Improving efficiency in drinking water analysis by high-end GC-QMS

~ Scan quantification of VOCs, 2-MIB&Geosmin, haloacetic acids, formaldehyde, Phenol by double column connection ~

Product：Mass Spectrometer (MS)

1.Introduction

Of the drinking water quality standards in Japan, the GC-MS method is adopted as the inspection method for 19 test items. The 19 test items covered by the GC-MS method are classified into 5 groups as volatile organic compounds (VOCs), substances causing musty odors (2-methylisoborneol, geosmin), haloacetic acids, formaldehyde, and phenols. One or more official methods have been established for each group. We already have reported an analysis application using the same column for the purpose of improving operational efficiency in these water quality analyses. The same column analysis of VOCs, 2-MIB, and geosmin using a mid-polar column was reported in MS Tips No. 334. The same column analysis of haloacetic acids, formaldehyde, and phenols using a non-polar column was reported in MS Tips No. 325.

JEOL Ltd. released the 6th generation high-end GC-QMS "JMS-Q1600GC UltraQuad™ SQ-Zeta" in 2021. We report on the construction of a system that enables measurement of all GC-MS items of water quality standards with a single instrument using the JMS-Q1600GC. The system can measure all test items without the need for column replacement by connecting a mid-polar column and a non-polar column to one JMS-Q1600GC in a double column configuration. In addition, by using the new attachment "High Performance Ion Source(EPIS)", an easier "Scan quantification" is possible instead of the "SIM quantification" that requires complicated condition settings. This MSTips reports the results of the evaluation of the linearity of the calibration curves for each item and the repeatability at a lower concentration limit.

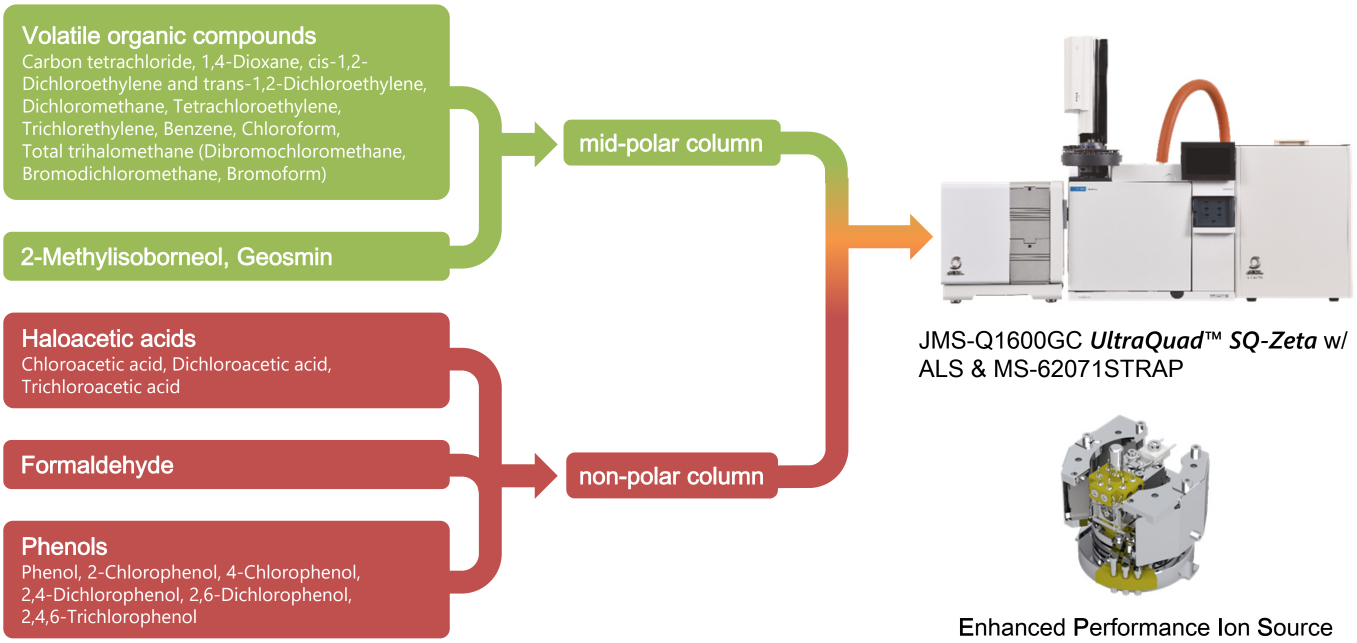

Figure 1. Measurement items by GC-MS method in Japanese drinking water regulation

2.Measurement

2.1.Sample Preparation

VOCs：In a headspace vial containing 3 g NaCl and 10 mL of purified water, VOCs except 1,4-dioxane were added at 0.1, 0.2, 0.5, 1, 2, 5, and 10 µg/L and 1,4-dioxane at 1, 2, 5, 10, 20, 50, and 100 µg/L, respectively, for adjustment. For internal standards, fluorobenzene and p-bromofluorobenzene were added to each measurement sample at 2.5 ppb and 1,4-dioxane-d8 at a concentration of 200 µg/L. 2-Methylisoborneol&Geosmin：In a headspace vial containing 4.5 g NaCl and 10 mL of purified water, 2-methylisoborneol (2-MIB) and geosmin were added at 1, 2, 5, and 10 ng/L, respectively, for adjustment. The internal standard was 2,4,6-trichloroanisole-d3 added to a concentration of 20 ng/L. Haloacetic acids：For methyl chloroacetate, methyl dichloroacetate, and methyl trichloroacetate, the concentrations were adjusted by stepwise dilution with MTBE to 0.002, 0.004, 0.008, 0.02, and 0.04 mg/L as converted to the concentration of haloacetic acids in the test water. For the internal standard, 1,2,3-trichloropropane was added to each measurement sample to a concentration of 0.1 mg/L. Formaldehyde：PFBOA-formaldehyde was adjusted by stepwise dilution with n-hexane to 0.002, 0.001, 0.005, 0.01, 0.05, and 0.1 mg/L as converted to the concentration of formaldehyde in the test water. For the internal standard, 1-chlorodecane was added to each measurement sample to a concentration of 0.1 mg/L. Phenols：Phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol were added stepwise with ethyl acetate to reach 0.0005, 0.001, 0.005, 0.01 mg/L as the concentration in the test water. After dilution, 50 μL of N,O-bis (trimethylsilyl) trifluoroacetamide was added to 1 mL of the aliquoted solution and allowed to stand for 1 hour. As an internal standard, acenaphthene-d10 was added to a concentration of 0.2 mg/L.

2.2. Measurement conditions

The measurement conditions for the samples are shown in Table 1. Scan mode was used for the MS data acquisition. Although Scan mode is less sensitive than SIM mode, it simplifies the workflow in analytical operations because it does not require the creation of measurement conditions necessary for SIM. The use of the EPIS in this MSTips enables both high-sensitivity measurement and operational cost reduction.

Table 1. Measurement condition

		VOCs	Geosmin, 2-MIB	haloacetic acids	Formaldehyde	Phenol
HS	Sample temp.	70℃	80℃			
	Heating time	30min				
	Sampling mode	Trap(3 times)				
GC	Column	DB-1301(Agilent Technologies, Inc.), 60m×0.32mm id, 1μm film thickness		InertCap 1MS(GL Sciences Inc.), 30m×0.25mm id, 1μm film thickness		
	Oven	40℃ for 3min, to 100℃ at 5℃/min, to 250℃ at 10℃/min, and hold for 5min		40℃ for 8min, to 250℃ at 15℃/min, and hold for 3min	50℃ for 1min, to 250℃ at 15℃/min, and hold for 5min	70℃ for 1min, to 250℃ at 15℃/min, and hold for 5min
	Carrier gas	83.44kPa(Constant Pressure)		1mL/min(Constant Flow)		
	Inlet temp.			250℃		
	Injection mode			Splitless		
	Injection volume			2μL		
MS	Interface temp.	250℃				
	Ion source temp.	250℃				
	Ionization current	50μA	100μA	100μA	50μA	100μA
	Ionization energy	70eV				
	Acquisition mode	Scan				
	Scan range	*m/z* 45 ～ 200	*m/z* 80 ～ 230	*m/z* 40 ～ 160	*m/z* 33 ～ 230	*m/z* 33 ～ 300

3.Result

Table 2 shows the correlation coefficient of the calibration curve and the coefficient of variation (= C.V.) of the quantification value when the lower concentration limit of the calibration curve was continuously measured at n=5 for the measured component. Figure 2 shows the calibration curve for 1,4-dioxane (VOCs), 2-methylisoborneol, chloroacetic acid (haloacetic acids), and 2,4,6-trichlorophenol (phenols), and Figure 3 shows the chromatogram of the lower concentration limit of the calibration curve. The correlation coefficients shown in Table 2 are greater than 0.999 for all components, and good linearity is obtained in the concentration range adjusted in this MSTips. The coefficients of variation at the lower concentration limit were also less than 5% for all components, indicating that it is possible to sufficiently measure concentrations of 1/10 of the standard value, which is the sensitivity required for water quality testing.

Table 2. Correlation Coefficient and Coefficient of Variation (C.V.) of each compound.

Compound Name	Correlation Coefficient	C.V. (%)	Sample Conc. (μg/L)	Standard Value (μg/L)	Compound Name	Correlation Coefficient	C.V. (%)	Sample Conc. (μg/L)	Standard Value (μg/L)
Carbon tetrachloride	0.9998	2.0	0.1	2	Total trihalomethane		1.6	0.4	100
1,4-dioxane	0.9999	3.4	1	50	Trichloroacetic acid	0.9997	0.8	2	30
trans-1,2-dichloroethylene	0.9999				Bromodichloromethane	0.9999	1.8	0.1	30
cis-1,2-dichloroethylene	0.9999				Bromoform	0.9990	2.5	0.1	90
1,2-dichloroethylene		0.8	0.2	40	Formaldehyde	0.9999	0.7	1	80
Dichloromethane	0.9997	3.4	0.1	20	2-Methylisoborneol	0.9992	4.3	0.001	0.01
Tetrachlorethylene	0.9998	0.9	0.1	10	Geosmin	0.9995	1.6	0.001	0.01
Trichlorethylene	0.9999	1.4	0.1	10	Phenol	0.9988	0.9	0.5	5
benzene	0.9999	1.0	0.1	10	2-Chlorophenol	0.9998	0.5	0.5	
Chloroacetic acid	0.9998	2.6	2	20	4-Chlorophenol	0.9998	0.6	0.5	
Chloroform	0.9999	1.0	0.1	60	2,6-dichlorophenol	0.9999	0.9	0.5	
Dichloroacetic acid	0.9999	1.9	2	30	2,4-dichlorophenol	0.9999	0.2	0.5	
Dibromochloromethane	0.9997	2.6	0.1	100	2,4,6-Trichlorophenol	0.9999	3.7	0.5	

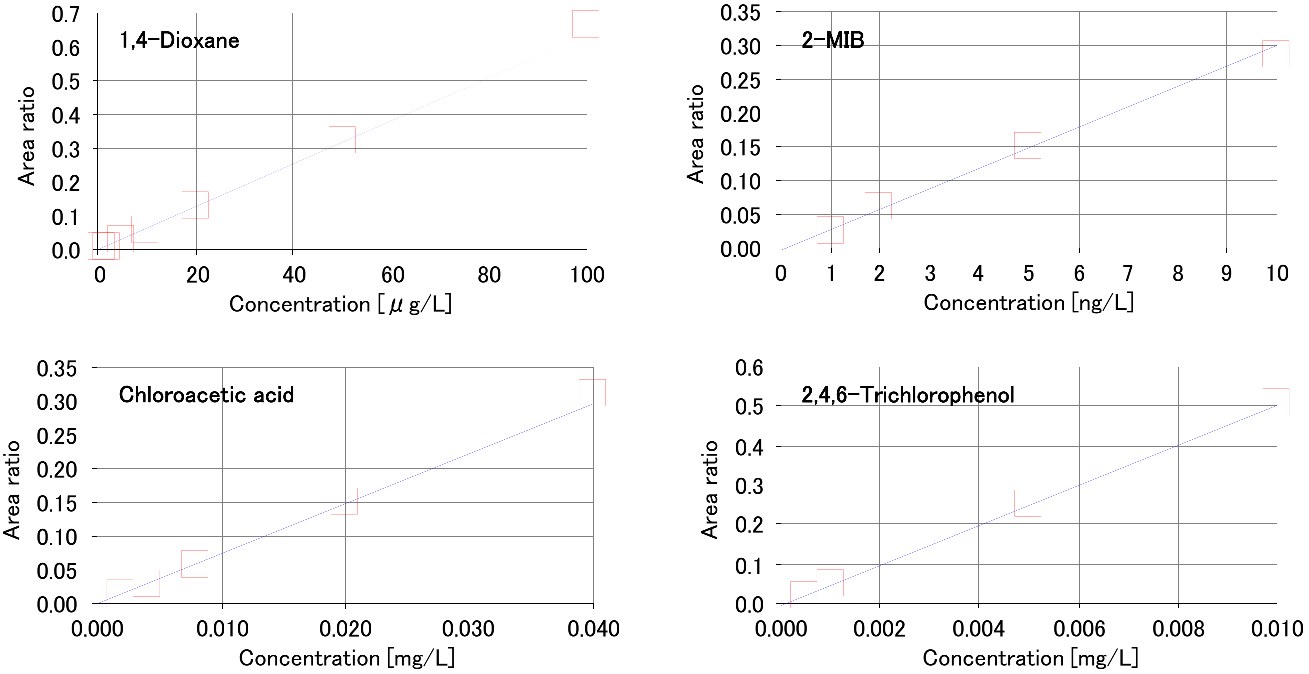

Figure 2. Calibration curve of 1,4-Dioxane, 2-MIB, Chloroacetic acid, 2,4,6-Trichlorophenol.

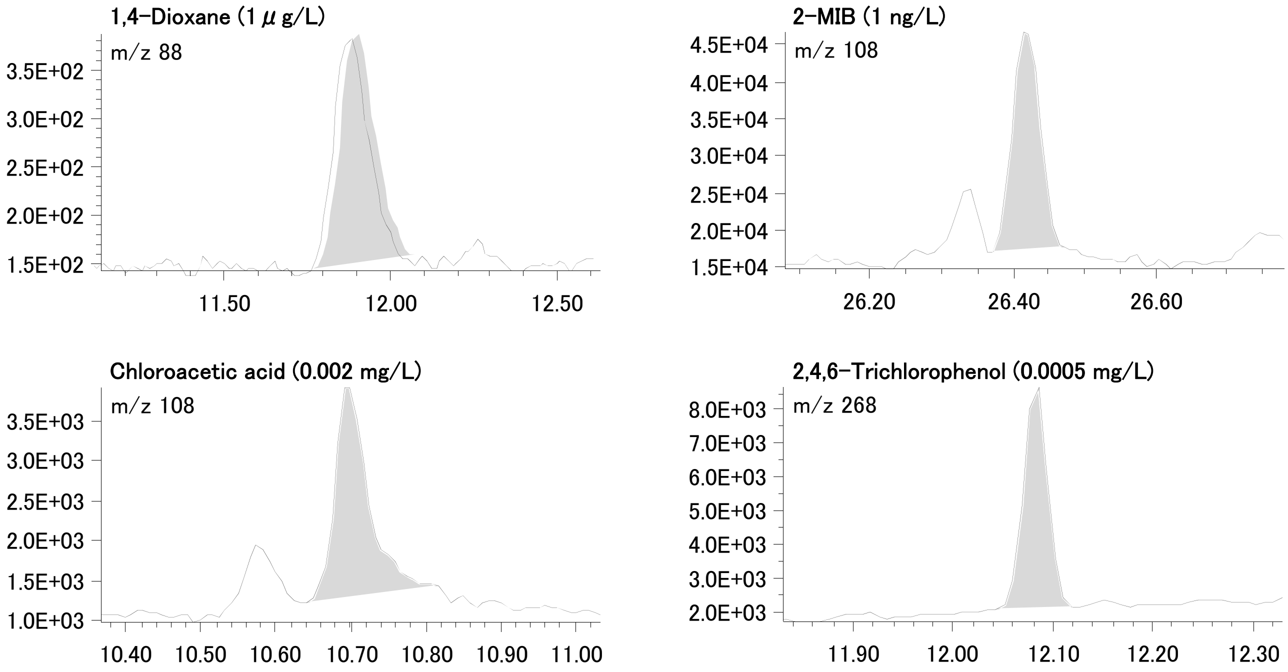

Figure 3. SIM chromatogram of 1,4-Dioxane, 2-Methylisoborneol, Chloroacetic acid, 2,4,6-Trichlorophenol at minimum plot of each calibration curve.

4.Conclusion

The JMS-Q1600GC UltraQuad™ SQ-Zeta, equipped with an EPIS, is connected to a mid-polar column for VOCs, 2-MIB, and geosmin and a non-polar column for haloacetic acids, formaldehyde, and phenols in a double column configuration to create a GC-MS system that can measure all test items subject to GC-MS in water quality standards. This system enables the measurement of all GC-MS target items without the need for column replacement involving a vacuum shutdown, and the use of scan quantitation, which does not require complicated settings of measurement conditions, significantly reduces operation costs.

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