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Application Data Sheet

No.108

GC-MS

Gas Chromatograph Mass Spectrometer

Fast Analysis of Volatile Organic Compounds (VOCs) in Water Using Headspace-GC/MS

The headspace-GC/MS method is utilized to analyze volatile organic compounds (VOCs) in drinking water and environmental water. VOCs are easy to evaporate from the water, so they must be analyzed as quickly as possible after sampling.[1)] Accordingly, the analysis time must be as short as possible, particularly when many samples must be analyzed. The headspace sampler allows up to 12 samples to be heated simultaneously. Therefore, analytical conditions were investigated in order to shorten analysis time using the HS-20 headspace sampler. As a result, it was possible to measure five samples per hour.

Experiment

A standard mixture containing 25 VOCs was diluted with methanol to concentrations of 0.5 μg/mL, 2.5 μg/mL, 25 μg/mL, and 50 μg/mL (10× for 1, 4-dioxane only). A three-compound mixed internal standard solution was prepared so that p-bromofluorobenzene and fluorobenzene are at 1 μg/mL, and 1,4-dioxane-d8 at 10 μg/mL. To prepare the standard samples (including the internal standards), 3 g of sodium chloride was added to 10 mL of mineral water (Volvic). Then 2 μL of the standard mixtures of 25 VOCs at each concentration, as well as 20 μL of the three-compound mixed internal solution were added. This resulted in concentrations of 0.1 μg/L, 0.5 μg/L, 1 μg/L, 5 μg/L, and 10 μg/L for the VOCs (10× for 1, 4-dioxane only), 2 μg/L for p-bromofluorobenzene and fluorobenzene (internal standards), and 20 μg/L for 1,4-dioxane-d8 (internal standard).

The prepared standard samples were measured using the analytical conditions listed in Table 1.

Table 1: Analysis Conditions

Headspace Sampler: HS-20					
GCMS: GCMS-QP2010 Ultra					
HS	Mode:	Loop (Capacity 1 mL)			
	Oven Temperature:	70 °C			
	Vial Warming Time:	30 min			
GC			MS		
	Column:	Rtx-624 (20 m × 0.18 mm I.D., 1 μm)*1		Ion Source Temp.:	200 °C
	Injection Mode:	Split		Interface Temp.:	230 °C
	Split Ratio:	30		Measurement Mode:	SIM mode
	Control Mode:	Constant linear velocity (50 cm/sec)		Event time:	0.2 sec
	Oven Temperature:	40 °C (2.5 min) → (35 °C/min) → 210 °C			

*1 Code No.: 40924 (RESTEK column, Shimadzu GLC)

Note: The preparation procedure for the standard mixture and mixed standard samples does not conform to the method specified in the Japanese Government's public notice for drinking water.

Analysis Results

The total ion current chromatogram obtained from measuring the 10 μg/L standard sample in SIM mode is shown in Fig. 1. The peaks for 1,4-dioxane-d8 and 1,2-dichloropropane, which have close retention times and are hard to separate based on *m/z*, were sharpened by increasing the split ratio, enabling separation in the chromatograph. In addition, sufficient sensitivity was obtained for 1,4-dioxane and bromoform, for which sensitivity is lower than other components even when the split ratio is increased. (Fig. 2)

The calibration graph linearity (correlation coefficient: R) and repeatability are shown in Table 2. Favorable results were obtained, as the calibration graph linearity was at least 0.999 for all components, and the repeatability was 2.12 % (1,1,2-trichloroethane) or less.

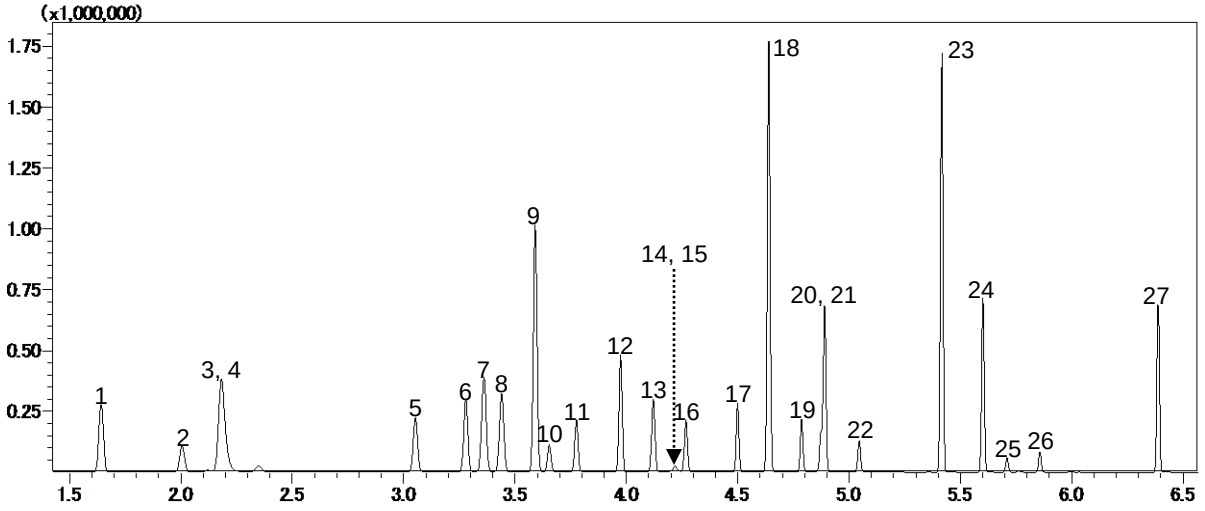

Fig. 1: Total Ion Current Chromatogram for the Standard Sample of 25 VOCs (10 μg/L)

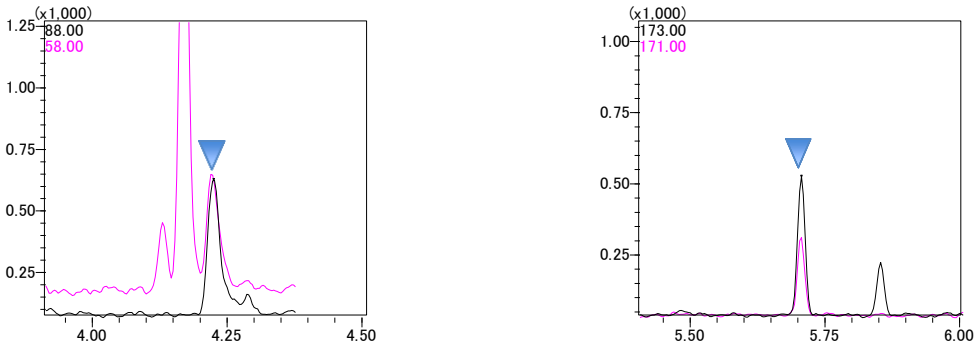

Fig. 2: SIM Chromatogram for the Standard Sample of 2 VOCs

Table 2: Repeatability (area ratio, n=5) and Calibration Graph Linearity (0.1 μg/L, 1, 4-dioxane: 5 μg/L)

Peak No.	Compound Name	%RSD	Correlation Coefficient R	Peak No.	Compound Name	%RSD	Correlation Coefficient R
1	1,1-dichloroethene	0.89	0.99996	15	1,4-dioxane	1.73	0.99993
2	Dichloromethane	1.58	0.99999	16	Bromodichloromethane	1.89	0.99996
3	Methyl t-butyl ether	2.03	0.99994	17	cis-1,3-dichloropropene	0.76	0.99992
4	trans-1,2-dichloroethylene	1.71	0.99997	18	Toluene	0.94	0.99995
5	cis-1,2-dichloroethylene	1.08	0.99996	19	trans-1,3-dichloropropene	1.22	0.99991
6	Chloroform	1.59	0.99951	20	1,1,2-trichloroethane	2.12	0.99996
7	1,1,1-trichloroethane	1.38	0.99998	21	Tetrachloroethylene	1.48	0.99997
8	Carbon tetrachloride	0.54	0.99999	22	Dibromochloromethane	1.59	0.99997
9	Benzene	1.72	0.99998	23	*m*-,*p*-xylene	0.45	0.99996
10	1,2-dichloroethane	1.43	0.99999	24	*o*-xylene	0.53	0.99994
11	Fluorobenzene	–	–	25	Bromoform	1.71	0.99997
12	Trichloroethylene	1.82	0.99997	26	*p*-Bromofluorobenzene	–	–
13	1,2-dichloropropane	1.50	0.99993	27	1,4-dichlorobenzene	1.16	0.99999
14	1,4-dioxane-d8	–	–				

Summary

Using the HS-20 headspace sampler and the GCMS-QP2010 Ultra with the optimized analysis conditions, it was possible to reduce the time to analyze VOCs in water to 12 minutes, enabling the analysis of five samples per hour.

Reference

1) Method Specified by the Japan ‘s Minister of Health, Labour and Welfare based on the ministerial ordinance for water-quality standards (Public Notice No. 261 by Japan’ s Ministry of Health, Labour and Welfare, July 22, 2002 (Final revision, Public Notice No.147 by Japan's Ministry of Health, Labour and Welfare, March 31, 2014))

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