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High Performance Liquid Chromatograph Mass Spectrometer LCMS™-8050RX

Application News

Quantitative Analysis of Nine Haloacetic Acids in Tap Water Using LCMS™-8050RX

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User Benefits

- Enable users to analyze nine haloacetic acids only 15 minutes per cycle using a simple dechlorination pretreatment.
- Enable users to detect nine haloacetic acids at 2 µg/L in water.
- Enable users to analyze nine haloacetic acids with good repeatability and recovery rates that are compliant with validation guidelines.

■ Introduction

Haloacetic acids in tap water are by-products from disinfection processes during water treatments. In Japan, the Ministerial Ordinance Concerning Water Quality Standards[1] specifies drinking water quality standards for three haloacetic acids: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA) (with limit values of 0.02 mg/L for MCAA, 0.03 mg/L for DCAA, and 0.03 mg/L for TCAA, respectively). The ordinance also specifies items for further study for the following six additional acids: bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), and tribromoacetic acid (TBAA).

The EU issued a directive, which became effective in 2020, that regulates five haloacetic acids, that is, the three acids governed by Japanese water quality standards as well as MBAA and DBAA.[2]

Haloacetic acids are analyzed using gas chromatography-mass spectrometry (GC/MS) or liquid chromatography-mass spectrometry (LC/MS). In particular, the LC/MS enables more efficient measurements since dechlorination is the only for required pretreatment.

This Application News describes an example of analyzing the nine haloacetic acids using the LCMS-8050RX, triple quadrupole mass spectrometer system (Fig. 1).

Fig. 1 LCMS™-8050RX Triple Quadrupole Mass Spectrometer and CoreSpray Technology

■ MRM Chromatogram and Calibration Curves for Standard Mixture Solution of Nine Haloacetic Acids

The analytical conditions are listed in Table 1 and the MRM transitions in Table 2.

MRM chromatograms of the nine haloacetic acids at concentrations of 2 µg/L each are shown in Fig. 2. Calibration curves for the concentrations ranging from 2 to 30 µg/L each are shown in Fig. 3. The coefficient of determination (r^2) of each calibration curve was higher than 0.999, demonstrating good linearity across each calibration range.

We obtained good accuracy with 80 to 120 % and repeatability with less than 10 % RSD, respectively (Table 3).

Table 1 Analytical Conditions

[HPLC Conditions] (Nexera™ X3)	
Column:	Shim-pack™ GIST-HP C18* (150 mm × 3.0 mm I.D. 3 µm)
Mobile Phases:	A) 0.2 % Formic acid-Water B) 0.2 % Formic acid-Methanol
Time Program:	B. conc. 1 % (0 min) - 100 % (7 - 11 min) - 1 % (11.01 - 15 min)
Flowrate:	0.5 mL/min
Column Temp.:	40 °C
Injection Volume:	20 µL
[MS Conditions] (LCMS-8050RX)	
Ionization:	ESI (Negative)
DL Temp.:	150 °C
Block Heat Temp.:	100 °C
Interface Temp.:	130 °C
Nebulizing Gas Flow:	3 L/min
Heating Gas Flow:	5 L/min
Drying Gas Flow:	15 L/min

*P/N: 227-30040-05

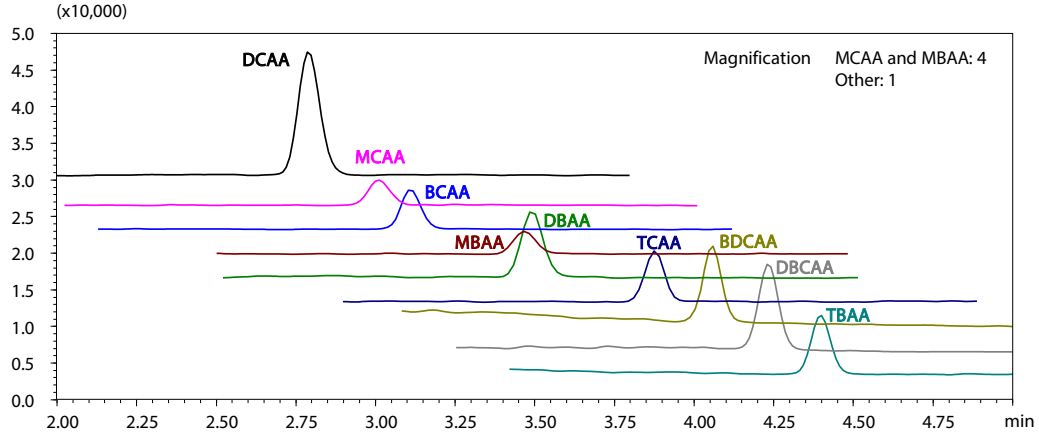

Fig. 2 MRM Chromatograms of Nine Haloacetic Acids (2 µg/L Each)

Table 2 MRM Transitions for Each Compound

Compound	Polarity	MRM Transition	Compound	Polarity	MRM Transition
MCAA	(-)	93.00 > 34.90	DBAA	(-)	262.80 > 172.80
DCAA	(-)	127.00 > 83.00	BDCAA	(-)	252.80 > 162.90
TCAA	(-)	161.00 > 116.90	DBCAA	(-)	296.80 > 206.80
MBAA	(-)	182.90 > 78.90	TBAA	(-)	340.70 > 250.80
BCAA	(-)	218.90 > 128.90			

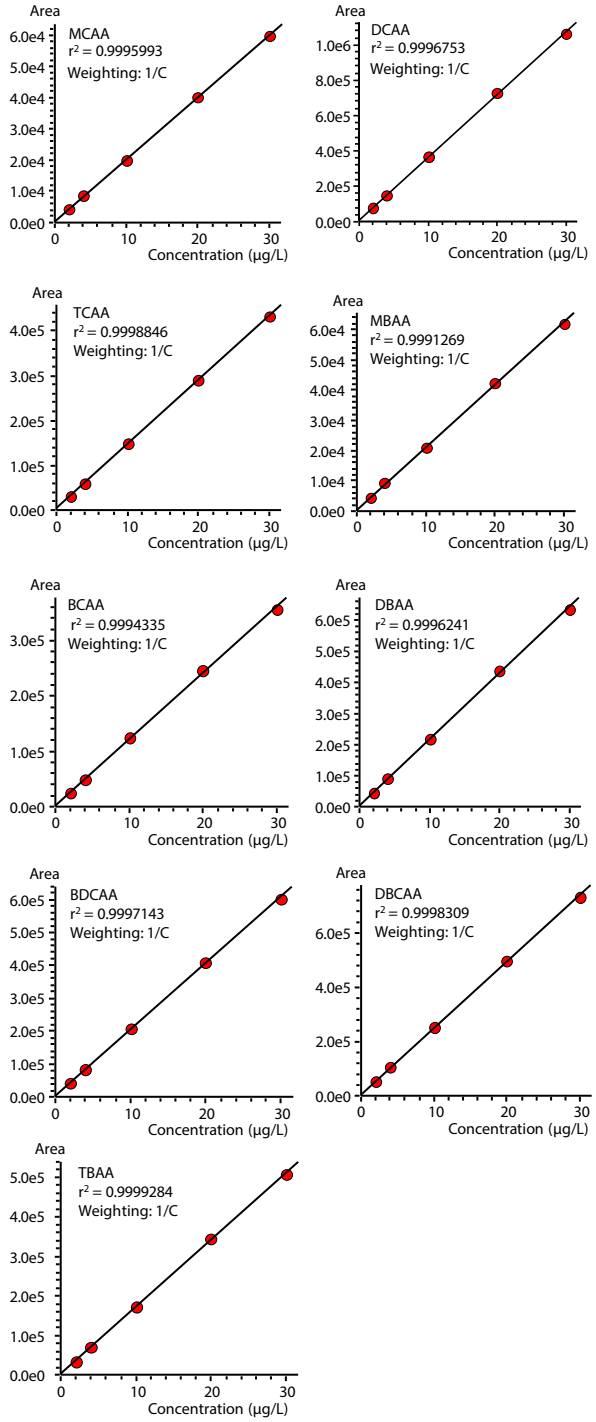

Fig. 3 Calibration Curve for Each Component

Table 3 Standard Sample Repeatability Results (2 µg/L, n = 5)

Compound	Mean Accuracy (%)	Repeatability (Conc. %RSD)	Compound	Mean Accuracy (%)	Repeatability (Conc. %RSD)
MCAA	101.6	3.8	DBAA	94.8	3.8
DCAA	103.3	3.7	BDCAA	99.6	3.7
TCAA	93.3	3.8	DBCAA	99.0	4.3
MBAA	84.4	5.2	TBAA	97.6	2.4
BCAA	101.0	4.3			

■ Using Tap Water for Validation Testing

A blank solution was prepared by adding sodium ascorbate to tap water as a dechlorinating agent. A haloacetic acid standard mixture solution was added to the blank solution to achieve a concentration of 2 µg/L, and then each acid was measured.

Good repeatability (concentration %RSD) values of 10 % or less and good recovery ratio within 80 to 120 % for all nine acids (Table 4) were obtained.

Table 4 Tap Water Spike and Recovery Test Results (n = 5)

Compound	Repeatability (Conc. %RSD)	Recovery Ratio (%)	Compound	Repeatability (Conc. %RSD)	Recovery Ratio (%)
MCAA	7.8	100.0	DBAA	3.2	97.2
DCAA	1.6	109.6	BDCAA	3.3	99.3
TCAA	2.9	88.5	DBCAA	2.9	96.6
MBAA	8.4	99.7	TBAA	3.7	98.5
BCAA	4.3	111.5			

■ Conclusion

Nine haloacetic acids specified for water quality testing criteria and monitoring were analyzed simultaneously in 15 minutes using the LCMS-8050RX system.

The results indicated that the system offered ample sensitivity for analyzing all haloacetic acids at concentrations of 2 µg/L, and it provided good calibration curve linearity within the 2 to 30 µg/L concentration range. In addition, spike-and-recovery tests of tap water samples (n = 5) provided good results with repeatability (concentration %RSD) of 10 % or less and recovery rates within the 80 to 120 % range. This confirms that analysis with good accuracy and repeatability can be performed with the LCMS-8050RX system.

Reference Documents

1) Ministerial Ordinance Concerning Water Quality Standards (Ministry of Health, Labour and Welfare Ordinance No. 101, May 30, 2003, and Ministry of Health, Labour and Welfare Ordinance 29, Revised March 2, 2015)
2) Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption

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