APPLICATION NOTE 73343

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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Goal

To identify and quantify low concentrations of haloacetic acids, bromate, and dalapon in drinking water according to U.S. EPA Method 557 using a Thermo Scientific™ Dionex™ ICS-6000 ion chromatography system and a Thermo Scientific™ Dionex™ IonPac™ AS31 column coupled with triple quadrupole electrospray mass spectrometry

Introduction

Haloacetic acids (HAAs) are a class of undesirable disinfection by-products (DBPs) formed during the disinfection of drinking water in which routine water disinfectants such as chlorine or chloramine are used to kill pathogenic microorganisms. There are nine major HAAs: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), and chlorodibromoacetic acid (CDBAA). 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. In the U.S., these guidelines are regulated by the Environmental Protection Agency (EPA) as a part of the Safe Drinking Water Act (SDWA). In 1998, the Stage 1 Disinfectants and DBPs Rule (Stage 1 DBPR) was published, which set the limit for total trihalomethanes (TTHM) at 80 µg/L and, for the first time, set the maximum contamination levels for the sum of the five HAAs (HAA5: MCAA, DCAA, TCAA, MBAA, and DBAA) at 60 µg/L. It also sets a maximum contaminant level goal (MCLG) for dichloroacetic acid (DCAA) to zero and trichloroacetic acid (TCAA) to 30 µg/L. In the Stage 2 DBPR, the MCLG for TCAA was reduced to 20 µg/L and MCAA was set at 70 µg/L.[6] Consequently, efforts have been made to develop fast and accurate

analytical methods to monitor concentration, behavior, and distribution of HAAs in water. Ozone is a powerful drinking water disinfectant that is effective in treating chlorine resistant organisms, such as *Cryptosporidia.*[7] For bottled water, ozonation is generally preferred over other available disinfection treatment methods because it does not leave a taste or residual disinfectant, due to the short lifetime of ozone.[2,3] Ozone also improves the quality of finished drinking water by reducing filtered water turbidity and decreasing the formation of many halogenated DBPs. Thus, some water utilities use a combination of chlorination and ozonation for the disinfection processes. However, ozonation of drinking water containing bromide can result in the formation of the DBP bromate, a potential human carcinogen even at low µg/L concentrations.[4] 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 is an herbicide used to control grasses in a wide variety of crops, including fruit trees, beans, coffee, corn, cotton, and peas. Dalapon is also registered for use in a number of non-crop applications such as lawns, drainage ditches, along railroad tracks, and in industrial areas. Some people who drink water containing dalapon well in excess of the MCL for many years could experience minor kidney changes. The U.S. EPA has set an enforceable regulation for dalapon, a MCL, at 0.2 mg/L or 200 ppb.

Ion chromatography (IC) has been applied to the determination of HAAs. In U.S. EPA Method 557, IC-ESI-MS/MS is used to directly determine HAAs, bromate, and dalapon in drinking water samples. All the targeted HAAs are separated and analyzed without preconcentration and derivatization in 57 min.[8] In 2017, the U.S. EPA approved Thermo Fisher Method 557.1 that uses a two-dimensional ion chromatography technique for determination of HAAs.[9]

In this study, we report the application of 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, a 39% faster analysis time than the original U.S. EPA Method 557, which uses the Thermo Scientific Dionex IonPac AS24 column. The direct detection of HAAs, bromate, and dalapon eliminates the tedious sample preparation such as sample acidification, extraction, and derivatization described in U.S. EPA Method 552.3. In this new IC-MS/MS method, the interfering ions are separated and diverted to the waste to ensure method robustness and decrease instrument down time. Excellent method precision and accuracy are obtained for the standard solution (DI water), laboratory synthetic sample matrix (LSSM), and municipal drinking water. Full method validation including calibration curves, lowest concentration minimum reporting levels (LCMRL), and method detection limits (DL) for all nine HAAs, bromate, and dalapon are presented per U.S. EPA Method 557 guidelines.

Experimental

Equipment and consumables

- Thermo Scientific™ Dionex™ ICS-6000 system including:
  - DP (Dual Analytical Pump, P/N 22181-60008)
  - EG (Eluent Generator, P/N 22181-60020)
  - AS-AP Autosampler with Sample Syringe, 250 µL (P/N 074306)
  - Low Temperature DC (Detector and Microbore Column Compartment, P/N 22181-60059)
- Thermo Scientific™ Dionex™ 6-port high-pressure valve (P/N 22153-60014)
- Thermo Scientific™ TSQ Fortis™ triple quadrupole mass spectrometer
- Thermo Scientific™ Dionex™ AXP Auxiliary Pump (P/N 063973)
- Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator Cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion Trap Column (P/N 088662)
- Thermo Scientific™ Dionex™ ADRS 600 2mm Anion Dynamically Regenerated Suppressor (P/N 088667)
- Thermo Scientific™ Dionex™ IonPac™ AS31 Analytical Column (2 × 250 mm, P/N 303147)
- Thermo Scientific™ Dionex™ IonPac™ AG31 Guard Column (2 × 50 mm, P/N 303148)
- Thermo Scientific™ Dionex™ AS-AP Autosampler Vials 10 mL (P/N 074228)
- Fisherbrand™ Narrow-Mouth Field Sample Bottles, high-density polyethylene (HDPE), 125 mL, 250 mL, and 1000 mL sizes for storage of standards (Fisher Scientific, P/N 02-895A, 02-895B, and 02-895D)

Reagents and standards

- Sodium Chloride (Crystalline/Certified ACS), Fisher Chemical (Fisher Scientific P/N S271-500)
- Sodium Nitrate (Crystalline/Certified ACS), Fisher Chemical (Fisher Scientific P/N S343-500)
- Sodium Sulfate Anhydrous (Granular/Certified ACS), Fisher Chemical (Fisher Scientific P/N S421-500)
- Sodium Bicarbonate Anhydrous (Powder/Certified ACS), Fisher Chemical (Fisher Scientific P/N S233-500)
- Ammonium Chloride (Crystalline/Certified ACS), Fisher Chemical (Fisher Scientific P/N A661-500)
- Thermo Scientific™ Dionex™ Haloacetic Acid Internal Standards, monochloroacetic acid-2-^{13}C, dichloroacetic acid-2-^{13}C, trichloroacetic acid-2-^{13}C, and monobromoacetic acid-1-^{13}C, 1000 mg/L in MTBE (P/N 069406, 069407, 069408, and 069409)
- Methanol, Optima™ LC/MS Grade, Fisher Chemical (Fisher Scientific A456-1)
- Acetonitrile, Optima™ LC/MS Grade, Fisher Chemical (Fisher Scientific A955-1)
- Isopropanol, Optima™ LC/MS Grade, Fisher Chemical (Fisher Scientific A461-1)
- Haloacetic acid mix standard HAA9 (including MCAA, DCAA, TCAA, MBAA, DBAA, TBAA, BCAA, BDCAA, and CDBAA), 1000 µg/mL each in MTBE (methyl-tert-butyl-ether) was purchased from Restek (Bellefonte, PA)
- Dalapon and bromate were purchased from Ultra Scientific, 1000 µg/mL each in MeOH (Ultra Scientific)

Conditions for the IC-MS/MS system

Parameter	Value
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

Instrumentation

Figure 1 shows the schematic of the setup used for this study. 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. Because the eluent stream is sent to the MS, a destructive detector, the eluent water cannot be used for regeneration of the suppressor, EG, and CR-ATC. For this reason, a second water reservoir (supplied by the second analytical pump, "5" in Figure 1) is required for regeneration of the suppressor and CR-ATC. A six-port auxiliary switching valve is placed between the CD and the mass spectrometer, and is used to divert suppressed eluent either to the MS or to waste ("7" in Figure 1). A Thermo Scientific™ Dionex™ ADRS 600 Anion Dynamically Regenerated Suppressor was used to convert the eluent (KOH) into water and the eluting anions into their corresponding acids, thus improving the sensitivity and selectivity of both detectors. It is important to note that HAAs, bromate, and dalapon are non-volatile organic compounds. After suppression, the eluent is a very dilute solution of HAAs in water. To improve desolvation and help analyte ionization, 100 µL/min isopropyl alcohol (IPA, item "8' in Figure 1) is added through a T-junction prior to MS.

The auxiliary valve can be configured in A position (MS) or B position (waste, not to MS). In the A position, eluent from the conductivity detector is sent through port 2 → 3 → 1 → 6 and to the MS. At the same time, the DI water supplied by the second pump is sent to the suppressor and the CR-ATC through ports 5 and 4. In the B position, eluent is sent to the suppressor through port 2 → 1 → 3 → 4 to regenerate the suppressor and CR-ATC (and is called "waste" as the eluent does not flow to MS). The second DI water is switched to supply the MS to avoid ion source overheating. Diverting ions to waste prevents signal suppression in the MS, helps decrease MS ion source contamination, and maintains its robustness. During this method the eluent is sent to waste at 0–5 min, 8.5–11.1 min, and 15.6–21.7 min.

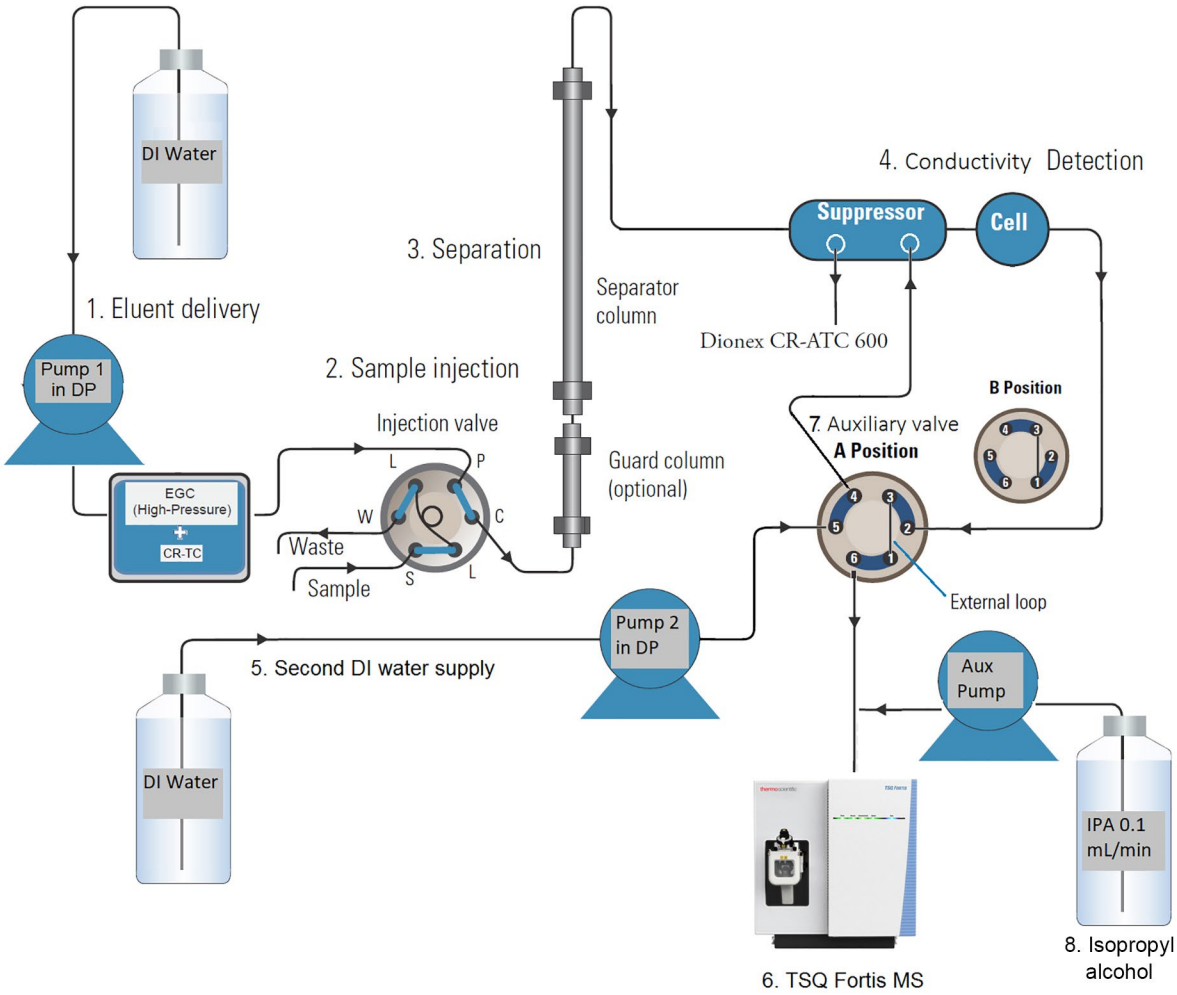


Figure 1. Flow schematic of the IC-MS/MS system

A TSQ Fortis mass spectrometer (a triple quadrupole MS detector) equipped with an electrospray ionization (ESI) source in the negative ion mode is used in this experiment. The data acquisition is the selected reaction monitoring (SRM) mode with both Q1 and Q3 resolution FWHM at 0.7. The method optimization has been performed by a direct infusion via a syringe pump to determine the best precursor and product ions and to optimize the collision energy, tube lens, and source fragmentation for each analyte (Table 1).

Standards, reagents, and stock solutions

Reagent water

Purified water is that which does not contain any measurable quantity of the target analyte or interfering compounds at concentrations >1/3 the minimum reporting level (MRL) for the target analyte. Water purity is very important for the successful execution of this method. For this work, municipal drinking water was further purified using a bench model Millipore water purification system (Millipore Corp, Billerica, MA, Model No. Milli-Q® Gradient A10 or equivalent). This water is referred to as DI water in this document.

Stock solution and working solution

All standard solutions (nine HAAs, bromate, and dalapon) were 1000 µg/mL in methanol or MTBE when purchased from reagent manufacturers.

The stock solution containing target analytes at 1 µg/mL: Add 100 µL of each standard solution (1000 µg/mL) into a 100 mL volumetric flask and bring to volume with DI water.

The working solution (WS) containing target analyte at 40 µg/L: Add 4.0 mL of stock solution into a 100 mL volumetric flask and bring to volume with 100 mg/L NH_4Cl.

All standard and working solutions were stored at 4 °C.

Internal Standard Primary Dilution Standard (IS PDS) (1.0 µg/mL)

The internal standard PDS at 1.0 µg/mL: Add 100 µL of each internal standard solution (1000 µg/mL) into a 100 mL volumetric flask and bring to volume with DI water.

Calibration standard solutions

Procedural calibration standards containing nine HAAs, bromate, and dalapon at concentrations ranging from 0.05 to 20 µg/L were prepared by diluting the working solution into 100 mg/L NH_4Cl as shown in Table 2. The holding time for the calibration standard solution is one month.

Table 1. Optimized MS instrumental and SRM conditions for determination of HAAs, bromate, and dalapon

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

Table 2. Calibration solutions preparation

Targeted conc. (µg/L)	WS (mL)	WS. conc. µg/L	100 mg/L NH_4Cl (mL)	Final volume (mL)	1 µg/mL IS PDS (mL)
20	20	40	20	40	0.16
10	10	40	30	40	0.16
5	5	40	35	40	0.16
2	2	40	38	40	0.16
1	1	40	39	40	0.16
0.5	0.5	40	39.5	40	0.16
0.25	0.25	40	39.8	40	0.16
0.1	0.1	40	39.9	40	0.16
0.05	0.05	40	39.95	40	0.16

Laboratory Synthetic Sample Matrix (LSSM)

The LSSM was prepared by dissolving 50 mg ammonium chloride (preservative), 13.7 mg sodium nitrate, 103 mg sodium bicarbonate, 206 mg sodium chloride, and 185 mg of sodium sulfate in 500 mL DI water. The concentrations of nitrate (20 mg/L), bicarbonate (150 mg/L), chloride (250 mg/L), and sulfate (250 mg/L) in the LSSM are based on the mass of the anion (not the sodium salt). The recommended holding time is one year.

Sample collection, preservation, and storage

Sample treatment

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. Samples must be chilled during shipment and must not exceed 10 °C during the first 48 h after collection. Samples must be confirmed to be at or below 10 °C when they are received at the laboratory. In the laboratory, samples must be stored at or below 6 °C and protected from light until analysis. Samples must not be frozen.

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).

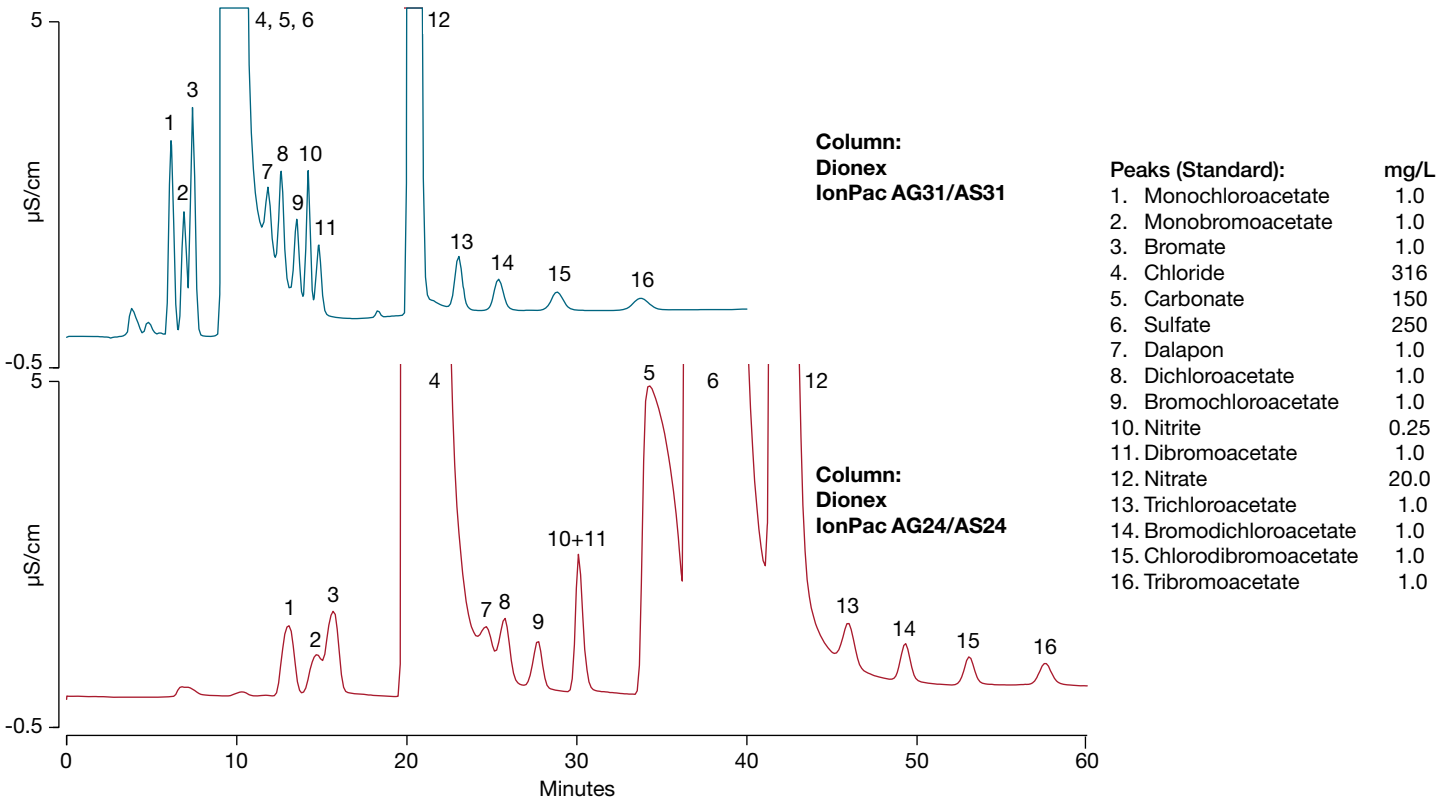
To assess analyte contamination, laboratory blanks were analyzed to ensure all analytes were 1/3 of the MRL. Recoveries were evaluated by spiking standard solutions into DI water, LSSM, and drinking water samples at two concentration levels for each HAA in replicates of seven. Because no sample extraction steps were included in this method, the recovery data reflected any ion suppression/enhancement.

Data were analyzed using Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) Software Version 7.2.9 and Thermo Scientific™ FreeStyle™ 1.5 application.

Results and discussion

Chromatography optimization

We optimized the chromatographic conditions so that nine HAAs, bromate, and dalapon were well resolved and separated from common interference anions such as chloride, sulfate, carbonate, and nitrate ions in 35 min by using a Dionex IonPac AS31 column set. The novel 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.



Peaks (Standard):	mg/L
1. Monochloroacetate	1.0
2. Monobromoacetate	1.0
3. Bromate	1.0
4. Chloride	316
5. Carbonate	150
6. Sulfate	250
7. Dalapon	1.0
8. Dichloroacetate	1.0
9. Bromochloroacetate	1.0
10. Nitrite	0.25
11. Dibromoacetate	1.0
12. Nitrate	20.0
13. Trichloroacetate	1.0
14. Bromodichloroacetate	1.0
15. Chlorodibromoacetate	1.0
16. Tribromoacetate	1.0

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

A matrix diversion auxiliary valve was placed in line prior to the mass spectrometer to divert the sample matrix anions that normally cause signal suppression from the MS source, and to improve method robustness (Figure 1). Experiments were designed and executed to evaluate the signal intensities with diversion (selected time periods to divert to waste (B position)) and without diversion (always in A position, eluent to the MS detector) conditions. Figure 3A lists the peak areas of 5 µg/L HAAs in DI water under both conditions. Similar peak areas were observed, as expected, because DI water has few matrix ions. While in LSSM matrix (Figure 3B), diverting the common interfering ions increases analyte intensity especially for dalapon, which elutes right after a large amount of chloride, carbonate, and sulfate with a 120% increase. DCAA, BCAA, and DBAA experience 58%, 63%, and 87% increases with matrix diversion, respectively.

Figure 4 shows chromatograms of 9 HAAs, bromate, and dalapon, each with a concentration of 5 µg/L in LSSM. Peak 1 presented in the CDBAA channel with the same retention time as BDCAA was BDCAA with precursor ion $[BDCAA\text{-}H]^-$ and product ion $[Br]^-$. The lower intensity for peak 1 than BDCAA peak above indicated this was not the major selected reaction monitoring (SRM) transition. A similar explanation can be applied to peak 2 (a non-major SRM transition for CDBAA)

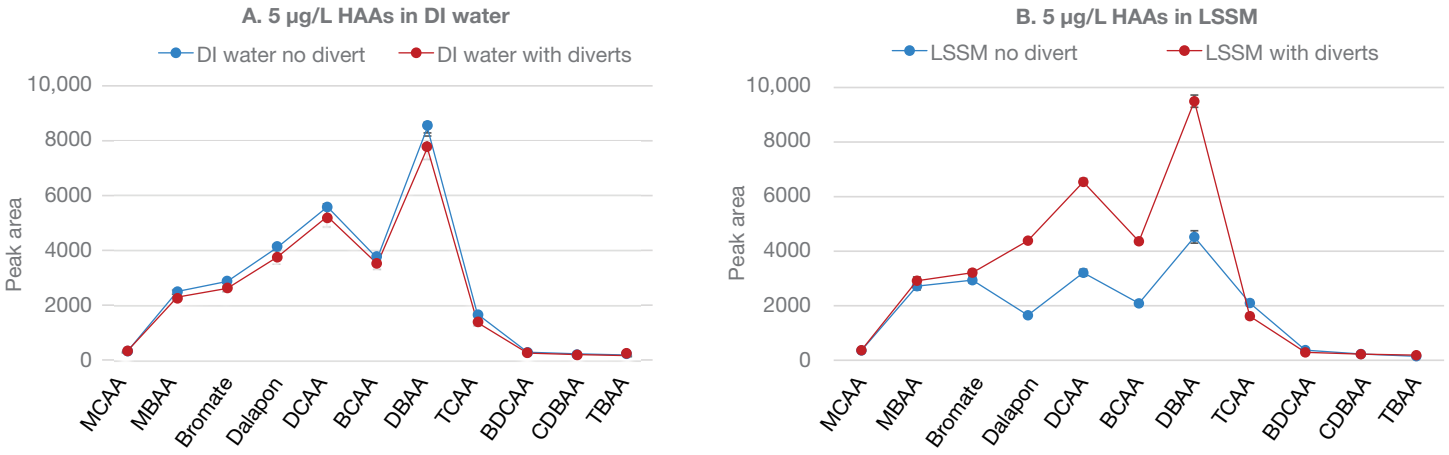


Figure 3. MS signal intensities with diversion and without diversion. (A: 5 µg/L HAAs, bromate, and dalapon in DI water; B: 5 µg/L HAAs, bromate, and dalapon in LSSM)

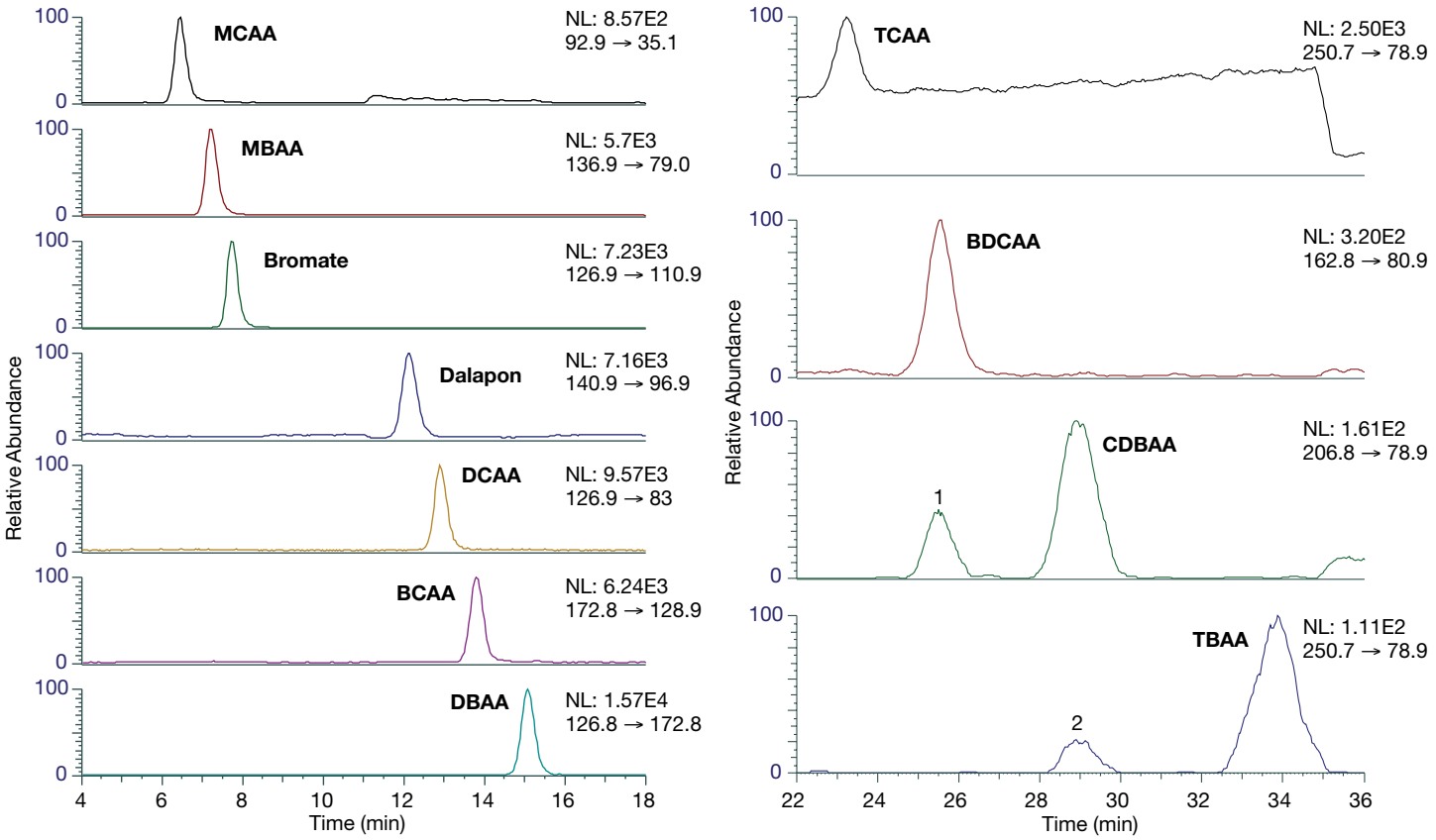


Figure 4. IC-MS/MS SRM chromatograms of nine HAAs, bromate, and dalapon with a concentration of 5 µg/L in LSSM

Quantification and method validation

Calibration

Table 3 shows the tested analytes with corresponding ISs, linear range, and coefficient of determination (r^2) when the injection volume was 100 µL and 0.1 mL/min IPA was used as the make-up flow. Linear responses over the listed calibration range with r^2 values of ≥0.99 were obtained for all target analytes. All calibration ranges meet or exceed the requirements specified in U.S. EPA Method 557.

Table 3. Calibration data obtained for nine HAAs, bromate, and dalapon with relevant internal standards (ISs), linearity range, and coefficient of determination (r^2)

Analyte	Internal standard	Linear range (µg/L)	r^2
MCAA	MCAA[2-^{13}C]	0.1–20	1.000
MBAA	MBAA[1-^{13}C]	0.1–20	0.999
Bromate	MBAA[1-^{13}C]	0.1–20	1.000
Dalapon	DCAA[2-^{13}C]	0.1–20	1.000
DCAA	DCAA[2-^{13}C]	0.1–20	1.000
BCAA	DCAA[2-^{13}C]	0.1–20	1.000
DBAA	DCAA[2-^{13}C]	0.1–20	1.000
TCAA	TCAA[2-^{13}C]	0.25–20	1.000
BDCAA	TCAA[2-^{13}C]	0.25–20	1.000
CDBAA	TCAA[2-^{13}C]	0.1–20	1.000
TBAA	TCAA[2-^{13}C]	0.1–20	1.000

Method DL and LCMRL determinations

Detection Limit (DL), is defined as the statistically calculated minimum concentration that can be measured with 99% confidence that the reported value is greater than zero. The Lowest Concentration Minimum Reporting Level (LCMRL), is the lowest spiking concentration at which recovery of 50–150% is expected 99% of the time. DL and LCMRLs both were used to evaluate detection/quantification limit, which were calculated by entering the concentrations for each of the HAAs obtained from seven replicate injections of HAA standard (0.05–2 µg/L) into the U.S. EPA's LCMRL calculator.[10] The calculated LCMRLs ranged from 0.035 to 0.25 µg/L and DLs from 0.009 to 0.099, which were comparable/better than those values included in U.S. EPA Method 557 (Table 4).

Table 4. IC-MS/MS method detection limits (MDL) and lowest concentration minimum reporting level (LCMRL) obtained for HAAs, bromate, and dalapon

Analyte (µg/L, n=7)	EPA reported DL	Calculated DL	EPA reported LCMRL	Calculated LCMRL
MCAA	0.20	0.099	0.58	0.15
MBAA	0.064	0.028	0.19	0.035
Bromate	0.02	0.012	0.042	0.039
Dalapon	0.038	0.031	0.41	0.20
DCAA	0.055	0.036	0.13	0.096
BCAA	0.11	0.087	0.16	0.15
DBAA	0.015	0.009	0.062	0.058
TCAA	0.09	0.061	0.25	0.14
BDCAA	0.05	0.027	0.19	0.055
CDBAA	0.041	0.042	0.080	0.10
TBAA	0.067	0.067	0.27	0.25

Method precision and accuracy

The LSSM is a solution of common anions prepared at high concentrations relative to their typical occurrence in drinking water. It is required by U.S. EPA Method 557 as accuracy and precision checks prior to analysis of drinking water samples. The precision of the method was determined by running seven replicates of HAAs, bromate, and dalapon spiked into water at 2 and 10 µg/L into DI water, LSSM matrix, and municipal drinking water (DW). The relative standard deviation (RSD) for the amount ranged from 0.6 to 8% for the 2 µg/L HAAs spike, with similar results for the 10 µg/L HAA spike (0.7% to 6.4%) (Table 5), which demonstrated great precision. The accuracy of the method was evaluated by determining the recoveries of the HAAs spiked into various water samples. Recoveries were all well within the generally accepted range of ±30% for U.S. EPA Method 557, ranging from 92% to 110% for 2 µg/L and from 87% to 106% with 10 µg/L HAA addition.

Analysis of drinking water samples

This method was applied to determine nine HAAs, bromate, and dalapon in the drinking water samples collected from different sources such as well water (groundwater), municipal drinking water (from three different cities in California, USA), and bottled water from different vendors. The mean concentrations (n=3) ± standard deviations are listed in Table 6. In the well water, which is groundwater without chlorination, no trace of DBPs was

detected as expected. Both bottled water (BW) samples had a trace amount of bromate, which probably indicates that ozone disinfection was applied during production. Of the three municipal drinking water samples, City 2 water was profoundly low in DBPs. Of the nine HAAs, MCAA, DCAA, TCAA, and BCAA were the most abundant species, and the sum made up more than 90% of all HAA concentrations in the City 3 water sample. The maximum concentration of DCAA and TCAA were 12.4 and 4.48 µg/L, respectively, which were much lower than the MCLs of 50 and 100 µg/L proposed by the WHO.[11] The total concentrations of HAA5 and HAA9 ranged from 1.19 to 23.5 µg/L, meeting the requirement of Stages 1 and 2 Disinfectants and Disinfection Byproducts Rules of the U.S. EPA. Both bromate and dalapon concentrations for all samples met the U.S. EPA requirements.

Table 5. 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	2 µg/L Spiked in						10 µg/L Spiked in					
	DI water		LSSM		Municipal DW		DI water		LSSM		Municipal DW	
n=7	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	4.7	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 6. Determination of HAAs, bromate, and dalapon in different drinking water (DW) samples

	Concentration (µg/L) [Mean ± standard deviation, n=3]					
Analyte	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

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Conclusion

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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