

# Application News

## No. C88

### Liquid Chromatography Mass Spectrometry

## Analysis of Haloacetic Acids in Tap Water Using LC/MS/MS [LCMS-8030]

Haloacetic acids are produced as by-products of chlorination in the water treatment purification process. Three haloacetic acids, monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA) (Fig. 1), are subject to water quality standard for drinking water with established limits (MCAA: 0.02 mg/L, DCAA: 0.04 mg/L, TCAA: 0.2 mg/L) by Japan Ministry of Health, Labour and Welfare. The specified test method (Notificated Method) for these 3 haloacetic acid compounds requires solvent extraction followed by methylation using diazomethane, and then quantitation by GC/MS.

On November 18, 2011, public comment was requested concerning the addition of LC/MS(/MS) as a new test method for haloacetic acids. This Application News introduces an example of analysis of the 3 haloacetic acids using the LCMS-8030 triple quadrupole mass spectrometer and is in accordance with this legislative measure.

The LC/MS(/MS) method eliminates the solvent extraction and derivatization steps currently conducted as part of the GC/MS method, and requires only the direct injection of the sample into the LC/MS<sup>(1), 2)</sup>. For the analytical conditions of the proposed method (Table 1), MCAA is eluted in 16.4 minutes, DCAA in 18.6 minutes, and TCAA in 30.3 minutes. Fig. 2 shows MRM chromatograms at 1/10th of the concentration of

the respective standard criteria values.

Fig. 3 shows the calibration curve linearity over a concentration range of 0.002-0.2 mg/L for each compound and peak area repeatability ( $n = 3$ ) at 0.002 mg/L. Excellent linearity was demonstrated for each compound, with  $R > 0.999$ , and %RSD for each was less than 10 % at 0.002 mg/L.

Fig. 4 shows the MRM chromatograms of tap water and tap water spiked with each of the 3 haloacetic acids at their respective standard threshold concentrations. According to the suggested LC/MS (/MS) method in the public comment, if there are high concentrations of anions in the tap water, then the sample water should be cleaned up as necessary. However, no significant interference due to contaminants was observed when conducting direct analysis of the tap water, and excellent recoveries were obtained.

#### [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: Validation 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, Posted in 2011.

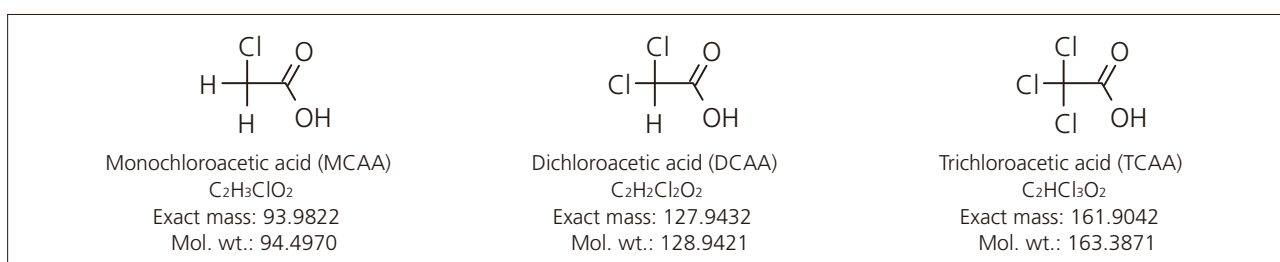


Fig. 1 Structures of Haloacetic Acids

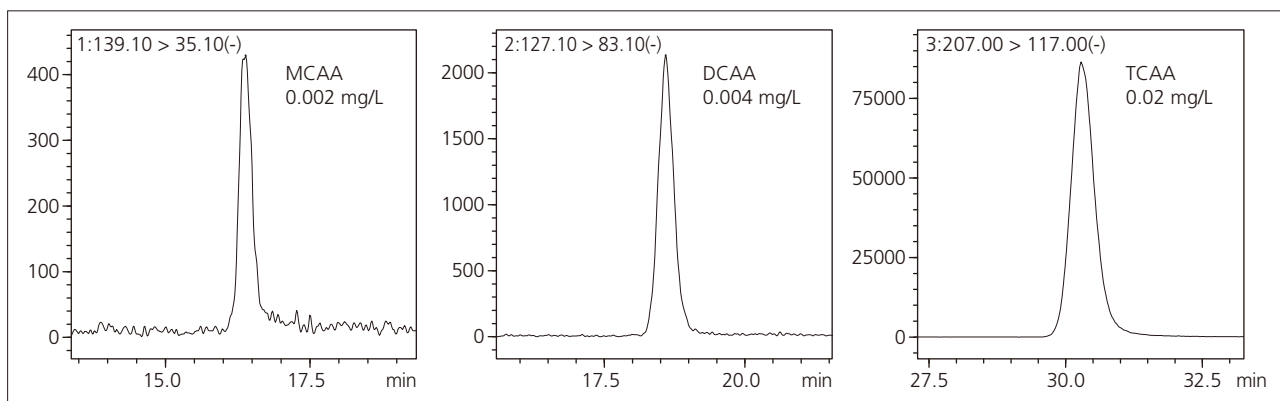


Fig. 2 MRM Chromatograms of MCAA (0.002 mg/L), DCAA (0.004 mg/L) and TCAA (0.02 mg/L)

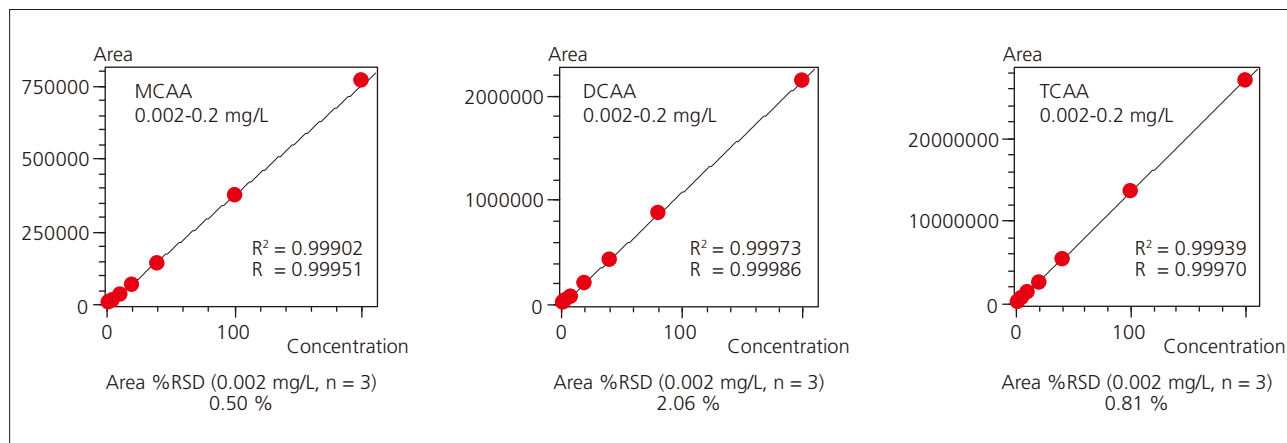


Fig. 3 Calibration Curve Linearity and Peak Area Repeatability

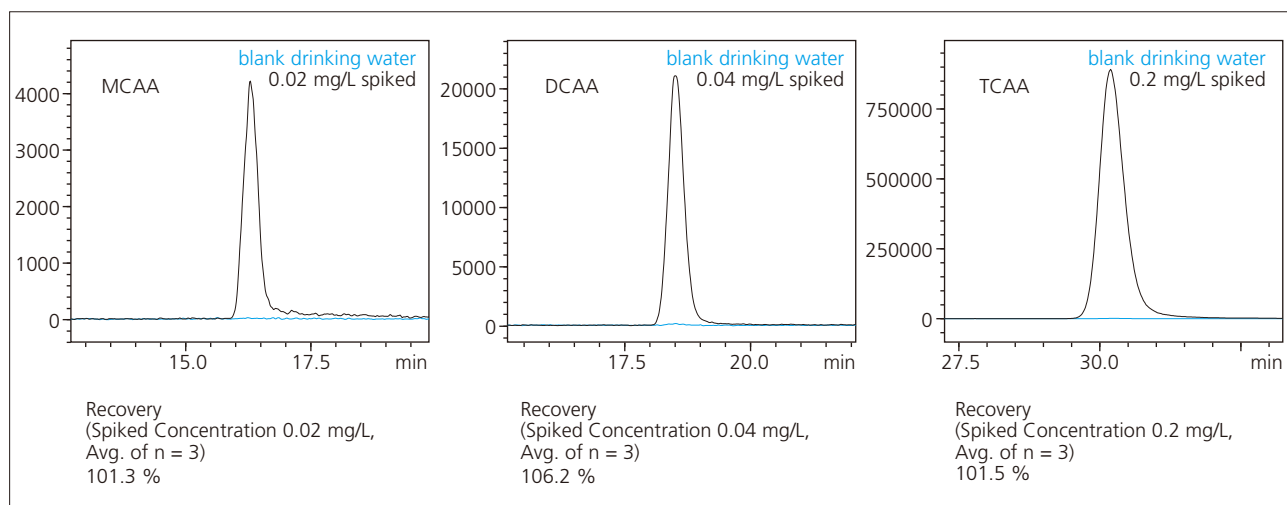


Fig. 4 MRM Chromatograms of Tap Water Blank and Tap Water Spiked with MCAA (0.02 mg/L), DCAA (0.04 mg/L) and TCAA (0.2 mg/L)

Table 1 Analytical Conditions

|                              |   |                          |            |
|------------------------------|---|--------------------------|------------|
| Column                       | : CAPCELL PAK MG III (150 mmL. × 4.6 mmI.D., 3 μm)  | Column Temperature       | : 30 °C    |
| Mobile Phases                | : A : 0.2 % Formic acid-water<br>B : Methanol   | Block Heater Temperature | : 100 °C   |
| Time Program                 | : 5 %B (0 min) → 100 %B (38 min) → 5 %B (38.01-50 min)                                      | Dryng Gas Flow           | : 15 L/min |
| Flow Rate                    | : 0.2 mL/min  |                          |            |
| Injection Volume             | : 50 μL   |                          |            |
| Probe Voltage                | : -3.5 kV (ESI-negative mode)   |                          |            |
| DL Temperature               | : 150 °C  |                          |            |
| Nebulizing Gas Flow          | : 1.5 L/min   |                          |            |
| DL Voltage / Q-array Voltage | : Using default values  |                          |            |
| MRM Transition               | : MCAA <i>m/z</i> 139.1 > 35.1, DCAA <i>m/z</i> 127.1 > 83.1, TCAA <i>m/z</i> 207.0 > 117.0 |                          |            |