

Analysis of Haloacetic Acids in drinking water without extensive sample preparation: the LC/MS/MS solution

Ruth Marfil-Vega¹; Kazuhiro Kwakami²; Junichi Masuda²

¹Shimadzu Scientific Instruments, Inc., Columbia, Maryland; ²Shimadzu Corporation, Kanagawa, Japan

1. Introduction

Haloacetic acids (HAAs) are known carcinogens that may occur as disinfection byproducts in drinking water. Currently five HAAs are regulated under the Stage 2 Disinfectants and Disinfection Byproducts Rule and occurrence of four more HAAs is being monitored under the Unregulated Contaminant Rule 4 (2018-2020) (Table 1). The vast majority of utilities and environmental commercial laboratories use EPA method 552.3 to ensure monitoring compliance with federal regulations. However, this method is tedious and prone to errors due to the complex sample preparation. Also, reagents required are potentially harmful for humans and ecosystems if not handled and disposed properly.

Method EPA 557, based on the use of suppressed ion chromatography mass spectrometry, is an alternative for the analysis of HAAs that has not been yet widely implemented due to practical challenges for implementing it as routine analysis in environmental laboratories.

An easier and faster alternative for the analysis of HAAs is based on the direct injection of the samples onto a LCMSMS. Countries like Japan and others use this method for compliance monitoring of HAAs in drinking water. Because of the ease of implementation and fast turn around time of results, this method is a promising alternative for the monitoring of HAAs, especially during events in which increased formation of HAAs could occur (e.x. chlorine burns, maintenance in water treatment plants and distribution system...). In this poster, the initial demonstration of the LCMSMS method performance is presented using the Shimadzu LCMSTM-8060.

Table 1. Haloacetic acids included in the HAA5 and HAA9 groups

| Compound | Acronyms | HAA Group | |
|--------------------------|----------|-----------|------|
| Monochloroacetic acid | MCAA | HAA5 | HAA9 |
| Monobromoacetic acid | MBAA | | |
| Dichloroacetic acid | DCAA | | |
| Trichloroacetic acid | TCAA | | |
| Dibromoacetic acid | DBAA | | |
| Bromochloroacetic acid | BCAA | HAA9 | |
| Bromodichloroacetic acid | BDCAA | | |
| Chlorodibromoacetic acid | CDBAA | | |
| Tribromoacetic acid | TBAA | | |

2. Experimental approach

Initial demonstration of performance of the Shimadzu LCMSTM-8060 (Figure 1) for the analysis of nine HAAs (MCAA, MBAA, DCAA, TCAA, DBAA, BCAA, BDCAA, CDBAA, TBAA) was conducted in this work. For this purpose, standards containing the target analysis were prepared in ultrapure water. Method optimization, including the identification of MRMs, was performed by Flow Injection Analysis with the MRM Optimization Wizard. Standard solutions with concentrations ranging from 1 to 50 µg/L were utilized in the subsequent experiments.

LCMS system and instrumental conditions are shown in Table 2 and retention time and MRM transitions are included in Table 3.



Figure 1. NexeraTM and LCMSTM-8060

Table 2. LC (top) and MSMS (bottom) conditions

| LC | Shimadzu LC 40 |
|------------------------------|---|
| Analytical Column | CAPCELLPAK C18 MGIII(150 mmL. X 3.0 mmI.D., 3 µm) |
| Injection Volume | 25 µL |
| LC Flow Rate | 0.5 mL/min |
| Mobile Phase A | 0.2% formic acid in water |
| Mobile Phase B | 0.2% formic acid in methanol |
| Run time | 15 minutes |
| MSMS | LCMS-8060 |
| Interface | ESI, Negative Mode |
| Interface Temperature | 130 °C |
| Desolvation Line Temperature | 150 °C |
| Heat Block Temperature | 100 °C |
| Heating Gas Flow | 15 L/min |
| Drying Gas Flow | 5 L/min |
| Neblizing Gas Flow | 3 L/min |

Table 3. Target compounds, retention times and MRMs.

| Compound | Retention (min) | MRM |
|----------|-----------------|---------------|
| MCAA | 3.0 | 93.00>34.90 |
| | | 139.00>34.80 |
| DCAA | 3.3 | 127.00>83.00 |
| | | 172.90>83.00 |
| MBAA | 3.4 | 182.90>78.90 |
| | | 137.30>78.85 |
| BCAA | 3.7 | 218.90>128.90 |
| | | 172.90>128.90 |
| DBAA | 4.1 | 262.80>172.80 |
| | | 216.80>172.95 |
| TCAA | 5.1 | 161.00>117.30 |
| | | 206.90>117.30 |
| BDCAA | 5.2 | 252.80>162.90 |
| | | 206.80>78.85 |
| CDBAA | 5.5 | 296.80>206.80 |
| | | 250.90>206.90 |
| TBAA | 5.9 | 340.70>250.80 |
| | | 294.90>250.85 |

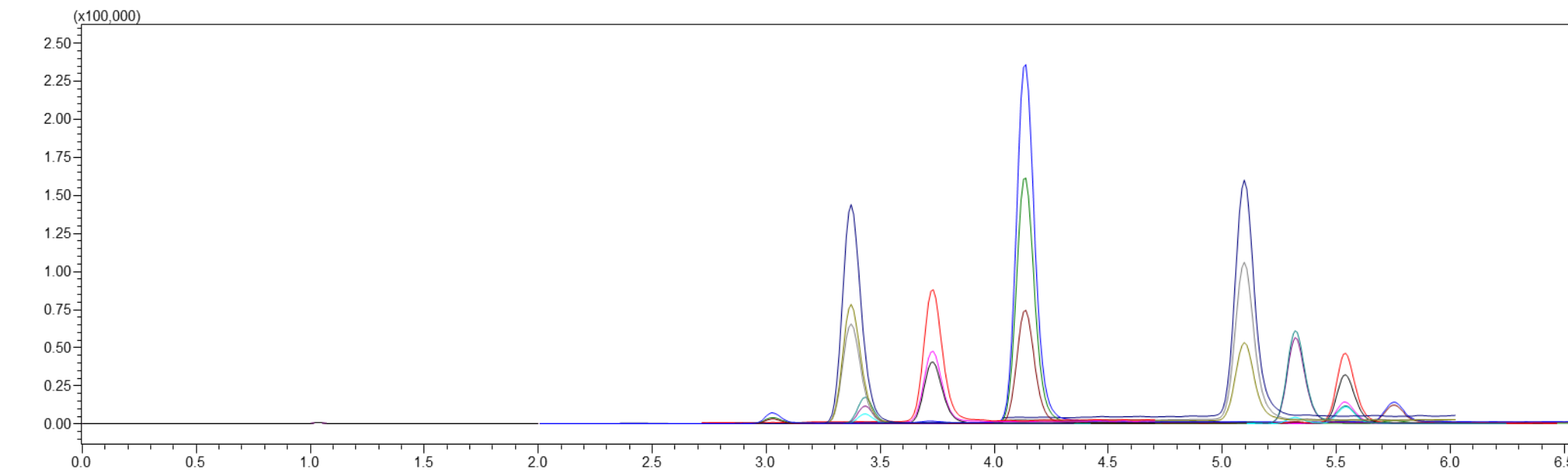


Figure 3. LCMS Chromatogram of a 10 µg/L HAAs standard.

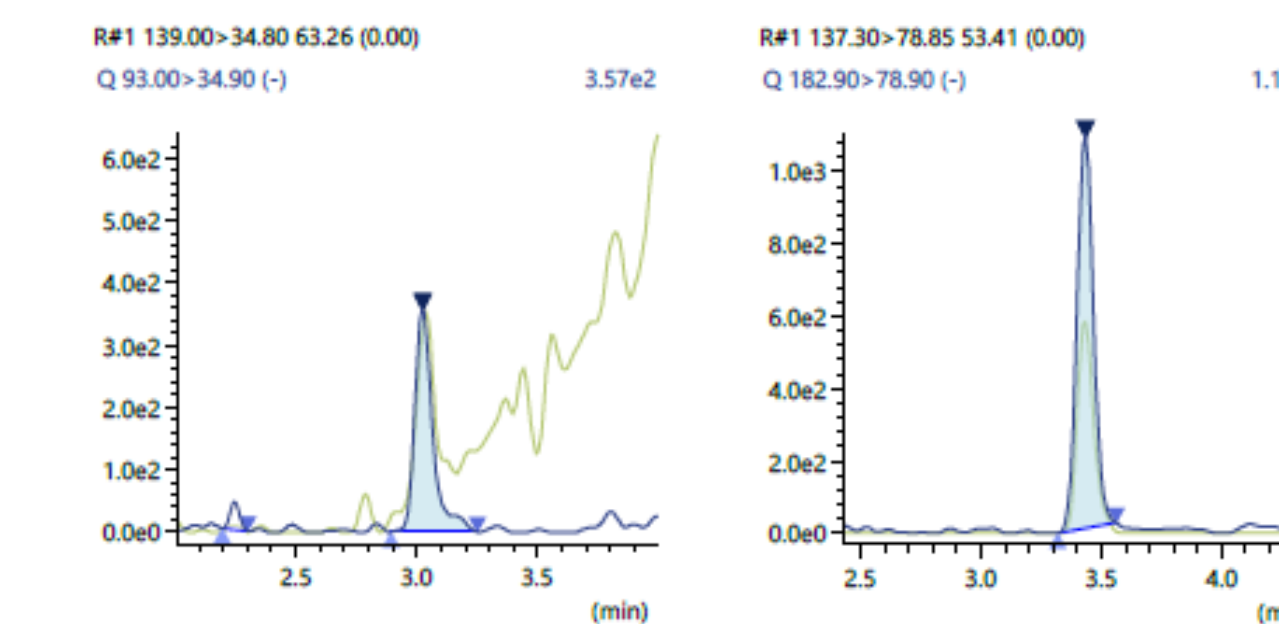


Figure 4. MRM transitions at 1 µg/L of MCAA (left) and MBAA (right).

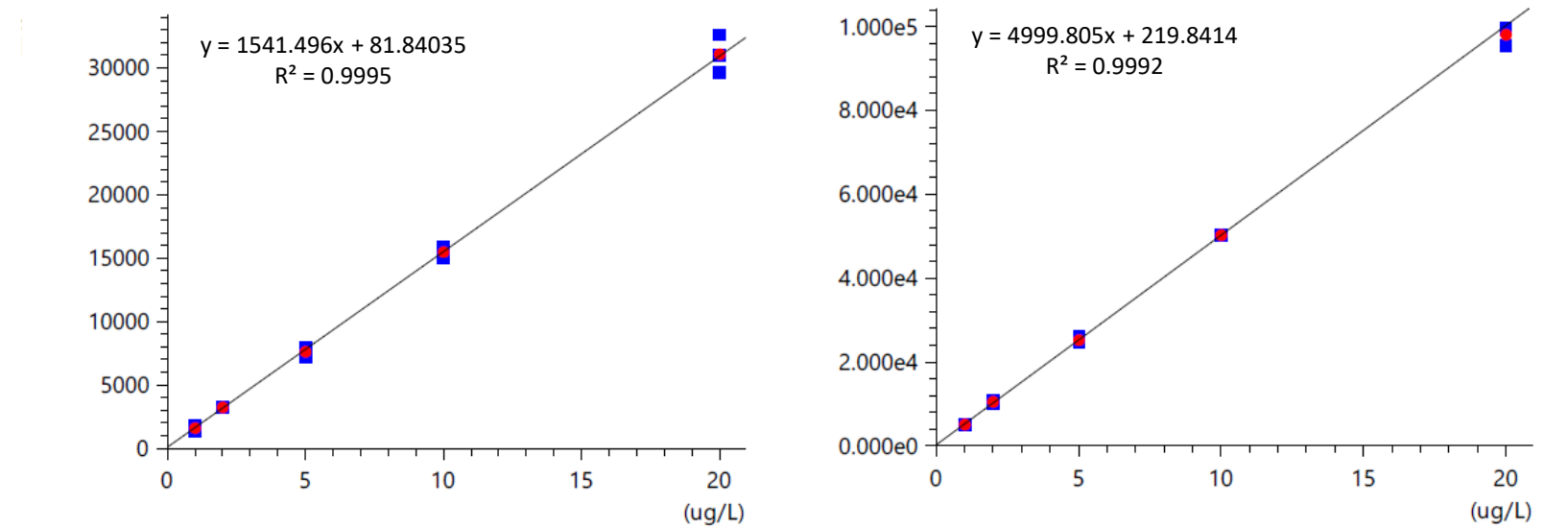


Figure 5. Calibration curve of MCAA (left) and MBAA (right).

Table 4. Linear range, r², S/N and MDL

| Compound | Linear Range (µg/L) | r ² | S/N (1 µg/L) | %Recovery 5 µg/L (n=7) | %RSD 5 µg/L (n=7) |
|----------|---------------------|----------------|--------------|------------------------|-------------------|
| MCAA | 1-50 | 0.999 | 16.5 | 106.2 | 4.0 |
| DCAA | 1-50 | 0.999 | 89.5 | 111.7 | 4.8 |
| MBAA | 1-50 | 0.999 | 37.7 | 113.4 | 4.5 |
| BCAA | 1-50 | 0.999 | 43.24 | 113.4 | 4.5 |
| DBAA | 1-50 | 0.999 | 52.45 | 107.7 | 5.1 |
| TCAA | 1-50 | 0.999 | 17.0 | 112.8 | 4.8 |
| BDCAA | 1-50 | 0.999 | 37.31 | 112.2 | 5.8 |
| CDBAA | 1-50 | 0.999 | 22.6 | 109.5 | 11.0 |
| TBAA | 2-50 | 0.999 | 13.7(*) | 95.3 | 36.0 |

(*) S/N at 2 µg/L

3. Results

After initial method optimization, calibration curves ranging between 1 and 50 µg/L were analyzed. Concentration range selected was such to ensure coverage of the concentration range required in Japan. Figures 3, 4 and 5 show a chromatogram of the nine targets, and MRMs and calibration curves from selected compounds, respectively. Linear range was between 1 to 50 µg/L for all compounds except for TBAA (2-50 µg/L). Acceptable linearity (r²>0.99) was obtained for all targets (Table 4). Seven replicates of the 5 µg/L standard were analyzed; %recoveries and %RSD (shown in Table 4) for all targets, except TBAA, ranged between 106-113% and 4-11%, respectively.

4. Conclusions

Initial demonstration of the performance of the Shimadzu LCMSTM-8060 for the analysis of nine HAAs (MCAA, MBAA, DCAA, TCAA, DBAA, BCAA, BDCAA, CDBAA, TBAA) in terms of linearity, accuracy and precision was achieved. Current limit of quantification for the nine HAAs attained with current conditions are above those expected for the analysis of these compounds by EPA 557; however, lower limits can be potentially achieved with further method optimization based on S/N determined.