SHIMADZU
Excellence in Science

Application News

No.C89

LC/MS
Liquid Chromatography Mass Spectrometry

# Analysis of 9 Haloacetic Acids in Tap Water Using the LCMS-8040 Triple Quadrupole Mass Spectrometer

Haloacetic acids are produced as byproducts of chlorination during water treatment purification processes. Three haloacetic acids are subject to tap water quality standards with established limits, monochloroacetic acid (MCAA: 0.02 mg/L), dichloroacetic acid (DCAA: 0.04 mg/L), and trichloroacetic acid (TCAA: 0.2 mg/L).

Historically, methods for determination of haloacetic acids required solvent extraction and methylation with diazomethane followed by GC/MS analysis. However, Japan's Ministry of Health, Labor and Welfare Notification No. 66, 2012, recently specified LC/MS (/MS) as a new, alternative analytical method for haloacetic acids. Since LC/MS (/MS) analysis permits direct sample injection without the necessity for solvent extraction and derivatization as required by the GC/MS method, a significant improvement in laboratory efficiency can be expected.[1), 2)]

In accordance with the method specified for LC/MS (/MS) analysis, simultaneous determination of the three specified targets in a water quality standard, together with six bromine-containing haloacetic acids, was conducted for a total of nine substances. The instrument used for analysis was the LCMS-8040 triple quadrupole mass spectrometer.

Fig. 1 shows an MRM chromatogram of a 0.001 mg/L standard solution. Calibration curve correlation coefficients (R) and peak area repeatability (%RSD, n=3) for each component are shown in Table 1. Excellent linearity was obtained for each component, and peak area repeatability at 0.001 mg/L was less than 5 %.

Quantitation of tap water and spiked tap water samples was conducted for each of the haloacetic acids. Although the test method specifies that cleanup of the test water sample be conducted if necessary when the sample contains high concentrations of anions, excellent recoveries from 90 to 110 % were obtained using direct analysis of the tap water without significant interference from contaminants (Table 2).

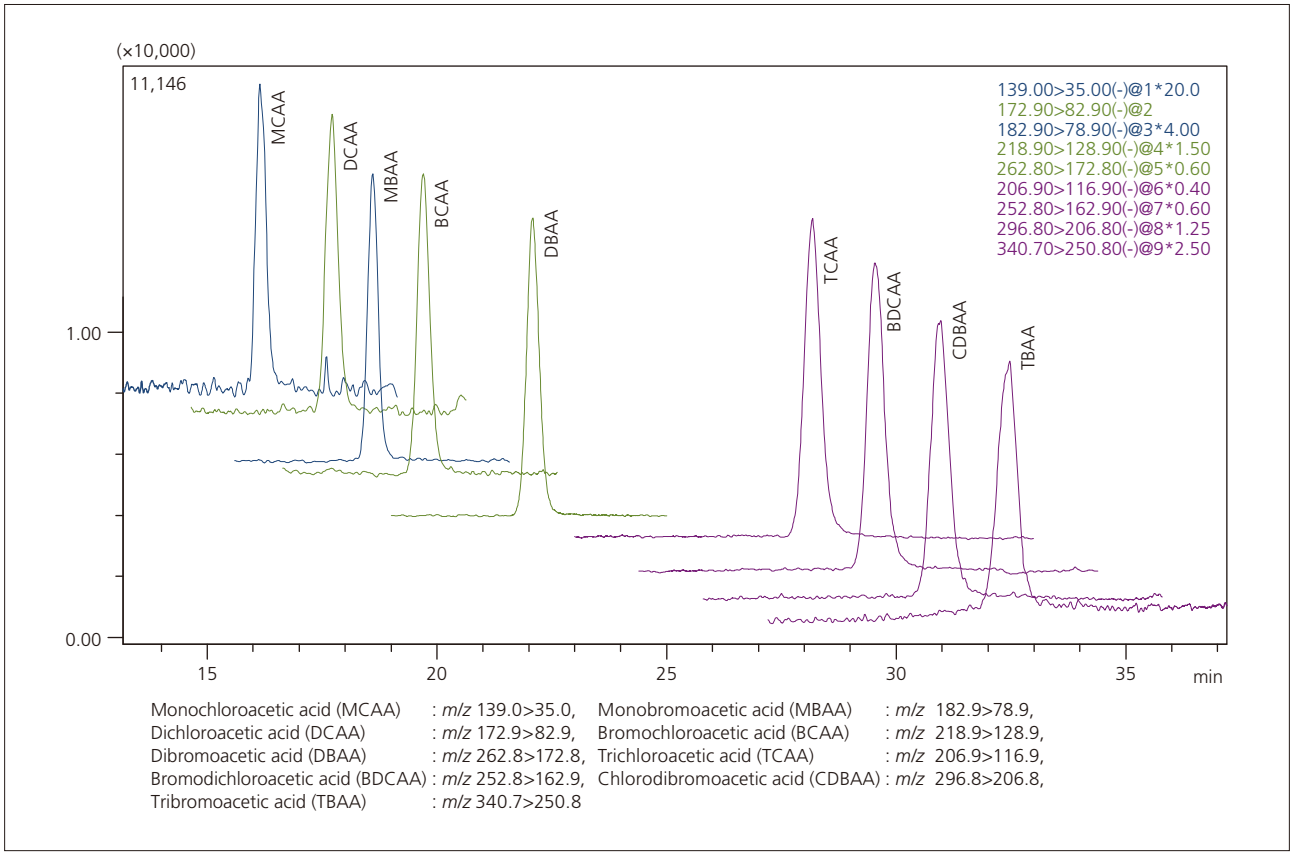


**Fig. 1 MRM Chromatograms of 9 Haloacetic Acids in a Standard Solution Mixture (0.001 mg/L)**

**Table 1 Calibration Curve Linearity and Peak Area Repeatability**

| | Correlation Coefficient R 0.001–0.2 mg/L | Area %RSD 0.001 mg/L |
|---|---|---|
| MCAA | 0.9956 | 2.6 |
| MBAA | 0.9988 | 0.3 |
| DCAA | 0.9950 | 2.7 |
| BCAA | 0.9960 | 1.9 |
| DBAA | 0.9965 | 0.8 |
| TCAA | 0.9987 | 0.7 |
| BDCAA | 0.9991 | 1.2 |
| CDBAA | 0.9983 | 3.3 |
| TBAA | 0.9956 | 0.9 |

**Table 2 Tap Water Quantitation and Spike Recovery Results**

| | Tap Water Sample Concentration mg/L | Recovery % (Spiked at 0.001 mg/L) |
|---|---|---|
| MCAA | N.D. | 92 |
| MBAA | N.D. | 102 |
| DCAA | Tr. | 109 |
| BCAA | N.D. | 104 |
| DBAA | Tr. | 99 |
| TCAA | 0.0031 | 105 |
| BDCAA | 00.0017 | 103 |
| CDBAA | 0.00034 | 105 |
| TBAA | Tr. | 98 |

N.D.: Not Detected, Tr.: Trace Level

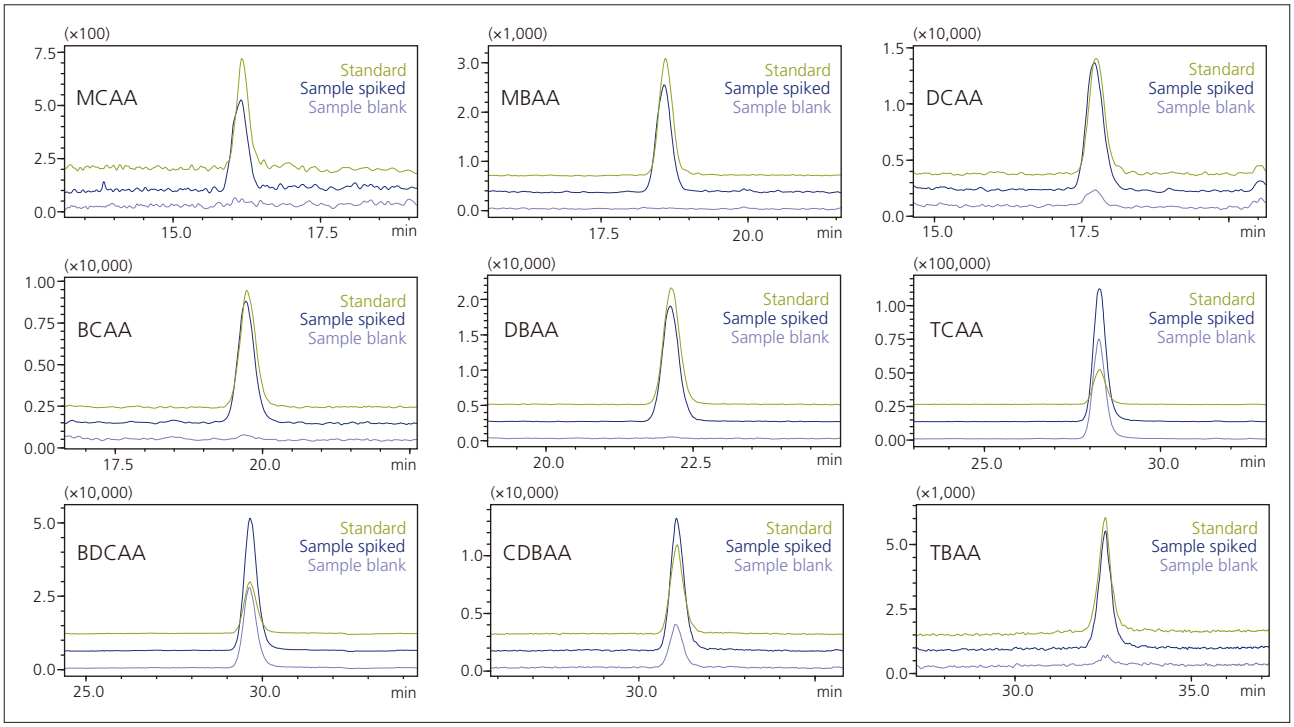


**Fig. 2 MRM Chromatograms of Haloacetic Acid Standard Solution (0.001 mg/L), Tap Water Blank, and Haloacetic Acid-Spiked Sample (0.001 mg/L each)**

**Table 3 Analytical Conditions**

| | |
|---|---|
| Column | : CAPCELL PAK MGⅢ (150 mm L. × 4.6 mm I.D., 3 µm) |
| Mobile Phases | : A: 0.2 % Formic acid-water, B: Methanol |
| Time Program | : 5 %B (0 min)→100 %B (38 min) →5 %B (38.01-50 min) |
| Flowrate | : 0.2 mL/min |
| Injection Volume | : 50 µL |
| Column Temperature | : 30 °C |
| Probe Voltage | : -3.5 kV (ESI-negative mode) |
| DL Temperature | : 150 °C |
| Block Heater Temperature | : 400 °C |
| Nebulizing Gas Flow | : 1.5 L/min |
| Drying Gas Flow | : 15 L/min |
| DL Voltage/Q-array Voltage | : Using default values |
| MRM Transition | : MCAA *m/z* 139.0>35.0, MBAA *m/z* 182.9>78.9, DCAA *m/z* 172.9>82.9, BCAA *m/z* 218.9>128.9, DBAA *m/z* 262.8>172.8, TCAA *m/z* 206.9>116.9, BDCAA *m/z* 252.8>162.9, CDBAA *m/z* 296.8>206.8, TBAA *m/z* 340.7>250.8 |

[References]
1) Maiko Tahara, Naoki Sugimoto, Reiji Kubota, Tetsuji Nishimura: Establishment of Direct Quantitation Method of Haloacetic Acids in Tap Water Using Liquid Chromatograph/Mass Spectrometer, Journal of the Japan Water Works Association, 907, 18-22 (2010).
2) Maiko Tahara, Reiji Kubota, Norihiro Kobayashi, Taku Tsukamoto, Naoki Sugimoto, Tetsuji Nishimura: Verification of Quantitative Accuracy of the LC/MS/MS and LC/MS Analysis of Haloacetic Acids in Tap Water in the Presence of Anions, Journal of the Japan Water Works Association, 931, 20-27 (2012).

First Edition: May. 2013

Shimadzu Corporation
www.shimadzu.com/an/