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Simultaneous LC-MS/MS Analysis of Bromate, Chlorate, Dalapon, and Haloacetic Acids in Drinking Water Samples using LCMS-8060RX

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1. Overview

A rapid LC-MS/MS method for analysis of haloacetic acids was developed using the LCMS-8060RX to achieve sufficient sensitivity, accuracy, and reproducibility.

2. Introduction

Drinking water treatment plants that use chlorination or bromination for disinfection can create disinfection byproducts, or DBPs. These DBPs and dalapon can be analyzed using EPA Method 557, which utilizes ion chromatography electrospray ionization tandem mass spectrometry; however, the runtime is 56 minutes. A reverse-phase LC-MS/MS method was developed to analyze bromate, chlorate, dalapon, and nine haloacetic acids at NPDWR-relevant concentrations with improved throughput and minimal sample preparation compared to the regulated methods.

3. Method

Bromate, chlorate, dalapon, and nine haloacetic acids (i.e., bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CBDAA), dibromoacetic acid (DBAA), dichloroacetic acid (DCAA), monobromoacetic acid (MBAA), monochloroacetic acid (MCAA), tribromoacetic acid (TBAA), and trichloroacetic acid (TCAA)) were separated by a Nexera HPLC and quantified by a Shimadzu LCMS-8060RX with a runtime of 15 minutes. HPLC and MS parameters are shown in **Tables 1 and 2**. Neat standards for calibration were prepared from 0.1-100 ppb. Reagent water, tap water, and laboratory fortified synthetic sample matrix (LFSSM) described in EPA 557 were used for evaluation of method performance.

Table 1. HPLC and MS acquisition parameters

Nexera X3			LCMS-8060RX	
Analytical Column:		C18 Column	Ionization Type:	CoreSpray
Mobile Phase	A:	0.2% formic acid in water	Nebulizing Gas:	6.0 L/min
	B:	0.2% formic acid in methanol	Heating Gas:	10.0 L/min
Elution Scheme		Gradient	Interface Temp.:	130 °C
Flow rate:		0.5 mL/min	DL Temp:	150 °C
Oven temp (°C):		40 °C	Heat Block Temp.:	100 °C
Injection volume:		20 µL	Drying Gas:	12 L/min

4. Results and Discussion

Table 2. LCMS transitions and calibration curve/control performance.

Compound	Internal Standard	RT (min)	Q1 m/z	Q3 m/z	Precursor ion	Calibration Range (ppb)	Accuracy Range (%)	RSE (curve) %	R^2	Accuracy Range of CCC (%)	LFB RSD% NH4Cl	LFB RSD% LFSSM	NH4Cl Accuracy Range (%)	LFSSM Accuracy Range (%)
BrO3-	MBAA-1-13C	1.49	126.9	110.85 95.0	[M-]-	0.5-100	85.0-111.7	6.7	0.9958	89.1-111.2	1.7	1.2	91.8-96.1	42.4-44.2
ClO3-	MCAA-2-13C	1.64	83.0	66.95 51.0	[M-]-	0.5-50	84.3-116.4	8.2	0.9976	88.6-105.2	1.2	3.7	97.3-100.8	55.5-63.2
DCAA	DCAA-2-13C	3.10	126.9 172.9	92.9 83.0	[M-H]- [M+COOH]-	0.5-100	91.2-107.6	2.8	0.9994	93.7-102.9	1.1	1.1	102.4-106.0	102.0-105.2
MCAA	MCAA-2-13C	3.36	92.9 139.0	35.0 92.9	[M-H]- [M+COOH]-	5-100	94.0-109.6	5.3	0.9972	90.0-108.3	5.4	4.0	89.7-102.8	92.7-103.9
BCAA	DCAA-2-13C	3.47	218.9 218.9 172.9	128.9 173.0 128.9	[M+COOH]- [M+COOH]- [M-H]-	0.5-100	79.7-115.2	7.1	0.9995	96.3-106.3	2.4	2.0	99.9-106.8	99.1-106.3
DBAA	DCAA-2-13C	3.89	262.8 216.8 262.8	173.0 173.0 216.9	[M+COOH]- [M-H]- [M+COOH]-	0.1-100	92.2-112.7	4.8	0.9995	96.2-101.6	2.4	1.8	103.5-110.3	110.4-116.4
MBAA	MBAA-1-13C	3.86	182.9 182.9 136.9	136.9 79.0 79.0	[M+COOH]- [M+COOH]- [M-H]-	5-100	91.2-107.1	4.8	0.9996	97.1-110.7	3.5	4.8	92.0-102.5	89.9-103.1
TCAA	TCAA-2-13C	4.31	206.9 206.9 160.9	116.9 161.0 116.9	[M+COOH]- [M+COOH]- [M-H]-	0.5-100	93.1-106.8	4.4	0.999	93.4-104.4	1.9	1.6	102.3-108.8	101.7-107.0
BDCAA	TCAA-2-13C	4.49	252.9 252.9 206.8	163.0 81.0 81.0	[M+COOH]- [M+COOH]- [M-H]-	0.5-100	81.4-117.2	6.5	0.9991	94.4-104.0	1.8	1.9	102.2-108.1	99.9-106.3
Dalapon	DCAA-2-13C	4.94	187.0 187.0 141.0	141.0 97.0 97.0	[M+COOH]- [M+COOH]- [M-H]-	2-100	85.3-113.8	7.3	0.9948	88.7-113.3	1.9	1.8	101.0-106.9	100.2-105.8
CDBAA	TCAA-2-13C	4.68	296.8 206.8 250.8	206.9 78.9 206.9	[M+COOH]- [M-COOH]- [M-H]-	0.5-100	91.3-108.9	4.8	0.9989	90.7-104.4	2.7	2.0	99.2-106.7	96.3-102.0
TBAA	TCAA-2-13C	4.85	340.8 250.8 250.8	250.9 78.9 80.9	[M+COOH]- [M-COOH]- [M-COOH]-	1-100	87.1-117.7	8.8	0.9975	85.4-105.8	4.3	2.6	100.1-113.7	95.6-103.7
DCAA-2-13C	--	3.11	127.9 127.9	83.9 35.0	[M-H]- [M-H]-	20	93.2-105.4	3.6	--	96.8-105.6	1.2	1.7	96.7-100.3	98.1-103.9
MCAA-2-13C	--	3.35	140.0 94.0	35.0 35.0	[M+COOH]- [M-H]-	20	90.4-118.4	6.9	--	97.9-105.8	1.5	3.6	95.2-99.9	96.9-107.8
MBAA-1-13C	--	3.86	137.9 182.9	78.9 78.9	[M-H]- [M+COOH]-	20	86.2-127.1	8.9	--	94.0-110.7	2.5	1.7	90.9-97.7	90.6-94.8
TCAA-2-13C	--	4.31	161.9 161.9	117.9 35.0	[M-H]- [M-H]-	20	80.0-115.9	9.9	--	93.6-110.0	1.8	2.2	89.6-94.9	93.1-98.6

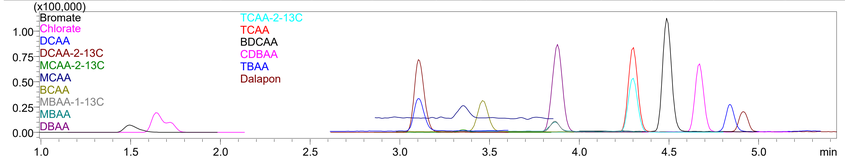

Figure 1. Chromatogram for all analytes at 5 ppb.

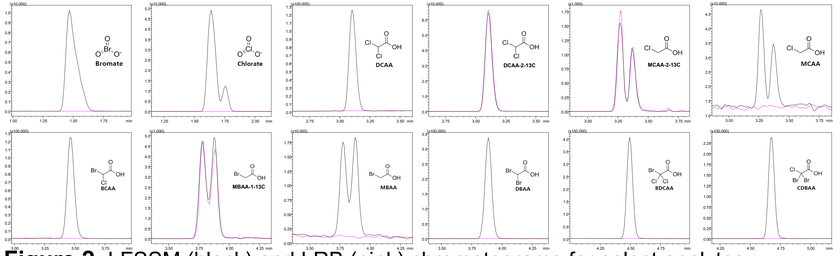

Figure 2. LFSSM (black) and LRB (pink) chromatograms for select analytes.

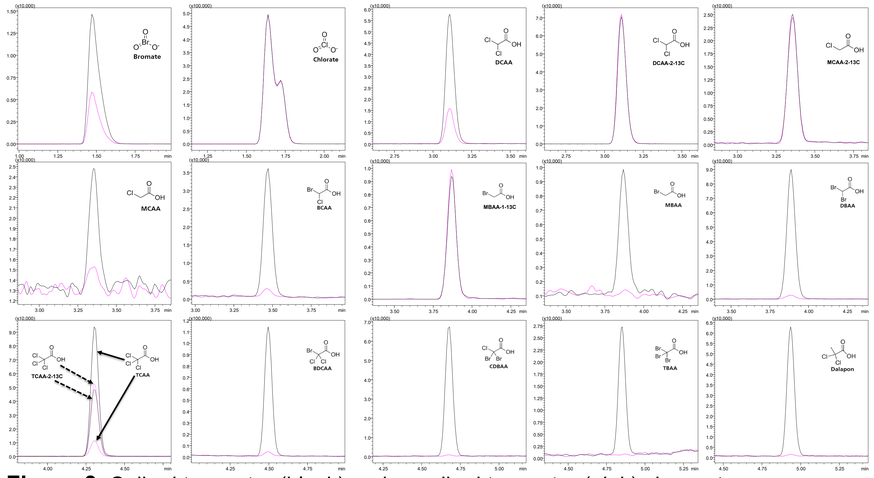

Figure 3. Spiked tap water (black) and unspiked tap water (pink) chromatograms.

Table 3. MDL and recovery of target analytes in reagent and tap water. Recovery of internal standards ranged from 95 to 110%. *Analyte was detected above the MDL but below the LOQ.

	BrO3-	ClO3-	DCAA	MCAA	BCAA	DBAA	MBAA	TCAA	BDCAA	Dalapon	CDBAA	TBAA
Concentration in Reagent Water (ppb)	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Average and Standard Dev. Recovery (%)	93.9 ± 1.5	100.9 ± 2.3	102.1 ± 1.8	99.1 ± 6.5	101.4 ± 2.7	100.3 ± 2.2	105.6 ± 6.1	101.7 ± 1.7	101.0 ± 1.5	99.1 ± 1.3	96.6 ± 2.2	96.4 ± 2.4
MDL in RW (ppb)	0.22	0.34	0.25	0.94	0.39	0.32	0.88	0.25	0.21	0.56	0.31	0.35
Concentration in Tap Water (ppb)	4.2	> 100	1.8	1.4*	<MDL	0.17	<MDL	0.6	<MDL	<MDL	<MDL	<MDL
Average and Standard Dev. Recovery (%)	117.7 ± 4.9	--	102.1 ± 1.5	87.5 ± 7.5	108.9 ± 3.4	100.4 ± 2.1	108.4 ± 4.3	99.4 ± 2.8	104.4 ± 1.9	100.5 ± 1.8	97.3 ± 3.2	98.3 ± 2.0
MDL in TW (ppb)	0.71	--	0.22	1.09	0.49	0.30	0.63	0.40	0.28	0.78	0.46	0.30

5. Conclusion

- A rapid, sensitive LC-MS/MS method for analysis of bromate, chlorate, dalapon and HAAs was shown to effectively quantify them in reagent water, tap water, and the LFSSM.
- Bromate and chlorate recoveries were reproducible, but recovery in the LFSSM can be improved with proper internal standards (e.g., $Br^{18}O_3$- and $Cl^{18}O_3$-).

6. References

1. U.S. Environmental Protection Agency, 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.
2. CFR Appendix B to Part 136, Title 40 -- Definition and Procedure for the Determination of the Method Detection Limit—Revision 2