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Application News

No. C235

LCMS™-8060 High Performance Liquid Chromatograph Mass Spectrometer

Analysis of Haloacetonitriles in Tap Water Using Triple Quadrupole LC/MS/MS

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User Benefits

- Three main components of haloacetonitriles can be measured simultaneously in an analysis time of only 13 minutes.
- Tap water samples can be measured without sample preparation.
- It is possible to change to APCI from ESI simply by exchanging probes.

■ Introduction

Haloacetonitriles in tap water are byproducts of the reaction of humic substances, algae, and amino acids with free carbon dioxide during chlorine disinfection treatment, and are known as one of the disinfection byproducts represented by trihalomethane and haloacetic acids, which are subject to water quality standards.

Among the haloacetonitriles, dichloroacetonitrile is now specified as an item for target setting for water quality management (provisional target: 0.01 mg/L or less), and trichloroacetonitrile, bromochloroacetonitrile, and dibromoacetonitrile (target value: 0.06 mg/L or less) are specified as items requiring study owing to their toxicity.

In particular, the solvent extraction-GC/MS method is currently listed as an inspection method for dichloroacetonitrile, which is specified as an item for target setting for water quality management, but liquid chromatography-tandem mass spectrometry (LC/MS/MS) is considered effective, as direct measurement is possible.

This article introduces an example of simultaneous determination of three components in tap water by using an LCMS-8060 triple quadrupole LC/MS/MS. (Trichloroacetonitrile was not measured because ionization is considered difficult in LC/MS.)

The results of a validation test confirmed that these three components can be measured with good accuracy in tap water without sample preparation.

■ Analysis Conditions

Table 1 shows the analysis conditions. A phenyl column was used in separation of the three components, and atmospheric pressure chemical ionization (APCI) was used as the ionization method.

Table 1 Analysis Conditions

Column	: Inertsil™ Ph-3 HP (150 mm × 2.1 mm, 3 µm, GLSciences)	
Mobile phases	: A Water B Methanol	
Time program	: B.conc 10 % (0 min) - 75 % (8 min) – 100 % (8.01 - 10 min) -10 % (10.01 - 13 min)	
Flow rate	: 0.30 mL/min	
Column temperature	: 40 ˚C	
Injection volume	: 50 µL	
Probe voltage	: -4.0 kV (APCI-Negative)	
DL temperature	: 200 ˚C	
Block heater temperature	: 200 ˚C	
Interface temperature	: 400 ˚C	
Nebulizing gas flow	: 3 L/min	
Drying gas flow	: 5 L/min	
MRM transition	:	
Dichloroacetonitrile	*m/z*	108.35 > 34.90
Bromochloroacetonitrile	*m/z*	151.80 > 78.85
Dibromoacetonitrile	*m/z*	195.75 > 78.85

■ MRM Chromatogram of 3 Component Mixed Standard Solution of Haloacetonitriles

Fig. 1 shows the MRM chromatograms obtained for the three substances.

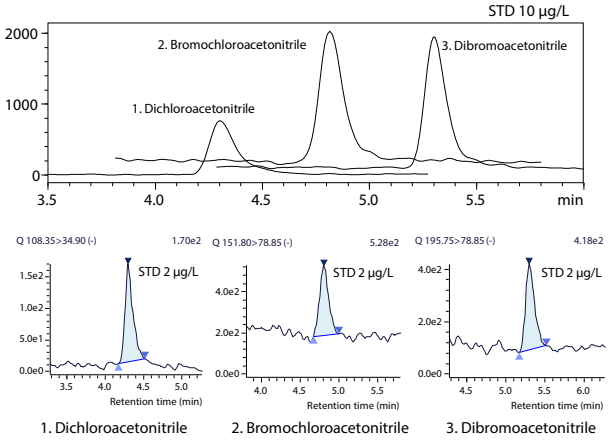

Fig. 1 MRM Chromatograms

■ Calibration Curves

Fig. 2 shows the calibration curves. Good linearity was obtained for all three substances.

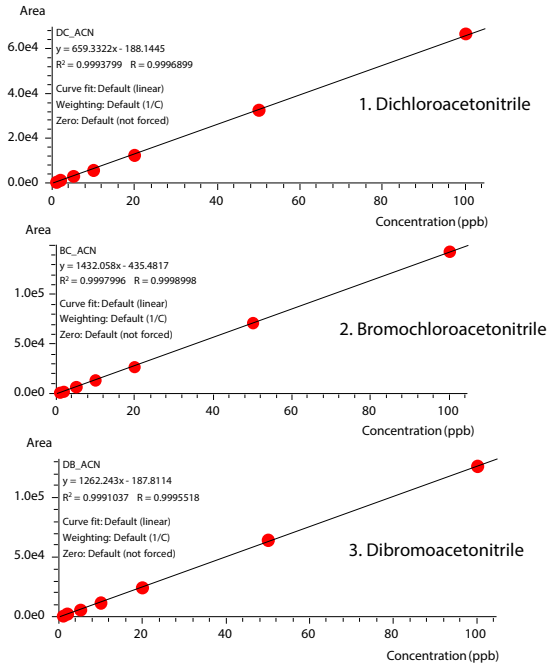

Fig. 2 Six-Point Calibration Curves (1 - 20 µg/L, n=3)

■ Validation Test Using Tap Water

As the analysis samples, tap water and dechlorinated tap water, in which sodium ascorbate was added to tap water as a dechlorination agent, were prepared.

The analysis samples were spiked with a mixed standard solution to obtain a concentration of 5 µg/L or 10 µg/L, and the samples were measured.

Fig. 3 shows the obtained MRM chromatograms, and Table 2 and Table 3 show the quantitative analysis results for the three substances of the tap water and the dechlorinated tap water, respectively.

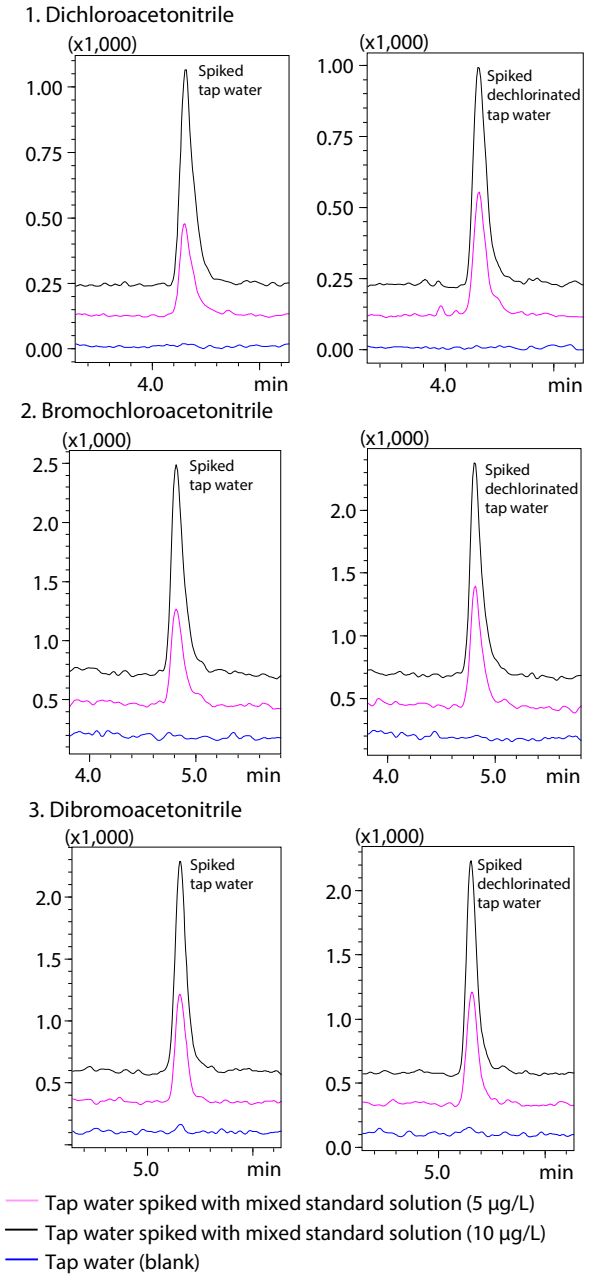

Fig.3 MRM Chromatograms of Tap Water Blanks and Spiked Samples

Table 2 Spike-and-Recovery Test Results for Tap Water (n=5, Average)

<Spiked concentration 5 µg/L>

Dichloro acetonitrile		Bromochloro acetonitrile		Dibromo acetonitrile	
Accuracy %	%RSD	Accuracy %	%RSD	Accuracy %	%RSD
99.7	7.9	101.8	5.1	98.4	4.3

<Spiked concentration 10 µg/L>

Dichloro acetonitrile		Bromochloro acetonitrile		Dibromo acetonitrile	
Accuracy %	%RSD	Accuracy %	%RSD	Accuracy %	%RSD
103.1	4.7	101.2	3.0	97.3	4.4

Table 3 Spike-and-Recovery Test Results for Dechlorinated Tap Water (n=5, Average)

<Spiked concentration 5 µg/L>

Dichloro acetonitrile		Bromochloro acetonitrile		Dibromo acetonitrile	
Accuracy %	%RSD	Accuracy %	%RSD	Accuracy %	%RSD
97.4	6.2	100.1	3.8	96.4	4.8

<Spiked concentration 10 µg/L>

Dichloro acetonitrile		Bromochloro acetonitrile		Dibromo acetonitrile	
Accuracy %	%RSD	Accuracy %	%RSD	Accuracy %	%RSD
91.7	4.7	91.0	3.9	91.1	3.3

■ Conclusion

A validation test was conducted using tap water and tap water to which the dechlorination agent sodium ascorbate was added as the samples. Satisfactory results were obtained with both, demonstrating that tap water can be analyzed by the LC/MS/MS method described here without sample preparation.

It is possible to measure the three haloacetonitrile components at or below the set (provisional) target concentration with good accuracy by using the LCMS-8060 and this method.

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First Edition: Feb. 2021