thermoscientific

Determination of Haloacetic Acids, Bromate, and Dalapon in Drinking Water Using Ion Chromatography Coupled to High-Resolution Accurate-Mass (IC-HRAM) Mass Spectrometry

Beibei Huang, and Jeffrey Rohrer, Thermo Fisher Scientific, Sunnyvale, CA , USA, 94085

ABSTRACT

Purpose: To demonstrate the capability and performance of a Thermo Scientific™ Q Exactive™ HF Hybrid Quadrupole-Orbitrap™ Mass Spectrometer-based IC-HRAM MS method to identify and quantify nine haloacetic acids, bromate, and dalapon in drinking water.

Methods: We developed a fast, simple, and ultra-sensitive quantitation assay for determination of HAAs, bromate, and dalapon in drinking water using a recently introduced Thermo Scientific™ Dionex™ IonPac™ AS31 Column, Thermo Scientific™ Dionex™ ICS-6000 HPIC™ System, and a Q Exactive HF Hybrid Quadrupole-Orbitrap Mass Spectrometer.

Results: Sensitivity, linearity, accuracy, and precision were validated following the guidelines of U.S. EPA Method 557. Single laboratory lowest concentration minimum reporting levels (LCMRLs) ranged from 0.0011 to 0.18 µg/L. All three quantitation modes showed good linearity for all analytes with coefficients of determination of 0.9981- 0.9993. Both t-SIM/dd-MS^2 and PRM modes are sensitive to confirm the trace-level presence of all nine HAAs, bromate, and dalapon in the tap water sample. Full-scan HRAM data acquisition provides the benefits of simultaneous data collection for both targeted and non-targeted components, and thus, suitability for simultaneous quantification of an unlimited number of compounds. Data-dependent MS/MS (dd-MS^2) product-ion spectra were used for confirmation. Single laboratory precision was 0.078- 8.04%, and accuracy was in the range 70–130%.

INTRODUCTION

Disinfection processes were introduced in drinking water treatment for removing or killing pathogenic microorganisms. However, the applied disinfectants can react with the natural organic matter and anthropogenic contaminants to form disinfection by-products (DBPs). Haloacetic acids (HAAs) are one of the most commonly detected classes of DBPs and have captured considerable attention due to their adverse biological effects on human and aquatic organisms. Of the nine chlorinated and/or brominated HAAs, five are currently regulated by the U.S. Environmental Protection Agency (EPA) (HAA5): monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA). Consequently, the U.S. EPA has established a maximum contamination level (MCL) of 60 µg/L for HAA5 in drinking water. According to regulations, drinking water plants must determine the concentration of DBPs in drinking water prior to release. U.S. EPA Method 557 has been validated for the determination of HAAs, bromate, and dalapon.[1]

By comparison to the conventional U.S. EPA methods using GC with ECD, the combination of ion chromatography (IC) and mass spectrometry (MS) offers sensitive and rapid detection without the need for sample derivatization. In this study, we developed a fast, simple, and ultra-sensitive quantitation assay for determination of HAAs, bromate, and dalapon in drinking water using IC coupled to an electrospray ionization Quadrupole-Orbitrap Mass Spectrometer (IC-ESI-HRAM). Our study compared three types of targeted quantitation experiments including full-scan MS with data-dependent MS/MS (full MS/dd-MS^2 with inclusion list), targeted selected ion monitoring (SIM) with data-dependent MS/MS (t-SIM/dd-MS^2), and parallel reaction monitoring (PRM).

MATERIALS AND METHODS

Test Method(s)

IC conditions	
IC system:	Dionex ICS-6000 HPIC system
Mobile Phase:	KOH, Source: Dionex EGC 500 KOH with Dionex CR-ATC 600
Column:	Dionex IonPac AG31 Guard, 2 × 50 mm Dionex IonPac AS31 Analytical, 2 × 250 mm
Gradient:	17 mM (-0.5–7 min), 17–85 mM (7–18 min), 85 mM (18–40 min), 17 mM (40-47 min)
Pump Flow:	0.3 mL/min
Injection Volume:	100 µL
Temperature:	4 ºC (autosampler tray temperature), 15 ºC (column compartment), 20 ºC (detector compartment)
Detection:	Suppressed Conductivity, Dionex ADRS 600 Suppressor (2 mm), AutoSuppression, 64 mA, external water mode via one Dionex ICS-6000 DP Pump, external water flow rate (0.60 mL/min)

Q Exactive HF Hybrid Quadrupole-Orbitrap Mass Spectrometer detection	
Ion Source:	Electrospray ionization (ESI), negative mode
Divert valve switch time:	Eluent to waste 0–4 min, 8.6–11.1 min, 18.73–21.73 min, and 40-47 min
MS Desolvation Solvent:	None
HESI source:	Sheath gas flow rate: 40
	Aux gas flow rate: 8
	Sweep gas flow rate: 0
	Spray voltage (kV): 3
	Capillary temp. (ºC): 220
	S-lens RF level: 50
	Aux gas heater temp (º C): 325
Three types of experiments:	1. Full MS/dd-MS^2 with inclusion list, Table 1
	2. t-SIM/dd-MS^2
	3. PRM

Table 1. Full MS/ddMS^2 method with inclusion list

Mass [m/z]	Formula [M]	Species	CS [z]	Polarity	Start [min]	End [min]	(N)CE
92.97488	$C_2H_3O_2Cl$	- H	1	Negative	5.00	7.50	
136.92437	$C_2H_3BrO_2$	- H	1	Negative	6.00	8.00	52
126.90363	BrO_3		1	Negative	7.00	9.00	78
140.95156	$C_3H_4Cl_2O_2$	- H	1	Negative	11.00	13.00	13
126.93591	$C_2H_2Cl_2O_2$	- H	1	Negative	12.00	14.00	19
172.88335	C_2H_2[81]$BrClO_2$	- H	1	Negative	13.00	15.00	22
216.83283	C_2H_2[79]Br[81]BrO_2	- H	1	Negative	14.00	16.00	17
116.90711	CCl_3		1	Negative	22.00	24.50	23
162.85454	C_1[81]$BrCl_2$		1	Negative	24.00	27.00	17
206.80403	C_1[79]Br[81]BrCl		1	Negative	26.00	30.50	58
250.75351	C_1[79]Br_2[81]Br		1	Negative	31.00	36.00	49
94.97193	$C_2H_3O_2$[37]Cl	- H	1	Negative	5.00	7.50	
93.97824	[13]$C_1C_1H_3O_2Cl$	- H	1	Negative	5.00	7.50	
137.92772	[13]$C_1C_1H_3BrO_2$	- H	1	Negative	6.00	8.00	52
127.93926	[13]$C_1C_1H_2Cl_2O_2$	- H	1	Negative	12.00	14.00	19
117.91046	[13]C_1Cl_3		1	Negative	22.00	24.50	23

Note: Formula [M] stands for the structure of the active compound, CS [z] for the charge state of the ion to be fragmented, and (N)CE for normalized collision energy

Software

IC-HRAM MS data was acquired using Thermo Scientific™ Xcalibur™ 4.2 software with SII 1.5 for Xcalibur software, and processed using Thermo Scientific™ TraceFinder™ 5.0 software, which allow creation of the acquisition and processing methods for high-throughput quantitative analysis along with data reviewing and reporting. Data visualization was performed by Thermo Scientific™ FreeStyle™ Version 1.6.

RESULTS

IC-HRAM MS Separation and Peak Identification

Assay specificity was assessed by comparing the chromatograms of standards with samples. Figures 1A, and 2A show chromatograms of 9 HAAs, dalapon, and bromate standard solution containing the preservative and the labeled internal standards with retention times using three different acquisition modes. All methods effectively separate these compounds, as highlighted by the example chromatograms shown in Figures 1B, and 2B. A tap water sample containing the preservative and internal standards (4 µg/L each) is analyzed by three different acquisition modes, respectively. Figure 2 (right) illustrates the ability of a full-scan acquisition to detect non-target compounds such as chlorite, acetate, malonate, succinate, malate, chlorate, bromide, etc. without re-running samples.

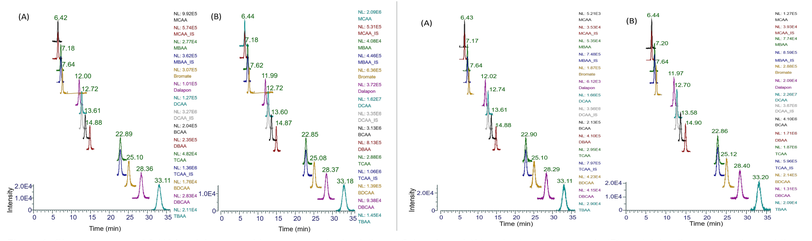

Figure 1. Chromatograms of 9 HAAs, dalapon, and bromate standard solution at 0.1 µg/L each(A) and a tap water sample (B) containing the preservative and the labeled internal standards (4 µg/L each) using t-SIM /dd-MS^2 mode (left) and PRM mode (right). Here the y-axis scale set to absolute (where the title is intensity) and normalization set to local. NL: Normalization level.

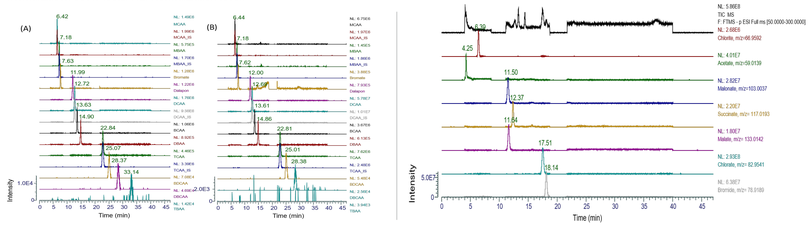

Figure 2. Chromatograms of 9 HAAs, dalapon, and bromate standard solution at 0.5 µg/L each(A) and a tap water sample (B) containing the preservative and the labeled internal standards (4 µg/L each) using Full MS/dd-MS^2 mode (left) , and non-target compounds are detected in tap water sample using Full MS/dd-MS^2 mode (right). Here the y-axis scale set to absolute (where the title is intensity) and normalization set to local. NL: Normalization level

Determination of the Single Laboratory Lowest Concentration Minimum Reporting Level (LCMRL)

Single laboratory LCMRLs for the analytes using three different acquisition modes ranged from 0.0011 to 0.18 µg/L. U.S. EPA 557 method reported that a volatile organic solvent was added as a make-up flow, after the conductivity detector (inline after the suppressor) and before the MS, to aid desolvation in the ion source.[1] Our results demonstrated high sensitivity of the Q Exactive Mass Spectrometer with no addition of organic solvent compared to QQQ MS/MS analysis with acetonitrile as a post-column organic modifier.

Calibration and Linearity

All the standard compounds showed good linearity (r^2 > 0.9981) in a relatively wide concentration range.[2] A calibration range of 0.1 to 20 µg/L works for most drinking water sources. The concentration of bromate in drinking water is estimated to be very low so that an extra calibration range of 0.025 to 2 µg/L was used.

Drinking Water Sample Analysis

The three quantitative methods were used to evaluate three types of drinking water samples: commercial bottled water, tap water, and tap water that has been through a filtered drinking water faucet, where the disinfectants were thought to be eliminated. The DBPs in tap water were shown to be dramatically reduced after they went through a filtered drinking water faucet, while commercial bottled water showed almost zero DBPs. The HAA5 in the tap water sample was about 34.5 µg/L and therefore was well within the specified limit of 60 µg/L. PRM mode provides the most sensitivity and selectivity for quantitation of compounds in the samples with a complex matrix. All three quantitative methods showed good quantitative performance and obtained similar values.

Precision and accuracy

Single laboratory precision and accuracy are assessed in three water matrices: reagent water (DI water), laboratory synthetic sample matrix (LSSM) , and tap water. Single laboratory precision was measured by relative standard deviation (RSD) of replicate analyses (n=7), and accuracy was measured by percent recoveries of fortified water samples. Single laboratory precision was 0.078-8.04%, and accuracy was in the range 70–130%.

CONCLUSIONS

- IC-HRAM MS is well suited for trace-level detection and quantification of HAAs in drinking water and offers good sensitivity.
- Both t-SIM/dd-MS^2 and PRM modes are sensitive to confirm the trace-level presence of all nine HAAs, bromate, and dalapon in the tap water sample. Full-scan HRAM data acquisition provides the benefits of simultaneous data collection for both targeted and non-targeted components, and thus, suitability for simultaneous quantification of an unlimited number of compounds.
- Sensitivity, linearity, accuracy, and precision were validated following the guidelines of U.S. EPA Method 557.

Note: See Thermo Scientific Application Note 73390 for more details [2].

REFERENCES

1. United States Environmental Protection Agency Method 557, Determination of Haloacetic Acids, Bromate, and Dalapon in Drinking Water by Ion Chromatography Electrospray Ionization Tandem Mass Spectrometry. 2009.
2. Thermo Scientific Application Note 73390: Determination of Haloacetic Acids, Bromate, and Dalapon in Drinking Water Using Ion Chromatography Coupled to High-Resolution Accurate-Mass (IC-HRAM) Mass Spectrometry. Sunnyvale, CA. 2020.

TRADEMARKS/LICENSING

PO65762-EN 0422S

ThermoFisher SCIENTIFIC