

Application News

Liquid Chromatograph Mass Spectrometer LCMS™-8060

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

No. C234A

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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.

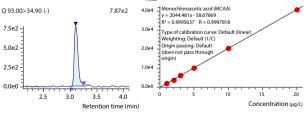
The solvent-extraction GC/MS method and the LC/MS method, which enables direct measurement, are provided as inspection methods for the 3 drinking water quality standard items. However, the LC/MS method is now widely used with the aim of improving analysis efficiency, as sample preparation is simple.

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.

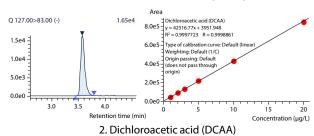
■ MRM Chromatograms and Calibration Curves of 9 Haloacetic Acids in Standard Solution Mixture

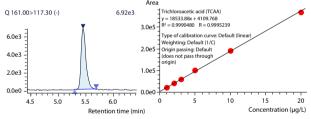
Fig. 1 shows the MRM chromatograms of 9 haloacetic acids with concentrations of 2 μ g/L each and 6 point absolute calibration curves for each HAA in the concentration range from 1 to 20 μ g/L.

It was possible to detect all 9 compounds at concentrations (2 μ g/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.

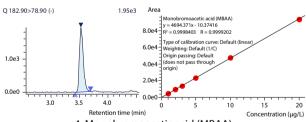




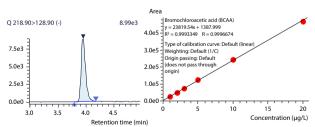




3. Trichloroacetic acid (TCAA)



4. Monobromoacetic acid (MBAA)



5. Bromochloroacetic acid (BCAA)

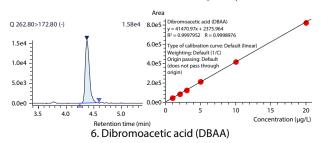
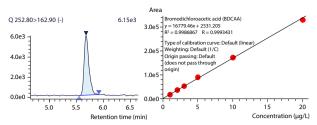
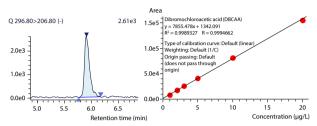


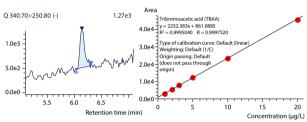
Fig. 1 MRM Chromatograms (2 μ g /L Each) and Calculation Curves (1 - 20 μ g/L, n = 3 Each)



7. Bromodichloroacetic acid (BDCAA)



8. Dibromochloroacetic acid (DBCAA)



Tribromoacetic acid (TBAA)

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

■ Analysis Conditions

Table 1 shows the analysis conditions.

Table 1 Analysis Conditions

: B.conc 1 % (0 min) \rightarrow 100 % (7 min)

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

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 : 3 L/min Heating gas flow : 15 L/min Drying gas flow : 5 L/min

MRM transition:

Time program

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	
TRAA	m/z	3/10 705	250.80					

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■ 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 $\mu g/L$.

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

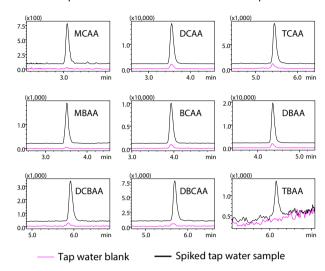


Fig. 2 MRM Chromatograms of Tap Water Blank and Spiked Samples

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

Table 2 Hesaits of Spine and Necovery Test of Tap Water (11 = 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		ТВАА				
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 \leq 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 $2 \mu g/L$, 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.



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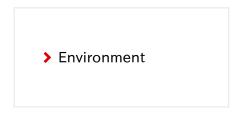
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