloroethane	5.94	63	Y = 0.630813 X -0.027151	0.99992
6	2-Butynyl chloride	6.04	53	Y = 0.313576 X -0.022736	0.99910
7	2,2-Dichloropropane	6.87	77	Y = 0.970312 X -0.016726	0.99768
8	cis-1,2-dichloroethylene	6.91	61	Y = 0.581532 X -0.046020	0.99883
9	Bromochloromethane	7.33	130	Y = 0.318706 X -0.020192	0.99878
10	Chloroform	7.54	83	Y = 0.692482 X -0.020303	0.99963
11	1,1,1-Trichloroethane	7.76	97	Y = 0.851604 X -0.011214	0.99839
12	Dibromofluoromethane (Substitute)	7.83	113	Y = 0.268262 X -0.018019	0.99899

No.	Compound	Retention Time	Quantitative Ion	Linear Equation	Correlation
13	Carbon tetrachloride	7.99	117	Y = 0.853076 X -0.024073	0.99908
14	1,3-Dichloropropene	8.05	75	Y = 0.529142 X -0.027920	0.99984
15	Benzene	8.42	78	Y = 1.87285 X -0.024750	0.99965
16	1,2-Dichloroethane	8.60	62	Y = 0.414744 X -0.040672	0.99771
17	Trichlorethylene	9.77	130	Y = 0.614695 X -0.044351	0.99929
18	1,2-Dichloropropane	10.34	63	Y = 0.420165 X -0.032144	0.99932
19	Dibromomethane	10.52	174	Y = 0.434229 X -0.038896	0.99857
20	Bromodichloromethane	10.94	83	Y = 0.586484 X -0.043943	0.99632
21	Epichlorohydrin	11.85	57	not have	not have
22	*cis*-1,3-Dichloropropene	11.94	75	Y = 0.701731 X -0.095604	0.99693
23	Toluene-d_8 (Substitute)	12.48	98	Y = 1.39781 X -0.105646	0.99918
24	Methylbenzene	12.63	91	Y = 2.159391 X -0.127617	0.99962
25	*trans*-1,3-Dichloropropene	13.35	75	Y = 0.673968 X -0.139124	0.99292
26	1,1,2-Trichloroethane	13.76	83	Y = 0.360292 X -0.052712	0.99699
27	Tetrachloroethylene	13.82	166	Y = 1.067741 X -0.086341	0.99820
28	1,3-Dichloropropane	14.16	76	Y = 0.764263 X -0.096066	0.99735
29	Dibromochloromethane	14.65	129	Y = 0.630521 X -0.053000	0.99761
30	1,2-Dibromoethane	14.90	107	Y = 0.390438 X -0.063523	0.99108
31	Chlorobenzene	16.17	112	Y = 1.719725 X -0.148314	0.99862
32	1,1,1,2-Tetrachloroethane	16.44	131	Y = 0.97712 X -0.078269	0.99691
33	Ethylbenzene	16.48	91	Y = 2.496144 X -0.167610	0.99922
34	*p*-Xylene	16.84	106	Y = 2.538984 X -0.236500	0.99801
35	*o*-Xylene	17.87	91	Y = 2.36711 X -0.147024	0.99801
36	Styrene	17.97	104	Y = 1.826415 X -0.223159	0.99604
37	Bromoform	18.41	173	Y = 0.557573 X -0.062362	0.99777
38	Cumene	18.92	105	Y = 3.511045 X -0.157545	0.99685
39	1-Bromo-4-fluorobenzene (Substitute)	19.42	95	Y = 0.593409 X -0.067575	0.99583
40	Bromobenzene	19.71	156	Y = 1.255506 X -0.141287	0.99670
41	1,1,2,2-Tetrachloroethane	19.95	83	Y = 0.865184 X -0.084297	0.99449
42	1,2,3-Trichloropropane	20.06	75	Y = 0.590668 X -0.061434	0.99678
43	Propylbenzene	20.12	120	Y = 1.194351 X -0.109655	0.99548
44	2-Chlorotoluene	20.28	126	Y = 1.213356 X -0.104968	0.99694
45	4-Chlorotoluene	20.67	91	Y = 2.641458 X -0.166345	0.99609

No.	Compound	Retention Time	Quantitative Ion	Linear Equation	Correlation
46	1,3,5-Trimethylbenzene	20.70	105	Y = 3.490165 X -0.135414	0.99642
47	*tert*-Butylbenzene	21.55	119	Y = 3.948194 X -0.192108	0.99591
48	1,2,4-Trimethylbenzene	21.75	105	Y = 3.699856 X -0.159675	0.99626
49	*sec*-Butylbenzene	22.21	105	Y = 5.596155 X -0.225514	0.99486
50	1,3-Dichlorobenzene	22.48	146	Y = 3.221243 X -0.027494	0.99581
51	*p*-Cymene	22.71	119	Y = 5.732419 X -0.224313	0.99402
52	1,4-Dichlorobenzene	22.80	146	Y = 2.661197 X -0.010481	0.99978
53	1,2-Dichlorobenzene	23.82	146	Y = 3.190339 X +0.020659	0.99972
54	Butylbenzene	23.94	91	Y = 3.611113 X -0.056239	0.99967
55	1,2-Dibromo-3-chloropropane	26.27	157	Y = 0.507351 X -0.028687	0.99812
56	1,2,4-Trichlorobenzene	28.70	180	Y = 2.717646 X -0.010488	0.99960
57	Hexachlorobutadiene	29.18	225	Y = 1.549069 X -0.002849	0.99927
58	Naphthalene	29.48	128	Y = 4.901722 X +0.095282	0.99903
59	1,2,3-Trichlorobenzene	30.14	180	Y = 2.793645 X -0.007342	0.99959

Table 3: Standard curves of 60 VOCs and their correlation coefficients

Conclusion

This GC-MS purge and trap methodology was created to analyze 57 volatile organic compounds in water, according to the environmental standard HJ 639-2012. This method has several advantages over traditional sample pretreatment; it is simple to operate, fast and accurate. The components were well separated. Except for epichlorohydrin, the other components had good linearity in the concentration range of 1–20 ppb, and the linear correlation coefficient greater than 0.99, which met the analysis and detection requirements. One note, the chloroethane and 1,1-dichloroethylene had relatively low response intensity, and low concentration of Epichlorohydrin does not produce peaks. This could be because this 4760 purge and trap hydrazine packing has not been replaced. It is recommended to monitor and replace the trap hydrazine regularly.

GBC Scientific Equipment Pty Ltd
A.B.N. 30 005 472 686
1/2 Naxos Way, Keysborough Victoria 3173, Australia
Phone: 61 3 9588 6666 Fax: 61 3 9588 6677
e-mail: gbc@gbcsci.com Website: www.gbcsci.com

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