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Application Data Sheet

No. 76

GC-MS
Gas Chromatograph Mass Spectrometer

Analysis of VOCs in Water Using Headspace-GC/MS

■Introduction

Volatile Organic Compounds (VOCs) in water are regulated by environmental water quality laws or standards because of health hazard factors. Purge and trap methods and Headspace methods are commonly used for analysis of VOCs because of their sensitivity and ease of use. This application presents an example of analysis of VOCs in drinking water using the Shimadzu HS-20 headspace sampler.

■Equipment and Analytical Conditions

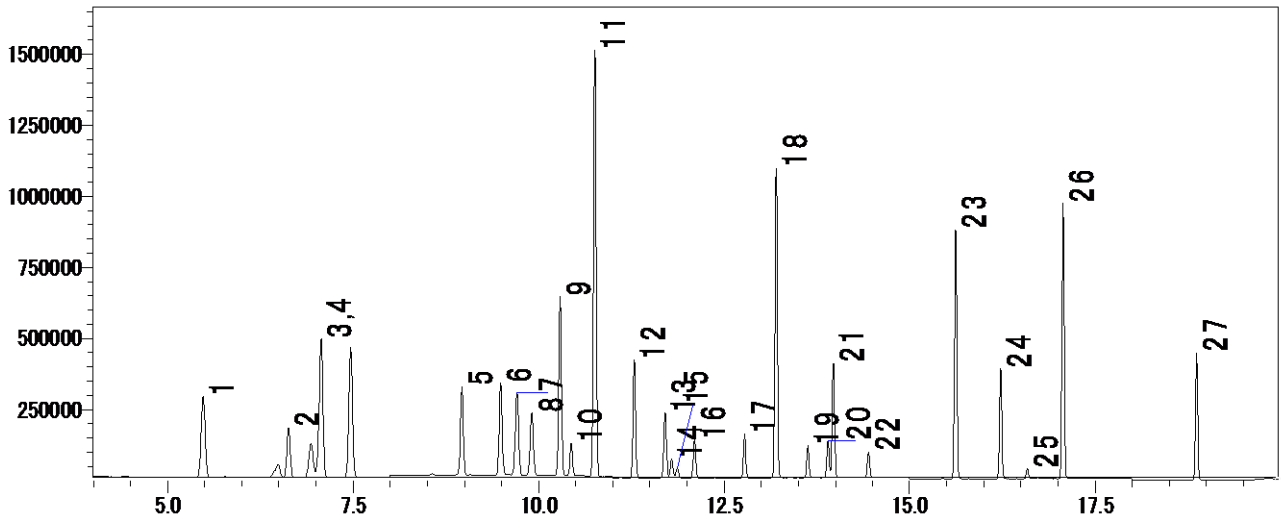
A 5-point calibration curve was generated for 24 target VOCs over the range of 0.1 to 10 µg/L (parts per billion, ppb). Three internal standards (IS) were spiked at a fixed concentration in all calibration standards. Because of its poor extraction efficiency, 1,4-dioxane was present at a concentration 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		
Load time	0.5 min	MS Unit	
Load equilibrating time	0.1 min	Interface temp.	230 °C
Injection time	1 min	Ion source temp.	200 °C
Needle flush	1 min	Acquisition mode	SIM
Loop Size	1mL	Emission current	60 µA
		Event time	0.3 sec

■Results

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-dichlorethane, 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. 1: Total ion current chromatogram (TIC)

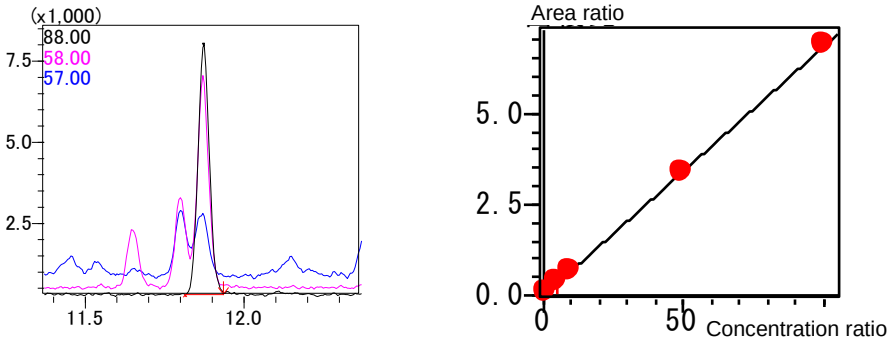


Fig. 2: SIM chromatogram of 1,4-dioxane (5 µg/L) and Calibration curve (1~100 µg/L)

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	*m,p*-xylene	0.999494	2.41
8	carbon tetrachloride	0.999611	0.36	24	*o*-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.

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