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LC-MS/MS Analysis of Haloacetic Acids with Simplified Sample Preparation

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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.

An easier and faster alternative for the analysis of HAAs is based on the direct injection of the samples onto a LC-MS/MS. 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.g. chlorine burns, maintenance in water treatment plants and distribution system…). In this poster, the initial demonstration of the LC-MS/MS method performance is presented using the Shimadzu LCMS-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		
Bromodichloroacetic acid	BDCAA		
Chlorodibromoacetic acid	CDBAA		
Tribromoacetic acid	TBAA		

Figure 1. Nexera and LCMS-8060

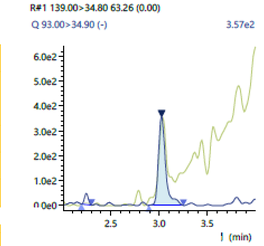
2. Experimental

Initial demonstration of performance of the Shimadzu LCMS-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 analytes 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 times are included in Table 3.

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
Nebulizing Gas Flow	3 L/min



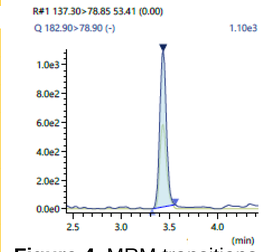


Figure 4. MRM transitions at 1 µg/Lof MCAA (top) and MBAA (bottom).

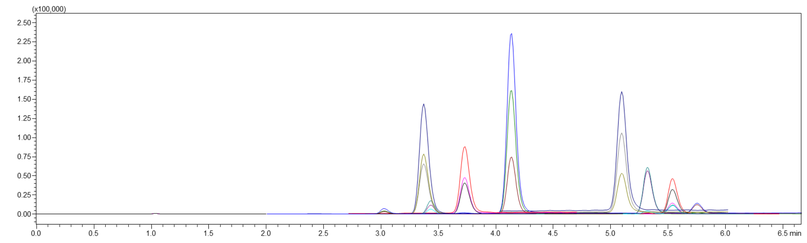


Figure 3. LCMS Chromatogram of a 10 µg/L HAAs standard.

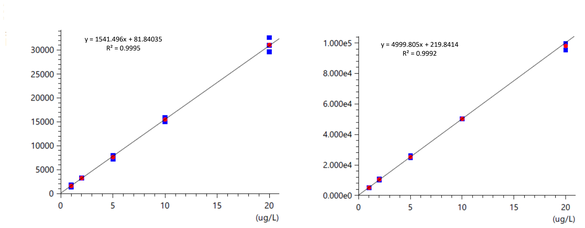


Figure 5. Calibration curve of MCAA (left) and MBAA (right).

Table 4. Retention Time, Linear Range, and r^2.

Compound	Retention Time, min	Linear Range (µg/L)	r^2
MCAA	3.0	1-50	0.999
DCAA	3.3	1-50	0.999
MBAA	3.4	1-50	0.999
BCAA	3.7	1-50	0.999
DBAA	4.1	1-50	0.999
TCAA	5.1	1-50	0.999
BDCAA	5.2	1-50	0.999
CDBAA	5.5	1-50	0.999
TBAA	5.9	2-50	0.999

Table 5. Signal to Noise, and Accuracy.

Compound	S/N (1 µg/L)	%Recovery 5 µg/L (n=7)	%RSD 5 µg/L (n=7)
MCAA	16.5	106.2	4.0
DCAA	89.5	111.7	4.8
MBAA	37.7	113.4	4.5
BCAA	43.24	113.4	4.5
DBAA	52.45	107.7	5.1
TCAA	17.0	112.8	4.8
BDCAA	37.31	112.2	5.8
CDBAA	22.6	109.5	11.0
TBAA	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 was selected according to regulations 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 (r^2>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 5) for all targets, except TBAA, ranged between 106-113% and 4-11%, respectively.

4. Conclusions

Initial demonstration of the performance of the Shimadzu LCMS-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. Good accuracy and linearity was obtained down to 1 µg/L for all HAAs except for TBAA (2 µg/L) with ample signal to noise ratios.

This work demonstrates the suitability of LC-MS/MS for the analysis of HAAs with minimal sample preparation and provides an alternative to complex methods, such as EPA 552.3.