

Analysis of VOCs in Water using Headspace-GC/MS

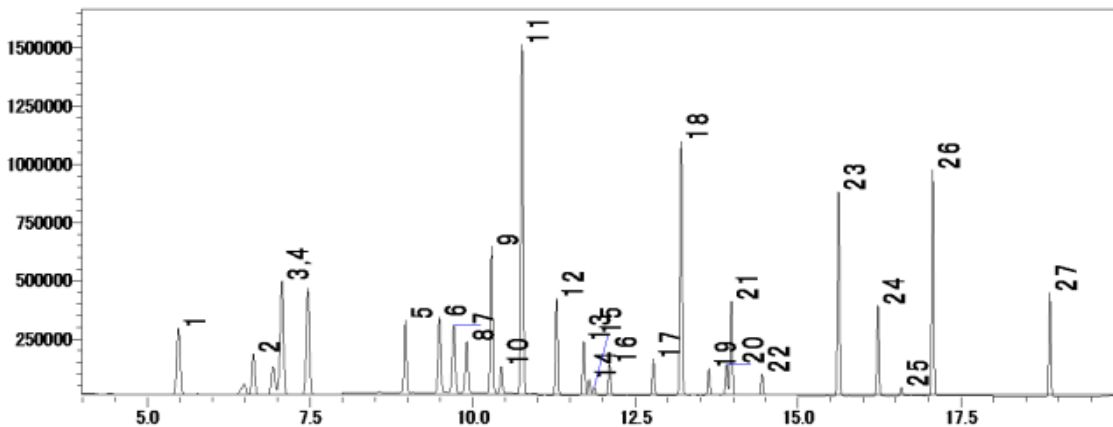
Instrument: [Shimadzu GC/MS System \(GC-2010, QP-2010S, AOC-20I, AOC-20S\)](#) with [CTC Twin HTS Pal](#)

A 5-point calibration curve was generated for 24 target VOCs over the range of 0.1 to 10 µg/L (parts per billion, ppb). Three internal standards (IS) were spiked at a fixed concentration in all calibration standards. Because of its poor extraction efficiency, 1,4-dioxane was present at a concentration 10x higher than the other VOCs in the standards. Instrument operating conditions for the Shimadzu HS-20 and GCMS-QP2010 Ultra are shown in Table 1.

Table 1: Analytical Conditions

HS-20		GCMS-QP2010 Ultra	
Sample amount	10mL+3g NaCl	GC Unit	
Mode	Loop	Column	Rtx-624
Equilibrating time	30 min		0.32 mm I.D. × 60 m L., df : 1.8 µm
Oven temp.	70 °C	Column oven temp.	35 °C (5 min) – 10 °C/min
Sample line temp.	150 °C		– 230 °C (5 min)
Transfer line temp.	150 °C	Carrier gas control	Constant pressure
Vial shaker	Off	Carrier gas linear velocity	48.8 cm/sec
Vial pressurizing time	1.0 min	Injection mode	Split (1:5)
Pressure equilibrating time	0.1min	MS Unit	
Load time	0.5 min	Interface temp.	230 °C
Load equilibrating time	0.1 min	Ion source temp.	200 °C
Injection time	1 min	Acquisition mode	SIM
Needle flush	1 min	Emission current	60 µA
Loop Size	1mL	Event time	0.3 sec

A total ion current (TIC) chromatogram is shown in Fig. 1. A SIM chromatogram and linearity of 5 µg/L 1,4-Dioxane is shown in Fig. 2. Statistical results from the calibration curve and the repeatability data are shown in Table 2. The coefficients of correlation (r) of the calibration curve were 0.999 or better for all compounds, and repeatability was < 5% for the 5 replicate analyses.



- 1 : 1,1-dichloroethylene, 2 : dichloromethane, 3 : methyl-t-butyl ether, 4 : trans-1,2-dichloroethylene, 5 : cis-1,2-dichloroethylene, 6 : chloroform, 7 : 1,1,1-trichloroethane, 8 : carbon tetrachloride, 9 : benzene, 10 : 1,2-dichloroethane, 11 : fluorobenzene(I.S.), 12 : trichloroethylene, 13 : 1,2-dichloropropane, 14 : 1,4-dioxane-d8(I.S.), 15 : 1,4-dioxane, 16 : bromodichloromethane, 17 : cis-1,3-dichloropropene, 18 : toluene, 19 : trans-1,3-dichloropropene, 20 : 1,1,2-trichloroethane, 21 : tetrachloroethylene, 22 : dibromochloromethane, 23 : *m,p*-xylene, 24 : *o*-xylene, 25 : bromoform, 26 : 4-bromofluorobenzene (I.S.), 27 : 1,4-dichlorobenzene

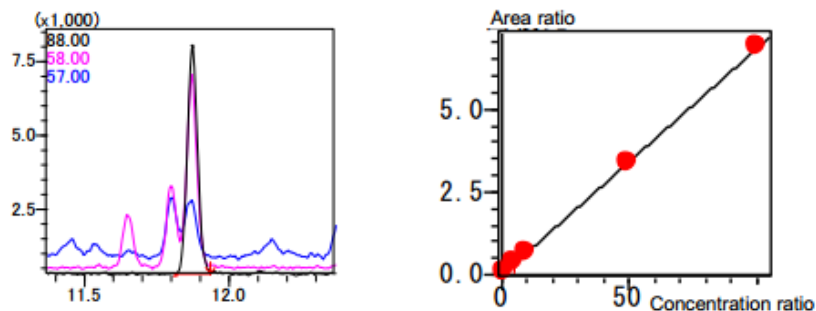


Fig. 2: SIM chromatogram of 1,4-dioxane (5 µg/L) and Calibration curve (1-100 µg/L)

Table 2: Linearity of calibration curves (0.1, 0.5, 1, 5, 10 µg/L) and repeatability (0.1 µg/L, n = 5)

PkNo.	Compounds name	r	C.V.(%)	PkNo.	Compounds name	r	C.V.(%)
1	1,1-dichloroethylene	0.999892	0.74	17	cis-1,3-dichloropropene	0.999689	1.89
2	dichloromethane	0.999797	3.56	18	toluene	0.999716	1.13
3	methyl-t-butyl ether	0.999686	4.06	19	trans-1,3-dichloropropene	0.999503	2.28
4	trans-1,2-dichloroethylene	0.999931	2.09	20	1,1,2-trichloroethane	0.999341	2.71
5	cis-1,2-dichloroethylene	0.999930	2.14	21	tetrachloroethylene	0.999678	3.08
6	chloroform	0.999858	4.10	22	dibromochloromethane	0.999573	1.52
7	1,1,1-trichloroethane	0.999733	1.85	23	<i>m,p</i> -xylene	0.999494	2.41
8	carbon tetrachloride	0.999611	0.36	24	<i>o</i> -xylene	0.999595	2.09
9	benzene	0.999873	1.79	25	bromoform	0.999268	5.06
10	1,2-dichloroethane	0.999386	2.24	27	1,4-dichlorobenzene	0.999827	1.63
12	trichloroethylene	0.999785	1.64	11	fluorobenzene(I.S.)		
13	1,2-dichloropropane	0.999784	1.28	14	1,4-dioxane-d8(I.S.)		
15	1,4-dioxane*	0.999882	2.43	26	4-bromofluorobenzene(I.S.)		
16	bromodichloromethane	0.999729	2.91				

* Calibration curve of 1,4-dioxane was evaluated at a concentration 10x higher than the other compounds. Repeatability of 1,4-dioxane was evaluated with 5.0 µg/L standard.

Reference: <http://www2.shimadzu.com/applications/GCMS/LAAN-A-MS-E033.pdf>