

Simultaneous LC-MS/MS Analysis of Haloacetic Acids, Bromate, Chlorate, and Dalapon in Water Samples

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1. Overview

Haloacetic acids, bromate, chlorate, and Dalapon were analyzed in one method on an LCMS-8060NX in various water matrices.

2. Introduction

During the disinfection of drinking water, disinfection by-products are formed. Common examples are chlorate, bromate, and haloacetic acids. All these compounds have been linked to various cancers. Dalapon is an herbicide used in agriculture and has been found to cause kidney defects.¹

The U.S. Environment Protection Agency (EPA) regulates five of the haloacetic acids, known as HAA5: monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), and trichloroacetic acid (TCAA). There are an additional four haloacetic acids currently not regulated: tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), chlorodibromoacetic acid (CDBAA), and bromodichloroacetic acid (BDCAA). Combined they are known as HAA9.² This method uses reverse phase chromatography to analyze HAA9, bromate, chlorate, and Dalapon, pictured in Figure 1, in one injection.

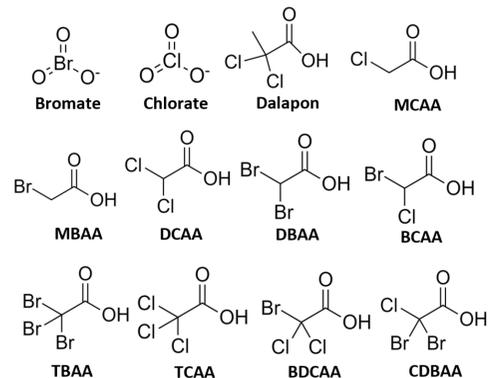


Figure 1. Structure of analytes.

3. Methods

A Shimadzu LC-30 Nexera HPLC system was coupled to an LCMS-8060NX with electrospray ionization (ESI) shown in Figure 2. All compounds were analysed in negative mode. The mobile phase composition, gradient, column, column oven temperature, and interface parameters were optimized to achieve the best sensitivity and peak shape (Table 1). MRM transitions are shown in Table 2.

Calibration curves of HAA9, bromate, chlorate, and Dalapon were created in LCMS grade water from 0.05-100 µg/L. A laboratory fortified blank (LFB) was created by adding 100 mg/L ammonium chloride to LCMS grade water. A synthetic sample matrix (SSM) was created by EPA specified amounts of ammonium chloride, nitrate, bicarbonate, chloride, and sulfate to water.² Six water samples were acquired from various locations near the laboratory. All standards and samples were spiked with internal standards at the following concentrations: chloroacetic acid-2-13C at 20 µg/L, monobromoacetic acid-1-13C at 10 µg/L, dichloroacetic acid-2-13C at 5 µg/L, and trichloroacetic acid-2-13C at 10 µg/L.



Figure 2. LCMS-8060NX triple quadrupole mass spectrometer.

Table 1. Liquid chromatography and mass spectrometry parameters.

LC Conditions		MS Conditions					
Mobile Phase A	0.05% formic acid in H ₂ O	Nebulizing Gas	2 L/min				
Mobile Phase B	0.3% formic acid in 80:20 MeOH:H ₂ O	Heating Gas Flow	Time (min)	Flow (L/min)			
Flow Rate	0.5 mL/min		0-10	20			
			10-15	5			
			15-20	20			
		Drying Gas Flow	20				
Gradient	Time (min)	% B	Interface Temp.				
			0-2	1	100°C		
			6	40	Desolvation Temp.	Time (min)	Temp (°C)
			7	60			
12	100	10-15	100				
16	100	15-20	130				
16.1	1	20	Stop	Heat Block Temp.	75°C		
20	Stop	Column	Capcell Pak C18 MGIII 150x3mm, 3 µm	Interface Voltage	1 kV		
Column	Capcell Pak C18 MGIII 150x3mm, 3 µm	Focus Voltage	2 kV	Injection Volume	30 µL		

Table 2. MRM transitions for all compounds

Compound	Q1 (m/z)	Q3 (m/z)	Compound	Q1 (m/z)	Q3 (m/z)
BrO ₃ ⁻	127.05	111.00	TCAA	207.05	117.30
	127.05	95.00		163.05	119.00
ClO ₃ ⁻	83.10	67.00	BDCAA	252.80	163.00
	83.10	51.05		252.80	81.00
MCAA	93.05	35.05	CDBAA	296.80	206.8
	139.15	35.10		207.00	79.2
DCAA	127.05	83.10	TBAA	340.85	250.85
	173.10	83.05		251.00	79.00
MBAA	183.00	79.00	MCAA-2-13C	94.05	35.10
	137.05	79.00			
BCAA	219.05	129.00	MBAA-1-13C	138.05	78.90
	173.05	81.05			
DBAA	262.95	172.80	DCAA-2-13C	128.05	84.00
	217.00	172.95			
Dalapon	141.05	97.00	TCAA-2-13C	162.05	118.05
	141.05	35.10			

4. Results

All compounds were quantified by an internal standard with a 20-minute separation method. Calibration curves were acquired in LCMS grade water in triplicate. Linear curves with a weighting of 1/C² were acquired with a coefficient of determination (R²) higher than 0.99 for all compounds, shown in Figure 2. Accuracies for calibration points are within 80-120%.

LFB samples were fortified with analytes at 5 µg/L and 100 µg/L. Each LFB was injected six times to give recoveries ranging from 80-120% with percent RSD (relative standard deviation) less than 15%.

The SSM was purposely made to contain a higher ionic concentration than typical drinking water. Peak shape was evaluated in the SSM, shown in Figure 3. Early eluting compounds had slight peak splitting and broadening, but later eluting compounds were not affected by the matrix. Six water samples were injected in triplicate, resulting concentrations are shown in Table 3.

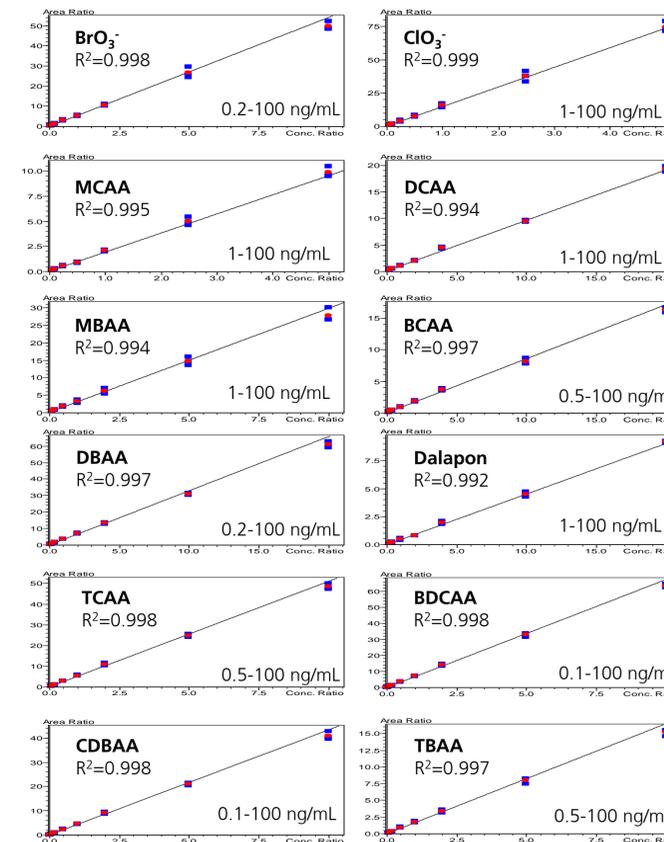


Figure 2. Calibration curves with R² for all analytes in LCMS grade water. All curves were acquired in triplicate with a weighting of 1/C².

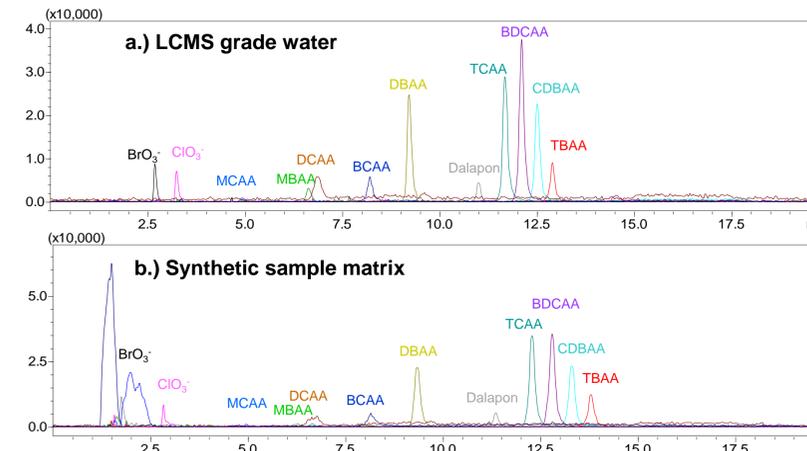


Figure 3. LCMS-8060NX triple quadrupole mass spectrometer. Chromatogram of HAAS, bromate, chlorate and Dalapon in at 5 µg/L in a.) LCMS grade water, b.) synthetic sample matrix.

Table 3. Internal Concentrations of HAAs, bromate, chlorate, and Dalapon in water samples (mean ± standard deviation, (µg/L), n=3).

Compound	DI Water	Tap Water A	Tap Water B	Tap Water C	River	Stream
BrO ₃ ⁻	ND	ND	ND	ND	ND	ND
ClO ₃ ⁻	ND	250 ± 20	220 ± 30	400 ± 50	16.1 ± 0.3	ND
MCAA	ND	ND	ND	ND	ND	ND
DCAA	ND	9.8 ± 0.7	ND	ND	ND	ND
MBAA	ND	ND	ND	ND	ND	ND
BCAA	ND	1.2 ± 0.1	ND	ND	ND	ND
DBAA	ND	ND	ND	ND	ND	ND
Dalapon	ND	1.5 ± 0.2	3.2 ± 0.8	ND	ND	ND
TCAA	ND	19 ± 1.0	15.5 ± 0.3	<LOQ	<LOQ	<LOQ
BDCAA	ND	3.57 ± 0.11	1.639 ± 0.010	0.16 ± 0.04	ND	ND
CDBAA	<LOQ	0.38 ± 0.09	<LOQ	<LOQ	ND	ND
TBAA	ND	ND	ND	ND	ND	ND
Total of HAAs	0	34.3	17.2	0.2	0	0

5. Conclusions

- A 20-minute method developed to analyze nine haloacetic acids, bromate, chlorate, and Dalapon on an LCMS-8060NX.
- Excellent linearity with R² greater than 0.99 and accuracy between 80 and 120%.
- Recovery at 5 and 100 µg/L in matrix was between 80 and 120%.
- Matrix effects in synthetic sample matrix affected early eluters more than late eluters.

References

1. EPA | Envirofacts | ICR https://archive.epa.gov/enviro/html/icr/web/html/gloss_dbp.html#haa (accessed 2021 -06 -17).
2. EPA. Method 557: Determination of Haloacetic Acids, Bromate, and Dalapon in Drinking Water by Ion Chromatography Electrospray Ionization Tandem Mass Spectrometry (IC-ESI-MS/MS). September 2009.