Fast determination of nine haloacetic acids, bromate, and dalapon at trace levels in drinking water samples by tandem IC-MS/MS

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INTRODUCTION

Haloacetic acids (HAAs) are disinfection by-products (DBPs) formed during the disinfection of drinking water using disinfectants such as chlorine or chloramine. Because of their suspected carcinogenicity, mutagenicity, as well as developmental, reproductive, and hepatic toxicity,[1-4] the World Health Organization (WHO)[5] has established guidelines for these DBPs in drinking water.

The U.S. EPA and European Commission have established a regulatory maximum contaminant level (MCL) of 10 µg/L (10 ppb) bromate in drinking water.[5,6] Dalapon, an herbicide, can cause minor kidney changes, when present in drinking water, well in excess of the MCL. The U.S.EPA has set an MCL, at 0.2 mg/L or 200 ppb.

In this study, we use a new ion exchange column (Thermo Scientific™ Dionex™ IonPac™ AS31 column) for the IC-MS/MS determination of nine haloacetic acids, bromate, and dalapon present at low concentrations in drinking water. The new IC-MS/MS method can determine all analytes in water samples in 35 min, 39% faster than the original U.S. EPA Method 557. The direct detection of HAAs, bromate, and dalapon eliminates the tedious sample preparation described in U.S. EPA Method 552.3.

MATERIALS AND METHODS

Sample collection, preservation, and storage

When water samples were collected, crystalline or granular ammonium chloride was added to the sample containers as a preservative to yield a concentration of 100 mg/L. For example, a 250 mL sample requires 25 mg of NH_4Cl. Prior to analysis by IC-MS/MS, no further sample preparation was performed.

Lowest Concentration Minimum Reporting Level (LCMRL) and Method Detection Limits (MDL)

Standard solutions containing 11 target analytes (including nine HAAs, bromate, and dalapon) at 0.05, 0.1, 0.25, 0.375, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, and 2.00 µg/L with of each ISS at 4 µg/L in 100 mg/L NH_4Cl solution were prepared.

Quantification

Identification and quantification of the nine HAAs, bromate, and dalapon in ground water, municipal drinking water, and bottled water samples were accomplished by MS/MS identification and retention time match with the corresponding standards, and each sample was analyzed three times (n=3).

Instrumentation

Thermo Scientific™ Dionex™ ICS-6000

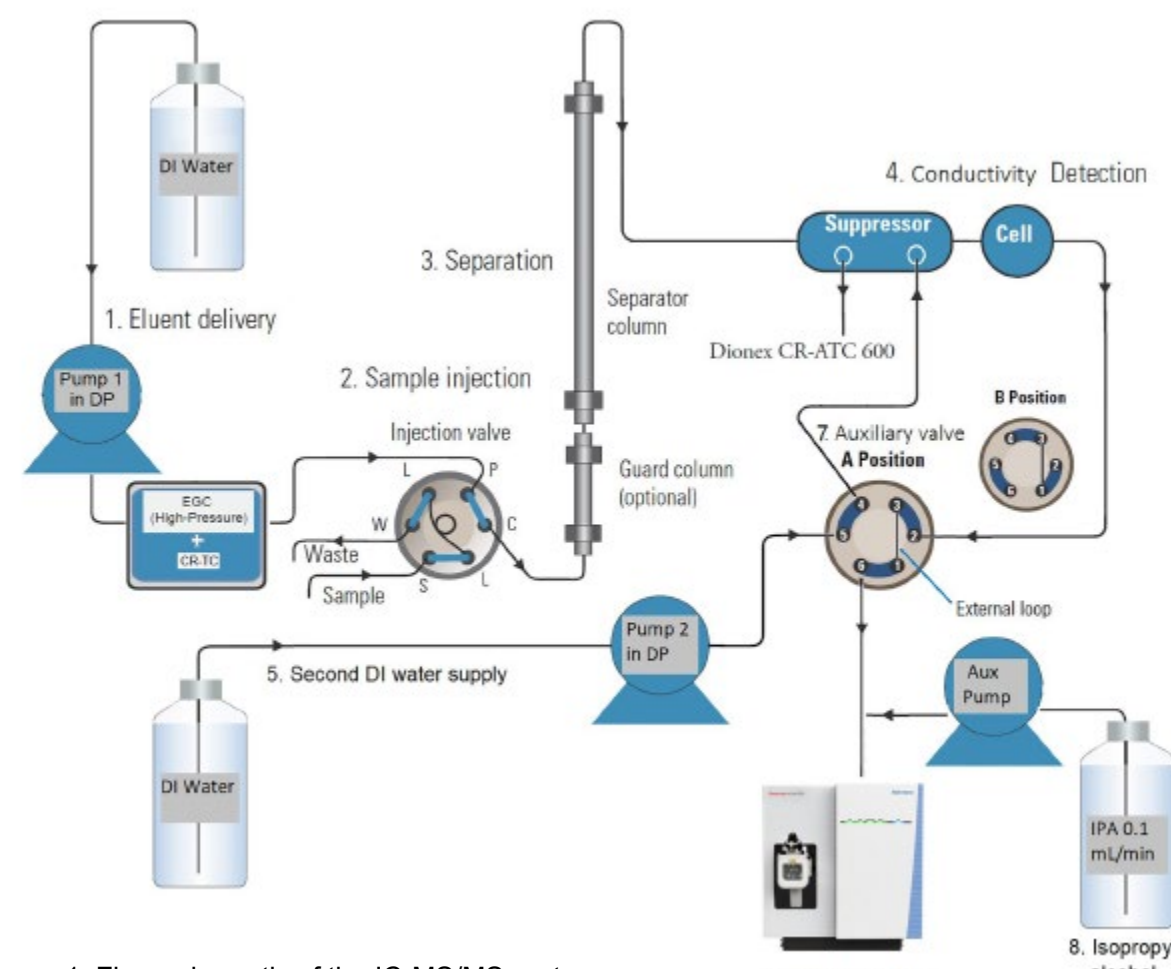Thermo Scientific™ TSQ Fortis™ Triple Quadrupole Mass Spectrometer

Figure 1. Flow schematic of the IC-MS/MS system

Table 1. Conditions for IC-MS/MS

Ion chromatography	
IC system	Dionex ICS-6000 system
MS detector	TSQ Fortis triple quadrupole mass spectrometer
Columns	Dionex IonPac AG31 Guard Column, 2 × 50 mm Dionex IonPac AS31 Analytical Column, 2 × 250 mm
Eluent source	Dionex EGC 500 KOH Eluent Generator Cartridge with Dionex CR-ATC 600 Continuously Regenerated Anion Trap Column
Eluent	17–85 mM KOH with gradient: The KOH concentration was maintained at 17 mM for the first 7 min, then linearly increased to 85 mM within 11 min, and maintained at 85 mM for another 17 min.
Flow rate	0.3 mL/min for both pumps in the DP
Injection volume	100 µL
Temperature	15 °C (column compartment) 20 °C (detector compartment) 10 °C (sampler compartment)
Detection	Suppressed Conductivity, Dionex ADRS 600 Anion Dynamically Regenerated Suppressor (2 mm), legacy mode with constant current 64 mA
Background conductance	<0.5 µS
Run time	36 min
IPA flow	0.10 mL/min

Mass spectrometric detection	
Ionization interface	Electrospray ionization (ESI), negative mode
Divert valve switch time	Eluent to waste 0–5 min, 8.5–11.1 min, and 15.6–21.7 min
Gas control	Sheath gas pressure: 50 arbitrary (Arb) units Aux gas pressure: 10 Arb
Sweep gas pressure	3 Arb
Source voltage	-3200 V
Vaporizer temperature	275 °C
Ion transfer tube temperature	225 °C
FWHM	0.7 for both Q1 and Q3
CID gas	2.0 mTorr

The Dionex ICS-6000 system is equipped with two analytical pumps (DP), eluent generator (EG), autosampler, low temperature microbore column compartment, suppressor, and conductivity detector (CD). DI water is added to the IC system and converted automatically to hydroxide eluent by the EG.

RESULTS

Table 2. Optimized MS instrumental and SRM conditions:

Compound	Precursor (m/z)	Product (m/z)	Collision energy (V)	Tube lens (V)	Source fragmentation (V)
MCAA	92.9	35.1	9.7	79	14.6
MCAA_IS	93.9	35.1	9.1	82	13.1
DCAA	126.9	83.0	8.5	86	24.5
Bromate	126.9	110.9	21.7	85	24.5
DCAA_IS	128.0	83.9	8.4	84	13.1
MBAA	136.9	78.9	8.7	86	9.8
MBAA_IS	137.9	78.9	9.4	84	14.7
Dalapon	140.9	96.9	7.7	84	13
TCAA_IS	161.9	117.9	5.3	78	18
BDCAA	162.8	80.9	8.6	79	22.9
TCAA	162.8	118.9	5.3	79	22.9
BCAA	172.8	128.9	9.6	89	22.8
CDBAA	206.8	78.9	15.6	91	22.9
DBAA	216.8	172.8	10.1	87	14.7
TBAA	250.7	78.9	19.4	87	26.1

The Dionex IonPac AS31 stationary phase is designed to provide faster sample analysis for HAAs, bromate, and dalapon yet still have high capacity to allow a large loop injection to maximize analyte sensitivity. As shown in Figure 2, the Dionex IonPac AS31 achieved 39% faster run times relative to the Dionex IonPac AS24 column (used in the experiments described in U.S. EPA Method 557) with equivalent resolutions.
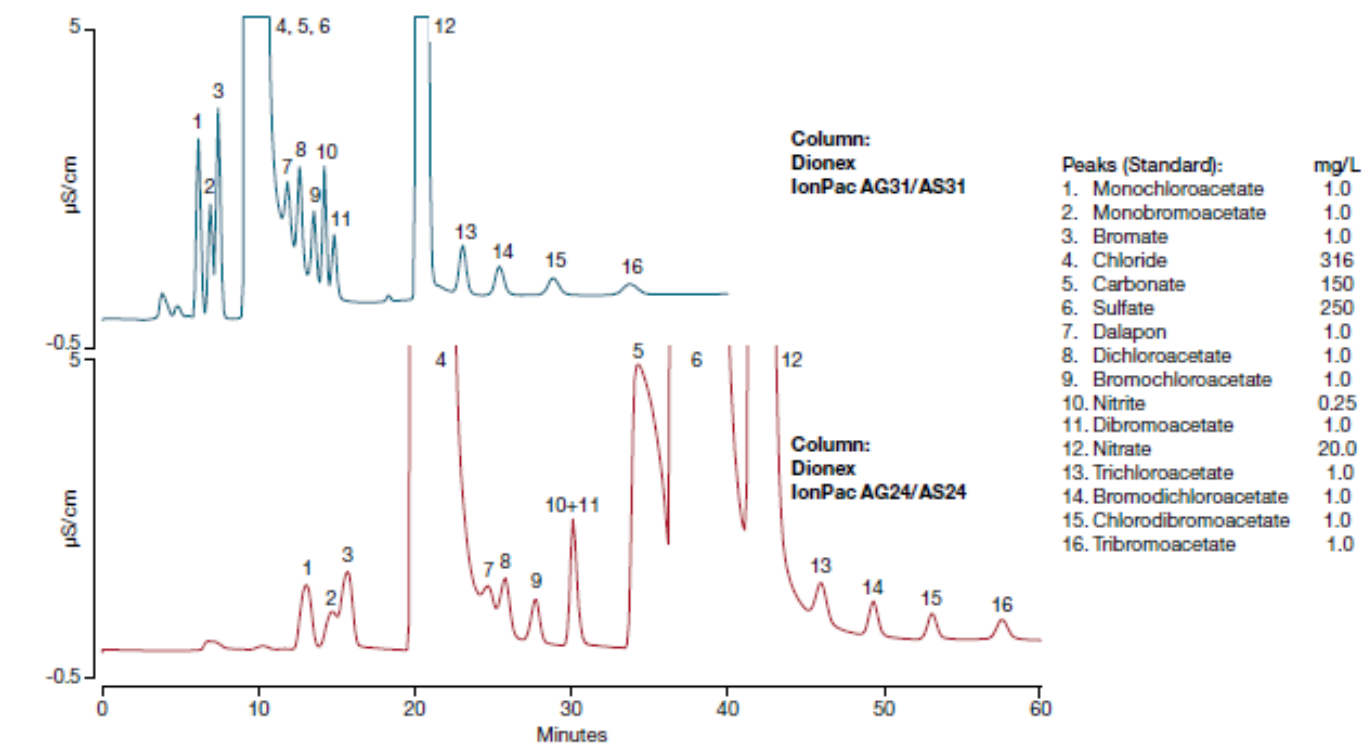

Figure 2. Separation of haloacetic acids, dalapon, and bromate in U.S. EPA Method 557 on the Dionex IonPac AS31 and Dionex IonPac AS24 columns (U.S. EPA 557 column) with conductivity detection

Table 3. Recovery and RSDs obtained for 2 µg/L and 10 µg/L HAAs spiked in three different matrixes: DI water, LSSM, and municipal drinking water (DW) (n=7)

Analytes n=7	2 µg/L Spiked in						10 µg/L Spiked in					
	DI water		LSSM		Municipal DW		DI water		LSSM		Municipal DW	
	REC (%)	RSD	REC (%)	RSD	REC (%)	RSD	REC (%)	RSD	REC (%)	RSD	REC (%)	RSD
MCAA	99.6	3.4	105	5.1	108	5.1	102	3.0	99.6	2.8	103	6.0
MBAA	101	3.8	105	4.2	104	4.0	101	0.7	97.0	3.2	99.2	3.7
Bromate	104	2.8	101	5.3	99.0	4.5	102	2.5	98.8	4.0	101	5.0
Dalapon	104	1.8	99.2	3.2	103	4.0	102	1.3	91.6	3.1	98.2	3.1
DCAA	110	1.8	110	2.0	107	2.0	101	2.0	100	2.7	90.7	3.3
BCAA	104	2.4	107	4.1	93.6	3.2	104	2.0	97.6	4.0	89.3	3.2
DBAA	102	0.6	101	2.8	94.8	2.2	101	1.4	90.1	3.0	91.4	4.2
TCAA	102	6.7	106	8.6	98.1	5.4	95	3.0	93.5	4.8	99.2	3.3
BDCAA	98.2	3.1	97.0	4.4	104	7.0	99.0	4.4	88.7	5.0	97.2	3.3
CDBAA	92.0	6.7	93.3	7.3	108	5.7	98.1	4.2	90.9	3.3	106	3.0
TBAA	92.0	3.7	98.4	7.4	103	5.7	104	5.7	86.7	4.4	100	6.4

Table 3. Determination of HAAs, bromate, and dalapon in different bottled water (BW) and drinking water (DW) samples

Analyte	Concentration (µg/L) [Mean ± standard deviation, n=3]					
	Well water	BW vendor 1	BW vendor 2	Municipal 1 DW	Municipal 2 DW	Municipal 3 DW
MCAA	ND	ND	ND	0.75 ± 0.06	ND	2.7 ± 0.1
MBAA	ND	ND	ND	0.21 ± 0.02	0.13 ± 0.01	0.08 ± 0.004
Bromate	ND	0.18±0.06	0.52±0.01	0.61 ± 0.01	0.12 ± 0.01	0.08 ± 0.005
Dalapon	ND	ND	ND	ND	ND	0.29 ± 0.01
DCAA	ND	ND	ND	3.7 ± 0.1	0.31 ± 0.04	12 ± 0.1
BCAA	ND	ND	ND	2.8 ± 0.1	ND	2.4 ± 0.1
DBAA	ND	ND	ND	1.2 ± 0.04	0.75 ± 0.04	0.34 ± 0.001
TCAA	ND	ND	ND	0.45 ± 0.01	ND	4.5 ± 0.02
BDCAA	ND	ND	ND	0.72 ± 0.01	ND	1.1 ± 0.1
CDBAA	ND	ND	ND	0.48 ± 0.06	ND	ND
TBAA	ND	ND	ND	ND	ND	ND
HAA5	ND	ND	ND	6.4	1.2	20
HAA9	ND	ND	ND	10.3	1.2	24

ND: Non detectable
HAA5: Sum of 5 regulated HAAs: MCAA, DCAA, TCAA, MBAA, and DBAA
HAA9: Sum of 9 HAAs

CONCLUSIONS

A fast, sensitive, and simple method was developed for direct analysis of nine HAAs, bromate, and dalapon in drinking water samples using IC-MS/MS without sample pretreatment. The unique selectivity of the Dionex IonPac AS31 column provides excellent separation of 9 HAAs, bromate, and dalapon from common interference anions such as chloride, sulfate, and carbonate in 35 min. The high sensitivity provided by the MS detection method made it possible to perform the direct injection of drinking water samples, thus eliminating the complexity and variabilities of sample preparation. The use of a hydroxide eluent generator and suppression in the Reagent-Free IC system provides a reliable, economic, and environmentally friendly platform for the separation and detection of HAAs, bromate, and dalapon.

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