SHIMADZU
Excellence in Science

Application News

No. C234

Liquid Chromatograph Mass Spectrometer LCMS™-8060

High-Speed Analysis of 9 Haloacetic Acids in Tap Water Using Triple Quadrupole LC/MS/MS

H. Horiike

User Benefits

- Analysis is possible in only 15 minutes thanks to simple sample preparation requiring only dechlorination.
- In addition to 3 items listed in drinking water quality standards, simultaneous analysis of 6 bromine-containing haloacetic acids is also possible.
- Analysis with higher sensitivity is possible at concentrations at or below 1/10 of the standard value and 1/2 of the target value.

■ Introduction

Haloacetic acids (HAAs) in tap water are widely known as disinfection byproducts formed by chlorination in the water purification process. At present, Japan's Drinking Water Quality Standards list 3 HAAs (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid) under items subject to Drinking Water Quality Standards, and 6 (bromochloroacetic acid, bromodichloroacetic acid, dibromochloroacetic acid, monobromoacetic acid, dibromoacetic acid, tribromoacetic acid) as Items for Further Study. These substances are measured and considered in water quality management.

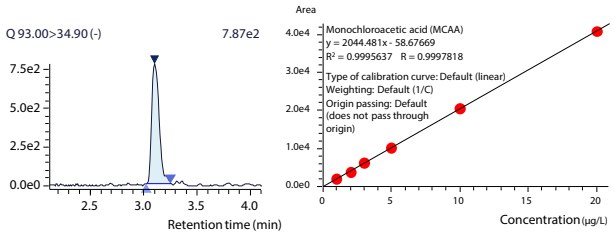
The solvent-extraction GC/MS method and the LC/MS method, which enables direct measurement, are provided as inspection methods for the 3 drinking water quality standard items. However, the LC/MS method is now widely used with the aim of improving analysis efficiency, as sample preparation is simple.

An example of measurement of the 9 HAAs was introduced in Application News No. C89. This article introduces results in which a satisfactory validity evaluation was obtained under high-speed analysis conditions with an analysis time of 15 min.

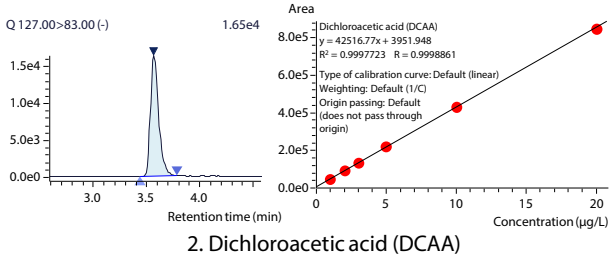
■ MRM Chromatograms and Calibration Curves of 9 Haloacetic Acids in Standard Solution Mixture

Fig. 1 shows the MRM chromatograms of 9 haloacetic acids with concentrations of 2 µg/L each and 6 point absolute calibration curves for each HAA in the concentration range from 1 to 20 µg/L.

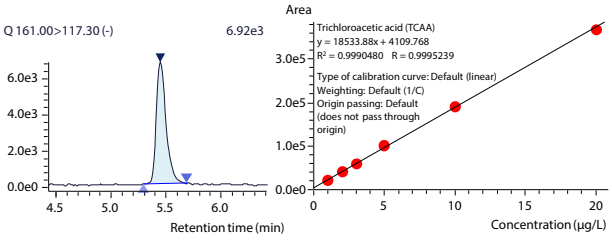
It was possible to detect all 9 compounds at concentrations (2 µg/L) at or below 1/10 of the standard values with higher sensitivity for the 3 target substances of the drinking water quality standards, and satisfactory linearity was also obtained.



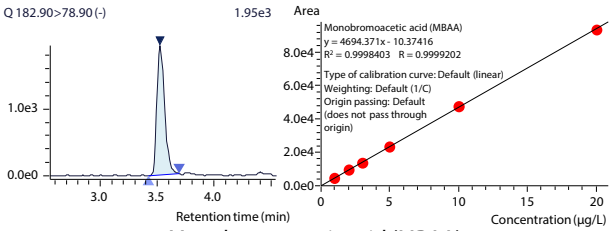
1. Monochloroacetic acid (MCAA)



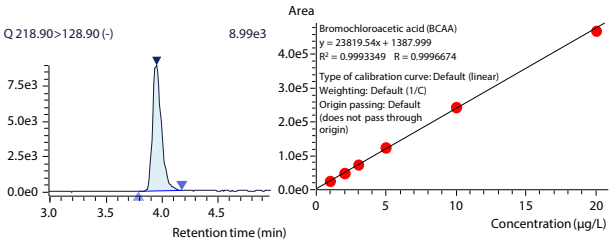
2. Dichloroacetic acid (DCAA)



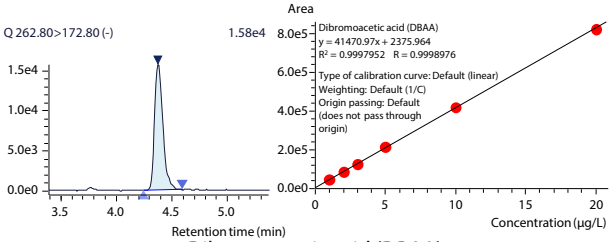
3. Trichloroacetic acid (TCAA)



4. Monobromoacetic acid (MBAA)

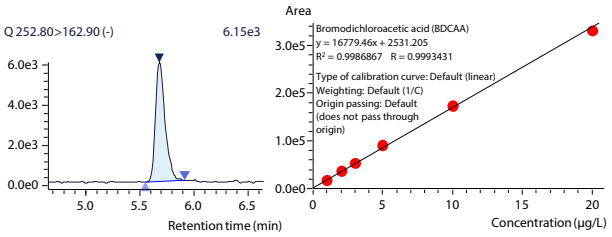


5. Bromochloroacetic acid (BCAA)

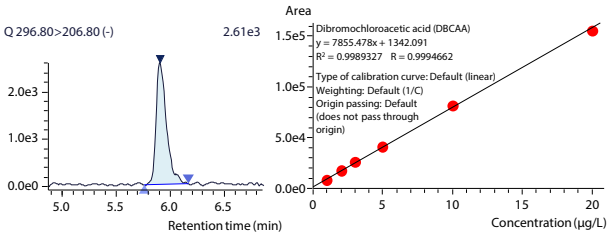


6. Dibromoacetic acid (DBAA)

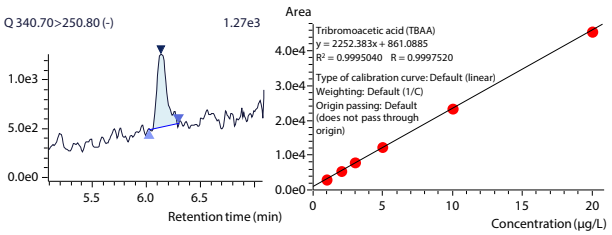
Fig. 1 MRM Chromatograms (2 µg /L Each) and Calculation Curves (1 - 20 µg/L, n = 3 Each)



7. Bromodichloroacetic acid (BDCAA)



8. Dibromochloroacetic acid (DBCAA)



9. Tribromoacetic acid (TBAA)

Fig. 1 MRM Chromatograms (2 µg /L Each) and Calculation Curves (1 - 20 µg/L, n = 3 Each)

■ Analysis Conditions

Table 1 shows the analysis conditions.

Table 1 Analysis Conditions

Column	: CAPCELLPAK MG III C18 (150 mm × 3.0 mm, 3 µm, Osaka Soda)
Mobile phases	: A 0.2 % Formic acid-Water B 0.2 % Formic acid-Methanol
Time program	: B.conc 1 % (0 min) → 100 % (7 min)
Flow rate	: 0.50 mL/min
Column temperature	: 50 ˚C
Injection volume	: 30 µL
Probe voltage	: -2.0 kV (ESI-Negative)
DL temperature	: 150 ˚C
Block heater temperature	: 100 ˚C
Interface temperature	: 130 ˚C
Nebulizing gas flow	: 15 L/min
Drying gas flow	: 5 L/min

MRM transition:

MCAA	*m/z*	93.00>	34.90	MBAA	*m/z*	182.90>	78.90
DCAA	*m/z*	127.00>	83.00	BCAA	*m/z*	218.90>	128.90
DBAA	*m/z*	262.80>	172.80	TCAA	*m/z*	161.00>	117.30
BDCAA	*m/z*	252.80>	162.90	CDBAA	*m/z*	296.80>	206.80
TBAA	*m/z*	340.70>	250.80				

■ Validity Evaluation Test Using Tap Water

A blank solution was prepared by spiking tap water with sodium ascorbate as a dechlorinating agent. Samples for measurement were prepared by spiking the blank solution with the standard solution mixture so as to obtain a concentration of 2 µg/L.

Fig. 2 shows the obtained MRM chromatograms, and Table 2 shows the quantitation results for each of the 9 compounds.

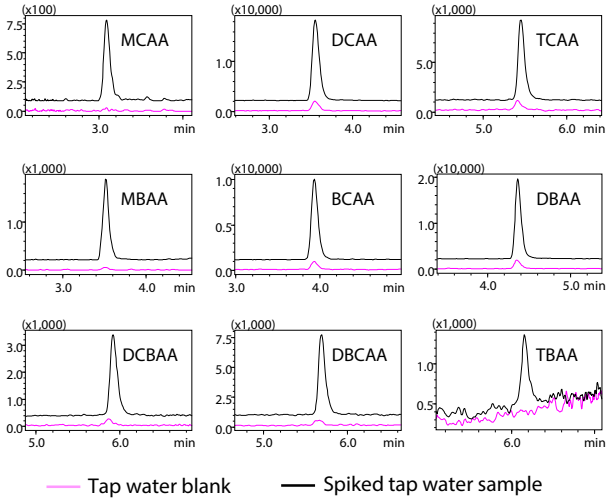


Fig. 2 MRM Chromatograms of Tap Water Blank and Spiked Samples

Table 2 Results of Spike-and-Recovery Test of Tap Water (n = 5)

MCAA		DCAA		TCAA	
Recovery %	%RSD	Recovery %	%RSD	Recovery %	%RSD
92	2.3	94	2.9	104	1.6
MBAA		**BCAA**		**DBAA**	
Recovery %	%RSD	Recovery %	%RSD	Recovery %	%RSD
87	2.6	91	2.1	93	1.5
BDCAA		**DBCAA**		**TBAA**	
Recovery %	%RSD	Recovery %	%RSD	Recovery %	%RSD
101	1.6	99	2.4	101	4.6

■ Conclusion

In an analysis of 9 bromine-containing haloacetic acid compounds, satisfactory linearity was obtained for all 9 compounds in the calibration curve range from 1 to 20 µg/L.

Accuracy of within ±15 % and peak area repeatability of %RSD ≤5 % were obtained in a spike-and-recovery test (n = 5) using tap water containing the three drinking water quality standard items monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA) at concentrations of 2 µg/L, which is 1/10 or less of the respective standard values.

This experiment demonstrated that simultaneous analysis of the 9 haloacetic acids listed as Drinking Water Quality Standard items or Items for Further Study is possible in a total analysis time of 15 minutes.

SHIMADZU
Shimadzu Corporation
Analytical & Measuring Instruments Division
Global Application Development Center

www.shimadzu.com/an/

First Edition: Nov. 2020