APPLICATION NOTE 73342

Determination of low-level haloacetic acids, bromate, and dalapon in drinking water using IC-MS

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Goal

To develop a method to determine haloacetic acids, bromate, and dalapon in drinking and surface waters using an ion chromatography (IC) system coupled with single quadrupole mass spectrometer (IC-MS)

Introduction

Disinfection treatment is essential to eliminate waterborne disease-causing microorganisms from drinking water. Municipal water authorities most commonly disinfect water using chemical disinfectants such as chlorine, chlorine dioxide, chloramine, and ozone.[1] However, these disinfectants can react with naturally occurring material in the water to form unintended disinfection byproducts (DBPs). For example, chlorination of drinking water can produce trihalomethanes, haloacetic acids (HAAs), and chlorate; bromate is formed when disinfecting ozone reacts with natural sources of bromide. These DBPs may pose health risks. For example, long term ingestion of bromate or haloacetic acids may cause cancer.

Dalapon, a herbicide used to control grasses in a wide variety of crops, can be introduced to waterways from runoff. People who for many years drink water containing dalapon above the maximum contaminant level (MCL), the highest level of a contaminant that is allowed in drinking water, could experience minor kidney changes.[2]

To ensure drinking water safety, major regulatory bodies worldwide, including the U.S. Environmental Protection Agency (EPA), European Commission (EC), U.S. Food and Drug Administration (FDA), and World Health Organization (WHO), have set the maximum allowable concentrations for toxic compounds and microorganisms in drinking water.[3-5]

Drinking water plants must determine the concentration of these compounds, including DBPs and dalapon, in drinking water before delivery to customers (Table 1). HAAs are a family of organic compounds based on the acetic acid molecule (CH_3COOH), where one or more hydrogen atoms attached to carbon atoms are replaced by a halogen (chlorine or bromine). There are nine species of HAAs that contain chlorine and/or bromine: monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetic acid (TCAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), and tribromoacetic acid (TBAA). Of these nine HAAs, five are currently regulated by the EPA (HAA5) with a cumulative legal limit of 60 µg/L (60 ppb) in drinking water (Table 1). The MCL for bromate is 10 µg/L (10 ppb), while dalapon is 0.2 mg/L (200 ppb).[3]

U.S. EPA Method 557 has been validated for the determination of HAAs, bromate, and dalapon. This method uses ion chromatography (IC) coupled with electrospray ionization tandem mass spectrometry (IC-ESI-MS/MS).[6] The Thermo Scientific™ Dionex™ IonPac™ AS24 column was used and the total run time was 60 min per sample. The newly developed Thermo Scientific™ Dionex™ IonPac™ AS31 hydroxide-selective anion-exchange column was specifically designed for fast analysis of HAAs, bromate, and dalapon in drinking water. The new Thermo Scientific™ ISQ™ EC Single Quadrupole Mass Spectrometer was developed for seamless integration with IC and ease of use. This study evaluated the determination of HAAs, bromate, and dalapon in drinking water using a Thermo Scientific™ Dionex™ ICS-6000 HPIC™ system with DP pump and Dionex IonPac AS31 column coupled with an ISQ EC single quadrupole mass spectrometer. This application note shows that the method is sensitive (< 1 µg/L) and fast (40 min) to determine HAA5, which is currently regulated by the U.S. EPA.

Experimental

Equipment

- A Dionex ICS-6000 Dual Channel RFIC System including:
  - Eluent Generator
  - DP Pump
  - Degasser
  - Conductivity Detector
  - Thermo Scientific™ Dionex™ IC PEEK Viper™ Tubing Kit for 2mm Dionex ICS-6000 system (P/N 302965)
  - Detector/Chromatography module (DC) with low temperature control for column oven and Detector-Suppressor compartment including two 6-port injection valves (P/N 22181-60059)
- Thermo Scientific™ Dionex™ AS-AP Autosampler (P/N 074926), with low temperature control, 5000 µL syringe (P/N 074308), 8500 µL buffer line assembly (P/N 075520), 100 µL injection loop (P/N 6820.2431), and 10 mL vial trays
- Thermo Scientific™ ISQ™ EC single quadrupole mass spectrometer (P/N ISQEC-IC) including Thermo Scientific™ HESI-II probe (P/N 70005-60155)

Table 1. U.S. EPA regulations for the disinfection byproducts determined by U.S. EPA Method 557

Disinfection byproduct	MCLG	MCL*
Dalapon	0.2 mg/L	0.20 mg/L
Bromate	Zero	0.010 mg/L or 10µg/L
Dichloroacetic acid (DCAA), Trichloroacetic acid (TCAA), Monochloroacetic acid (MCAA),	Zero, 0.02 mg/L or 20 µg/L, 0.07 mg/L or 70 µg/L	**HAA5** are currently regulated at the total level of 60 µg/L (sum of the concentrations of all five haloacetic acids as an annual average)
Bromoacetic acid (MBAA), Dibromoacetic acid (DBAA)	Regulated with this group but has no MCLG	
Bromochloroacetic acid (BCAA), Chlorodibromoacetic acid (CDBAA), Bromodichloroacetic acid (BDCAA), Tribromoacetic acid (TBAA)	These four HAAs are not currently regulated, but are on the Unregulated Contaminant Monitoring Rule (UCMR) 4 list for monitoring by public water systems between 2018 and 2020	

*Maximum Contaminant Level (MCL) - The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to maximum contaminant level goals (MCLG) as feasible using the best available technology and taking cost into consideration. MCLs are enforceable standards.

Software

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) Version 7.2.9

Consumables

- Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion Trap Column (P/N 088662)
- Thermo Scientific™ Dionex™ ADRS 600 Anion Dynamically Regenerated Suppressor, 2 mm (P/N 088667)
- Dionex AS-AP Autosampler Vials 10 mL (P/N 074228)
- Fisherbrand Narrow-Mouth field sample bottles, high density polyethylene (HDPE), 125 mL, 250 mL sizes for storage of standards and samples (Fisher Scientific P/N 02-895A, B)

Reagents and standards

- Deionized (DI) water, ASTM Type 1 reagent grade, 18 MΩ·cm resistivity or better
- Mixed Haloacetic acids standard was purchased from Restek (Cat. No. 31896).
- Bromate and dalapon standards were purchased from Sigma-Aldrich.
- Thermo Scientific Dionex internal standards of MCAA-2-^{13}C, MBAA-1-^{13}C, DCAA-2-^{13}C, and TCAA-2-^{13}C (Table 2)

Samples

The residential tap drinking water samples were collected from different cities in the San Francisco Bay Area.

Table 2. Internal standards (1000 µg/mL in MtBE)

Internal standard	Thermo Scientific P/N
Monochloroacetic acid-2^{13}C, (MCAA-2-^{13}C)	069406
Monobromoacetic acid-1^{13}C, (MBAA-1-^{13}C)	069407
Dichloroacetic acid-2^{13}C, (DCAA-2-^{13}C)	069408
Trichloroacetic acid-2^{13}C, (TCAA-2-^{13}C)	069409

Chromatographic conditions

Table 3. Chromatographic conditions

Parameter	Value
Columns	Dionex IonPac AG31 Guard Column, 2 × 50 mm (P/N 303148) Dionex IonPac AS31 Analytical Column, 2 × 250 mm (P/N 303147)
Eluent	17 mM KOH from -5 to 11.5 min, 17–85 mM KOH from 11.5 to 18 min, 85 mM KOH from 18 to 39 min, 17 mM KOH from 39 to 40 min
Eluent source	Dionex EGC 500 KOH cartridge with Dionex CR-ATC 600
Flow rate	0.3 mL/min
Injection volume	100 µL in Push-Full mode
Column temperature	15 °C
Detection 1, suppressed conductivity	
Suppressor	Dionex ADRS 600 (2 mm) Suppressor, external water mode (flow 0.3 mL/min), legacy mode, 75 mA current
Detection/suppressor compartment temperature	15 °C
Cell temperature	15 °C
Background conductance	<1 µS/cm
System backpressure	~3700 psi
Noise	<1 nS/cm
Run time	40 min
Detection 2, mass spectrometry	
MS detector	ISQ EC single quadrupole MS
Ionization interface	Electrospray ionization (ESI), negative mode
Diverter valve switch time	0–2, 9–11.5, and 20–23 min to waste
Sheath gas pressure	35.0 psi
Aux gas pressure	2.0 psi
Sweep gas pressure	1.0 psi
Foreline pressure	~1.72 Torr
Source voltage	-3528 V
Vaporizer temperature	350 °C
Ion transfer tube temperature	150 °C
Chrom. filter peak width	30 s
Method type	Scan mode (Table 4)

Table 4. MS scans details

Time (min)	Scan name	Mass list (amu)	Dwell or scan time (s)	SIM width (amu)	Ion polarity	Spectrum type	Source CID voltage	Tube lens voltage
4.50	MCAA	93	0.4	1.00	Negative	Centroid	10	Last Tune
	MCAA_IS	94	0.4	1.00	Negative	Centroid	10	Last Tune
6.00	MCAA	93	0.2	1.00	Negative	Centroid	10	Last Tune
	MCAA_IS	94	0.2	1.00	Negative	Centroid	10	Last Tune
	MBAA	137	0.2	1.00	Negative	Centroid	10	Last Tune
	MBAA_IS	138	0.2	1.00	Negative	Centroid	10	Last Tune
6.5	MCAA	93	0.16	1.00	Negative	Centroid	10	Last Tune
	MCAA_IS	94	0.16	1.00	Negative	Centroid	10	Last Tune
	MBAA	137	0.16	1.00	Negative	Centroid	10	Last Tune
	MBAA_IS	138	0.16	1.00	Negative	Centroid	10	Last Tune
	Bromate	127	0.16	1.00	Negative	Centroid	10	Last Tune
8.5	Bromate	127	0.8	1.00	Negative	Centroid	10	Last Tune
11.00	Dalapon	141	0.8	1.00	Negative	Centroid	10	Last Tune
11.5	Dalapon	141	0.26	1.00	Negative	Centroid	10	Last Tune
	DCAA	127	0.26	1.00	Negative	Centroid	10	Last Tune
	DCAA-IS	128	0.26	1.00	Negative	Centroid	10	Last Tune
12.00	Dalapon	141	0.2	1.00	Negative	Centroid	10	Last Tune
	DCAA	127	0.2	1.00	Negative	Centroid	10	Last Tune
	DCAA-IS	128	0.2	1.00	Negative	Centroid	10	Last Tune
	BCAA	173	0.2	1.00	Negative	Centroid	10	Last Tune
15	DCAA	127	0.2	1.00	Negative	Centroid	10	Last Tune
	DCAA-IS	128	0.2	1.00	Negative	Centroid	10	Last Tune
	BCAA	173	0.2	1.00	Negative	Centroid	10	Last Tune
	BDAA	217	0.2	1.00	Negative	Centroid	10	Last Tune
16.00	BCAA	173	0.4	1.00	Negative	Centroid	10	Last Tune
	BDAA	217	0.4	1.00	Negative	Centroid	10	Last Tune
17.00	BDAA	217	0.8	1.00	Negative	Centroid	10	Last Tune
23.00	TCAA	163	0.4	1.00	Negative	Centroid	10	Last Tune
	TCAA-IS	164	0.4	1.00	Negative	Centroid	10	Last Tune
25.00	TCAA	163	0.26	1.00	Negative	Centroid	10	Last Tune
	TCAA-IS	164	0.26	1.00	Negative	Centroid	10	Last Tune
	BDCAA	207	0.26	1.00	Negative	Centroid	10	Last Tune
26.00	TCAA	163	0.2	1.00	Negative	Centroid	10	Last Tune
	TCAA-IS	164	0.2	1.00	Negative	Centroid	10	Last Tune
	BDCAA	207	0.2	1.00	Negative	Centroid	10	Last Tune
	CDBAA	251	0.2	1.00	Negative	Centroid	10	Last Tune
29.00	BDCAA	207	0.4	1.00	Negative	Centroid	10	Last Tune
	CDBAA	251	0.4	1.00	Negative	Centroid	10	Last Tune
30	CDBAA	251	0.4	1.00	Negative	Centroid	10	Last Tune
	TBAA	295	0.4	1.00	Negative	Centroid	10	Last Tune
35	TBAA	295	0.8	1.00	Negative	Centroid	10	Last Tune

System preparation and setup

Figure 1 shows the flow diagram of IC-CD/MS. The IC system is plumbed as a Reagent-Free IC (RFIC) system using eluent generation following the installation and operator's manual.[7] Install the suppressor in external water mode and use the second pump to provide the DI water regenerant.[8] The ISQ EC single quadrupole mass spectrometer is installed according to the installation guide.[9]

The second 6-port injection valve is installed as a diverter valve between the CD and mass spectrometer. The diverter valve can be operated in two positions (Figure 2). The IC-CD/MS system is connected/configured as follows: when in "load" position, eluent flows from the CD to the MS, and the second pump delivers water to the suppressor Regen In; when in "inject" position, eluent flow is switched to the suppressor Regen In, and the second pump delivers water to the MS. Edit the instrument method accordingly to "cut" the high salt matrix out from entering the mass spectrometer to protect the MS and thereby increase source ruggedness. Detailed instructions for configuring the IC-MS system are shown in Technical Note 72611.[10]

Notes:

1. When developing the IC instrument method, such as optimizing the gradient to best separate analytes or determining the diverter valve switch time, the divert valve should always keep at the "inject" position. This can prevent the non-volatile eluent from precipitating inside the ESI capillary.
2. To ensure the IC system is optimal for MS analysis, the total conductivity should be low (< 1.0 µS/cm) for the blank run before analyzing samples.

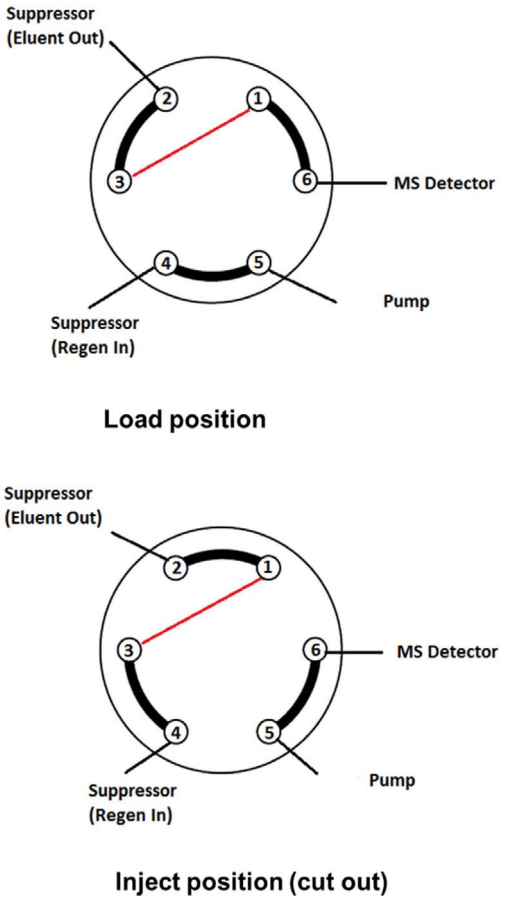


Figure 2. Illustration of the two positions of the 6-port diverter valve

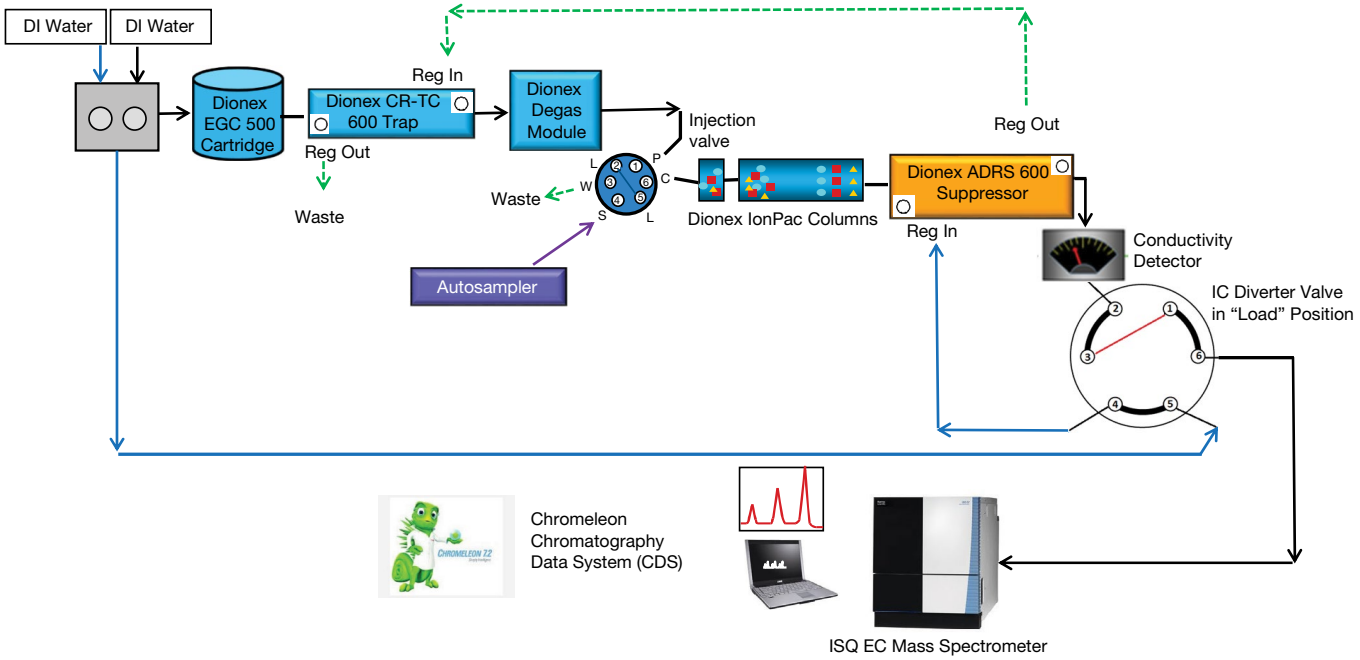


Figure 1. Flow diagram for IC-CD/MS with diverter valve in "load" position

Preparation of solutions and reagents

Stock standard solutions (1000 mg/L)

Analyte stock standard solutions and internal standards stock solutions (ISSS) (1000 mg/L) were purchased or prepared by dissolving the appropriate amounts of the required analytes in 100 mL of DI water. Stock standards were stored at 4 ˚C and they are stable for at least six months at 4 ˚C.

Primary dilution solution (PDS) (5.00 mg/L)

Prepare the analyte PDS by diluting the stock standard solutions into DI water to make the final concentration 5.00 mg/L (e.g., combine 100 µL each of mixed HAAs, bromate, and dalapon stock standard solutions into 19.700 mL DI water). Prepare the internal standard PDS by adding enough of each ISSS to a known volume of DI water to make the final concentration 5.0 mg/L (e.g., combine 100 µL of each of the four ISSS into 19.600 mL DI water). Store the PDS in a plastic vial. The analyte PDS is used to prepare calibration standards and to fortify QC samples with the method analytes.

Working standard solutions

Diluted working standard solutions were prepared using the analyte PDS as shown in Table 5. Levels of calibration standard mixture concentrations used in this study were 0.01, 0.5, 1, 4, 10, 20, 40, and 100 µg/L.

Laboratory Synthetic Sample Matrix (LSSM)

Prepare the LSSM at the concentrations listed in Table 6. The required concentrations of nitrate (20 mg/L), bicarbonate (150 mg/L), chloride (250 mg/L), and sulfate (250 mg/L) are based on the mass of the anion, not the sodium salt. The NH_4Cl preservative is included in the matrix. The laboratory fortified QC samples (LFSSM) at 5.0, 10.0, or 20.0 µg/L were prepared by diluting the analyte PDS with the LSSM.

Table 5. Preparation of calibration standards

Calibration standard	Dilution aliquot used	Dilution aliquot concentration (µg/L)	Dilution aliquot (mL)	Final volume* (mL)	Final concentration (µg/L)	Internal standard concentration** (µg/L)
WS _Stock	Analyte PDS	5000	0.8	20	200	20
WS8	WS _Stock	200	2.5	5	100	20
WS7	WS _Stock	200	1	5	40	20
WS6	WS _Stock	200	2	20	20	20
WS5	WS6	20	2.5	5	10	20
WS4	WS6	20	1	5	4	20
WS3	WS6	20	1	20	1	20
WS2	WS3	1	2.5	5	0.5	20
WS1	WS3	1	0.5	5	0.1	20

*In 100 mg/L ammonium chloride, aqueous
**Add 20 µL of 5 ppm IS PDS in each 5 mL sample or standard.

Table 6. Preparation of the LSSM

Compound	Empirical formula	Salt (gfw)*	Anion (gfw)	Salt mass (mg)	DI H_2O, (mL)	Conc. stock (mg/L)**	Conc. LSSM***
Ammonium chloride (preservative)	NH_4Cl	53.49		100	100	1000	100
Nitrate	NO_3^-	84.99	62.00	27.4		200	20
Bicarbonate	HCO_3^-	84.01	61.02	206		1500	150
Chloride	Cl^-	58.44	35.45	412		2500	150
Sulfate	SO_4^{2-}	142.04	96.06	370		2500	150

*gfw = gram formula weight of the sodium salt
**Stock concentration = (salt mass) (gfw anion)/(gfw salt) (0.1 L)
***1:10 dilution of stock (e.g., 50 mL to 500 mL), LSSM = Laboratory Synthetic Sample Matrix

Sample preparation

Drinking water samples are treated with the preservative (100 mg/L ammonium chloride) and kept in HDPE bottles before analysis. When samples are used for several days, they are stored at 4 ˚C.

Standard and sample with ISTD

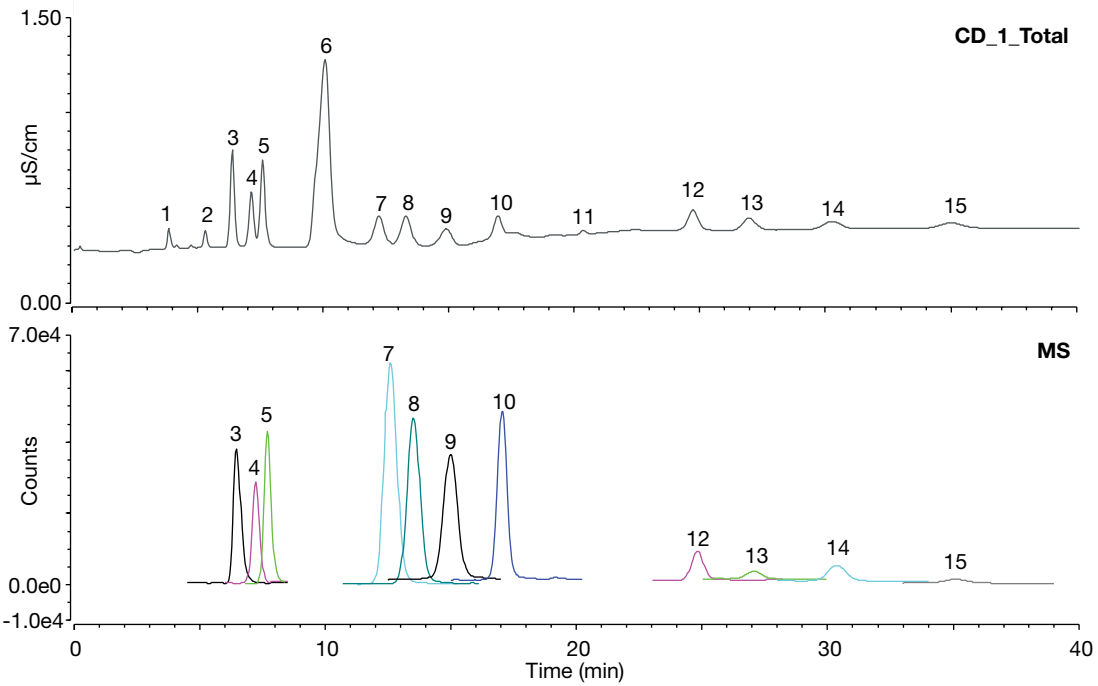
Add 20 µL 5 mg/L of internal standard PDS to each 5 mL of calibration standard or sample.

Results and discussion

Separation

The Dionex IonPac AS31 hydroxide-selective anion-exchange column was specifically designed for fast analysis of HAAs, bromate, and dalapon in drinking water. Figure 3 shows a separation of HAAs, bromate, and dalapon using the Dionex IonPac AS31 column. The top chromatogram displays the CD profile. The bottom chromatogram displays the MS profile. Compared to the Dionex IonPac AS24 column, which was used in U.S. EPA Method 557 to separate nine HAAs, bromate, and dalapon in a one-hour gradient method, the Dionex IonPac AS31 column can separate the same analytes within 40 min, representing a time savings of more than 30%.

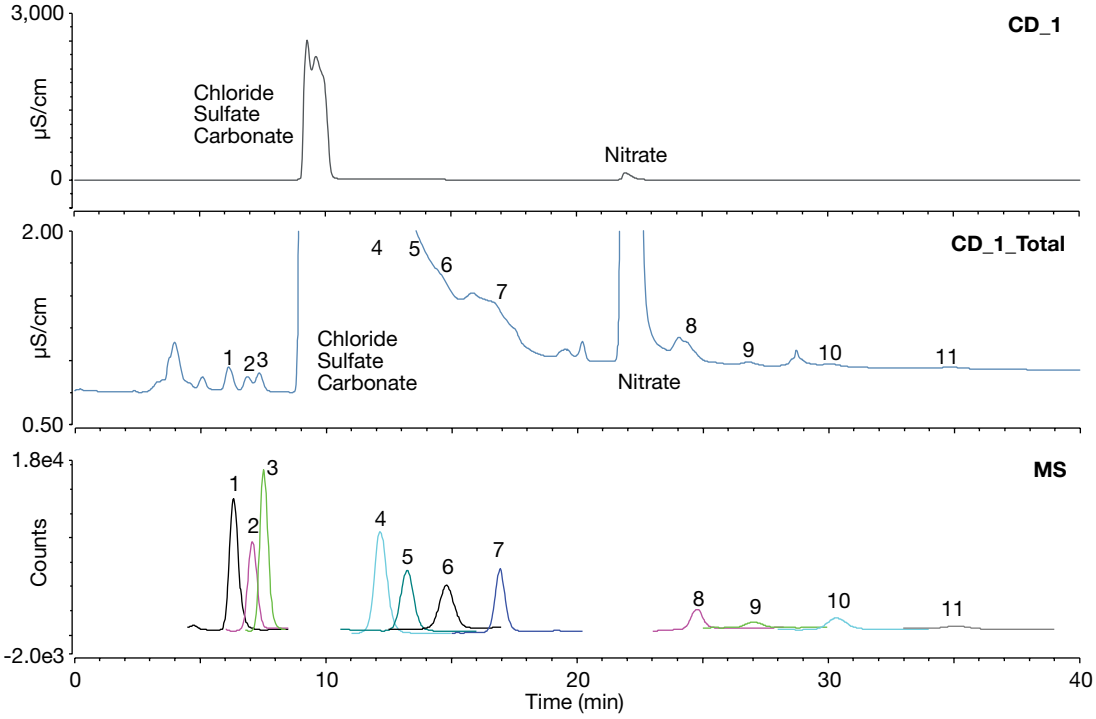
Figure 4 shows a chromatogram of the LSSM spiked with 40 µg/L of nine HAAs, bromate, and dalapon. While CD cannot determine these analytes due to incomplete resolution of analyte peaks from the matrix peaks (chloride, sulfate, carbonate, and nitrate), the ISQ EC single quadrupole mass spectrometer can determine them without difficulty. A small retention shift due to the high ionic strength matrix (the analytes elute out about 0.2 min early) was observed, but it does not impact the analyte quantification by the MS channel.



No.	Quantitation peak	RT (min)	Conc. (µg/L)
1	Fluoride		NQ
2	Unknown		NQ
3	MCAA	6.5	100
4	MBAA	7.2	100
5	Bromate	7.7	100
6	Carbonate		NQ
7	Dalapon	12.3	100
8	DCAA	13.4	100
9	BCAA	15.0	100
10	DBAA	17.1	100
11	Unknown	24.8	NQ
12	TCAA	24.8	100
13	BDCAA	27.0	100
14	CDBAA	30.4	100
15	TBAA	35.1	100

NQ: Not Quantified

Figure 3. Chromatogram of DI-water spiked with 100 µg/L of nine HAAs, bromate, and dalapon



No.	Quantitation peak	RT (min)	Conc. (µg/L)
1	MCAA	6.3	40
2	MBAA	7.1	40
3	Bromate	7.5	40
4	Dalapon	12.1	40
5	DCAA	13.2	40
6	BCAA	14.8	40
7	DBAA	16.9	40
8	TCAA	24.7	40
9	BDCAA	27.0	40
10	CDBAA	30.3	40
11	TBAA	34.9	40

Figure 4. Chromatogram of the LSSM spiked with 40 µg/L of nine HAAs, bromate, and dalapon

Calibration and method detection limits (MDL)

Calibration standard mixtures in the range of 0.01–100 µg/L were prepared in DI water with 100 mg/L of NH_4Cl as a preservative. The ISTD was spiked to each calibration standard at 20 µg/L. The internal standard method provides a means to account for losses in ionization efficiencies due to components in the matrix that may compete for ion formation in the source. The use of isotopically labeled internal standards ensures that both compound identification and compound quantification are of the highest degree of precision and accuracy possible. Table 7 summarizes the calibration results. Calibration curves were generated using internal standard calibration for MS detection in the range of 0.01–100 µg/L. All analytes show a linear response (Figure 5) with coefficients of determination (r^2 value) ranging from 0.998 to 1.

Table 7. Summary of method performance values and comparison of its MDL to U.S. EPA Method 557

Analyte	Retention time (min)	Internal standard	U.S. EPA Method 557 DL (µg/L)	MDL (µg/L)	Calibration range (µg/L)	r^2-value
MCAA*	6.5	MCAA-2-13C	0.2	0.1	0.1–100	0.999
MBAA*	7.2	MBAA-1-13C	0.06	0.03	0.1–100	0.998
Bromate	7.7	MBAA-1-13C	0.02	0.12	0.5–100	0.998
Dalapon	12.3	DCAA-2-13C	0.04	0.12	0.5–100	0.999
DCAA*	13.4	DCAA-2-13C	0.06	0.03	0.1–100	0.998
BCAA	15.0	DCAA-2-13C	0.11	0.16	0.5–100	0.998
DBAA*	17.1	DCAA-2-13C	0.02	0.16	0.5–100	0.999
TCAA*	24.8	TCAA-2-13C	0.09	0.67	1–100	0.999
BDCAA	27.0	TCAA-2-13C	0.05	2.79	4–100	0.998
CDBAA	30.4	TCAA-2-13C	0.04	1.04	4–100	1
TBAA	35.1	TCAA-2-13C	0.07	4.55	10–100	1

*HAA5

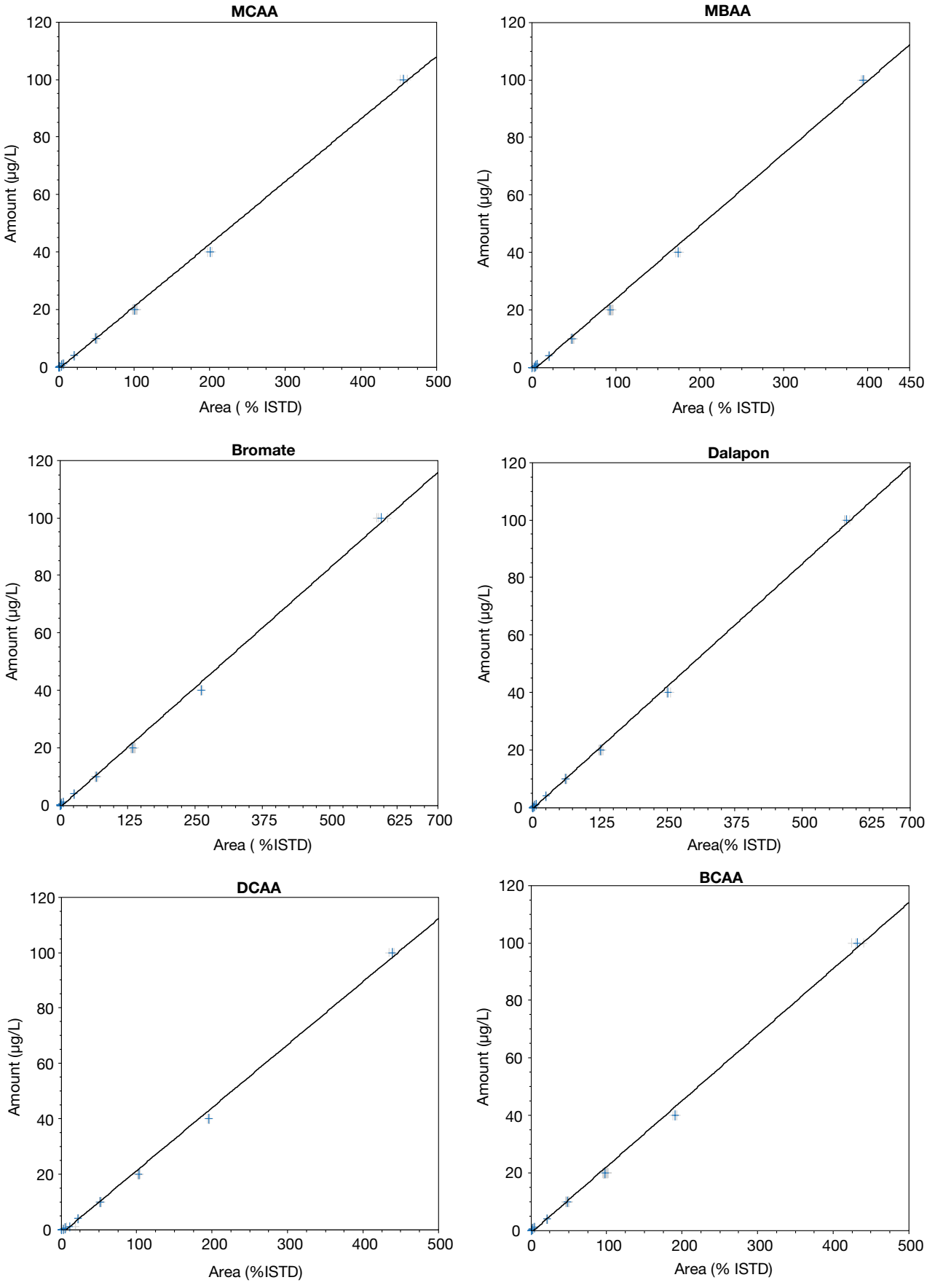


Figure 5 (part 1). Calibration curves of HAAs, bromate, and dalapon

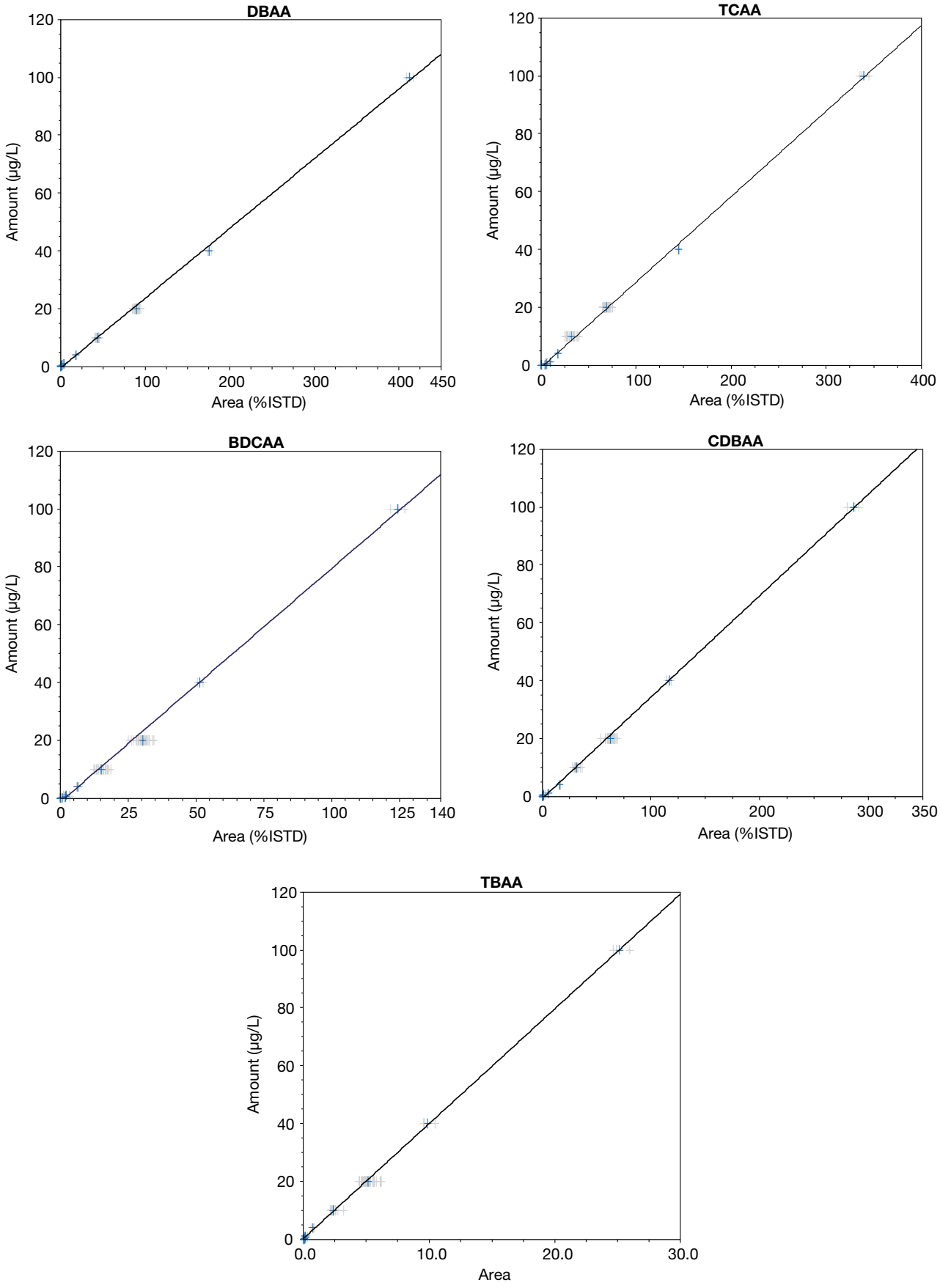


Figure 5 (part 2). Calibration curves of HAAs, bromate, and dalapon

The method detection limits (MDLs) were determined by performing seven replicate injections of standards at a concentration of three to five times the estimated instrument detection limits. Calculate the MDL as follows: MDL = (*t*) × (S), where *t* = Student's value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven injections), S = standard deviation of the replicate analysis.

This shows that the method is sensitive enough to determine the U.S. EPA regulated HAA5 (MCAA, MBAA, DCAA, BCAA, DBAA, and TCAA), bromate, and dalapon with MDLs ranging from 0.03 to 0.67 µg/L. The MS chromatograms at low concentrations are shown in Figures 6 to 8. The gray areas show the times when the diverter valve switched to send the sample stream (the high salt matrix) to waste. Figure 6 shows that U.S. EPA regulated HAA5 (MCAA, MBAA, DCAA, DBAA, and TCAA), BCAA, bromate, and dalapon are easily detected at 1 µg/L.

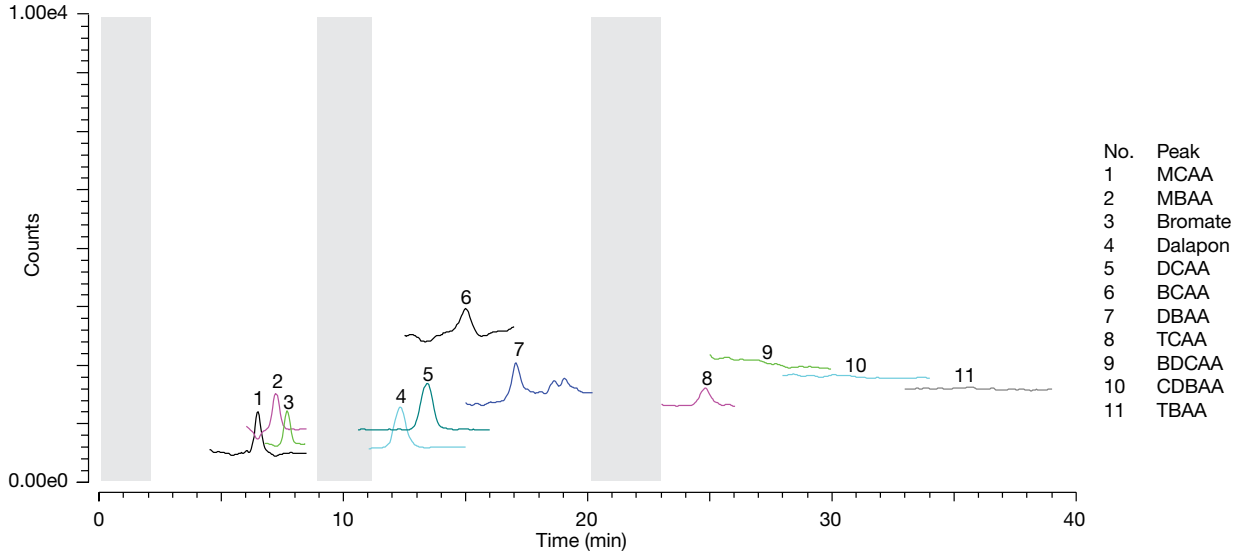


Figure 6. Chromatogram (MS profile) of 1.0 µg/L of HAAs, bromate, and dalapon

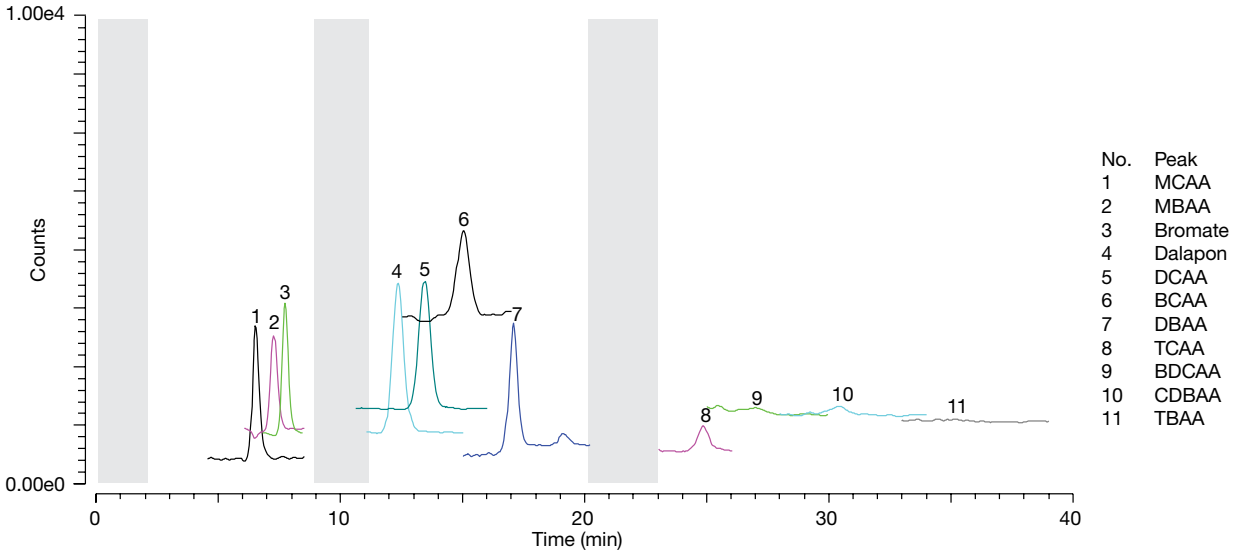


Figure 7. Chromatogram (MS profile) of 4.0 µg/L of HAAs, bromate, and dalapon

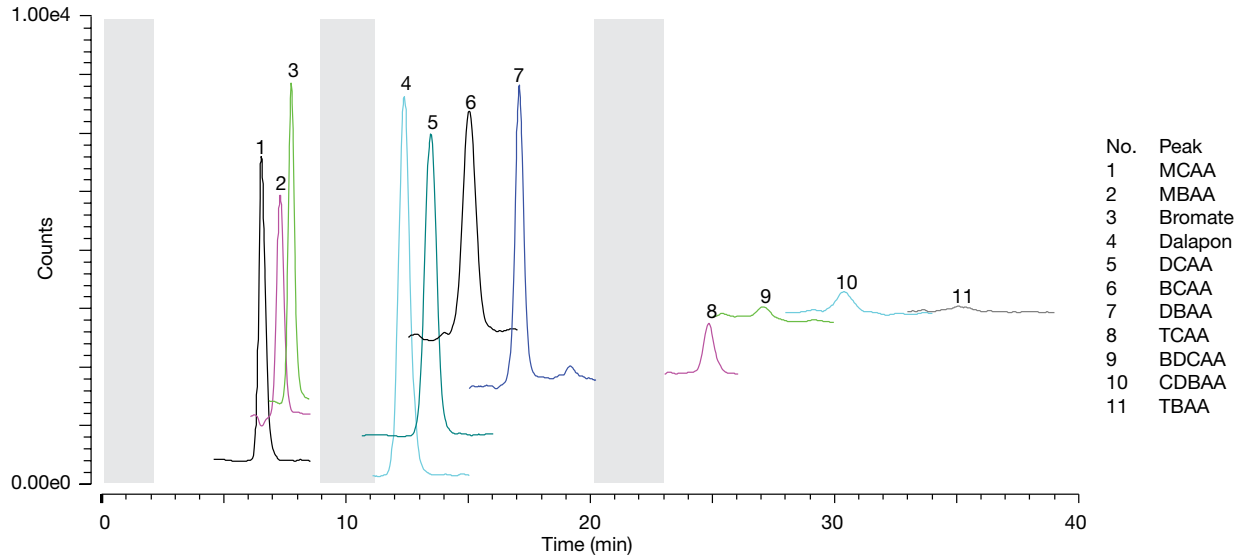


Figure 8. Chromatogram (MS profile) of 10.0 µg/L of HAAs, bromate, and dalapon

Sample analysis

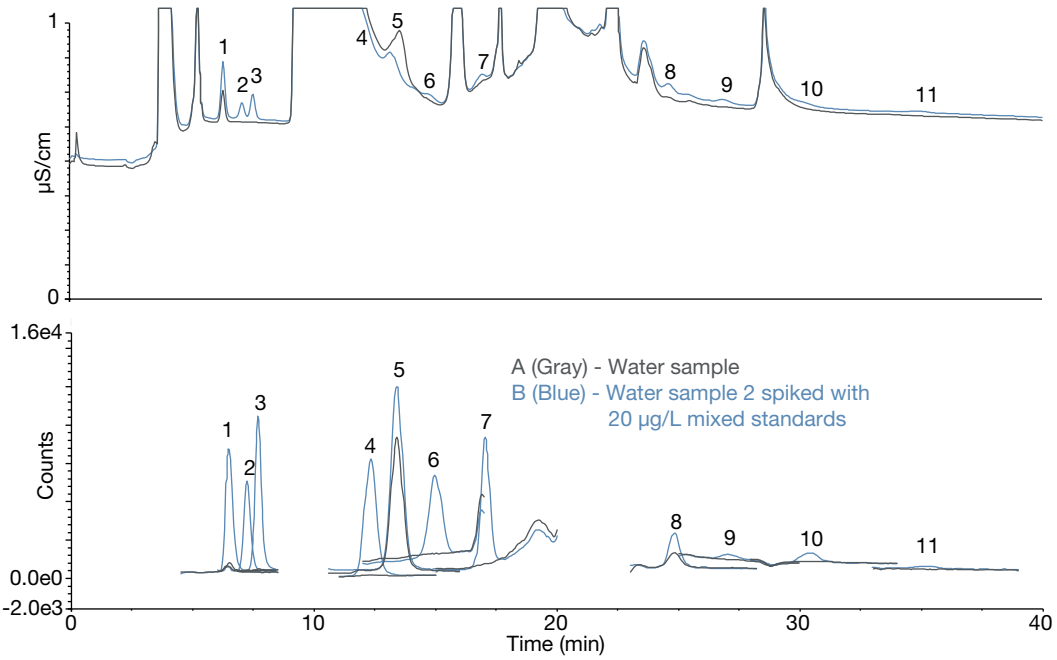
The developed method was used to evaluate three residential tap water samples collected from two cities in the San Francisco Bay Area, California. Samples 1 and 2 were from city 1 and sample 3 was from city 2. Samples 1 and 3 were tested more than three times over more than three days. The results are listed in Table 8. The results show that although all samples had concentrations lower than the action levels required by the U.S. EPA, each sample had DBPs. For example, city 1 water contains MCAA (1.5 µg/L), DCAA (22.1 µg/L) and TCAA (3.8 and 9.0 µg/L); and city 2 contains DCAA (21.9 µg/L), BCAA (4.4 µg/L), TCAA (4.4 µg/L) and trace of bromate (0.4 µg/L) and DBAA (0.4 µg/L). The method is reproducible as the test results of the two samples over three days were consistent with percent relative standard deviation (RSD) <13.4% for the contaminants >1 ppb.

Table 8. Analysis results of drinking water samples

Analyte	Retention time (min)	Water sample 1	RSD range**	Water sample 2	RSD (%)	Water sample 3	RSD range**
MCAA *	6.5	1.5 ± 0.1	3.9–5.0	1.5 ± 0.1	4.0	ND	-
MBAA *	7.2	ND	-	ND	-	ND	-
Bromate	7.7	ND	-	ND	-	0.36 ± 0.03	1.0–25
Dalapon	12.3	ND	-	ND	-	ND	-
DCAA *	13.4	22.1 ± 1.3	0–1.0	22.1 ± 0.2	1.0	21.9 ± 0.9	0–1.0
BCAA	15.0	ND	-	ND	-	4.4 ± 0.3	0.2–8.9
DBAA *	17.1	ND	-	ND	-	0.4 ± 0.1	12–47
TCAA *	24.8	13.8 ± 1.9	1.6–5.8	9.0 ± 0.3	3.5	4.4 ± 0.4	2.9–13.4
BDCAA	27.0	ND	-	ND	-	ND	-
CDBAA	30.4	ND	-	ND	-	ND	-
TBAA	35.1	ND	-	ND	-	ND	-

*HAA5, **The samples were tested for more than three times over more than three days, n=3/each day.

Figures 9 and 10 show chromatograms of two water samples and those samples spiked with 10 µg/L of nine HAAs, bromate, and dalapon. Again, it is difficult for the conductivity detector to determine the concentrations of dalapon, DCAA, BCAA, DBAA, and TCAA due to the other anions in the sample. In contrast, the ISQ EC single quadrupole mass spectrometer can determine these analytes with minimum interference.

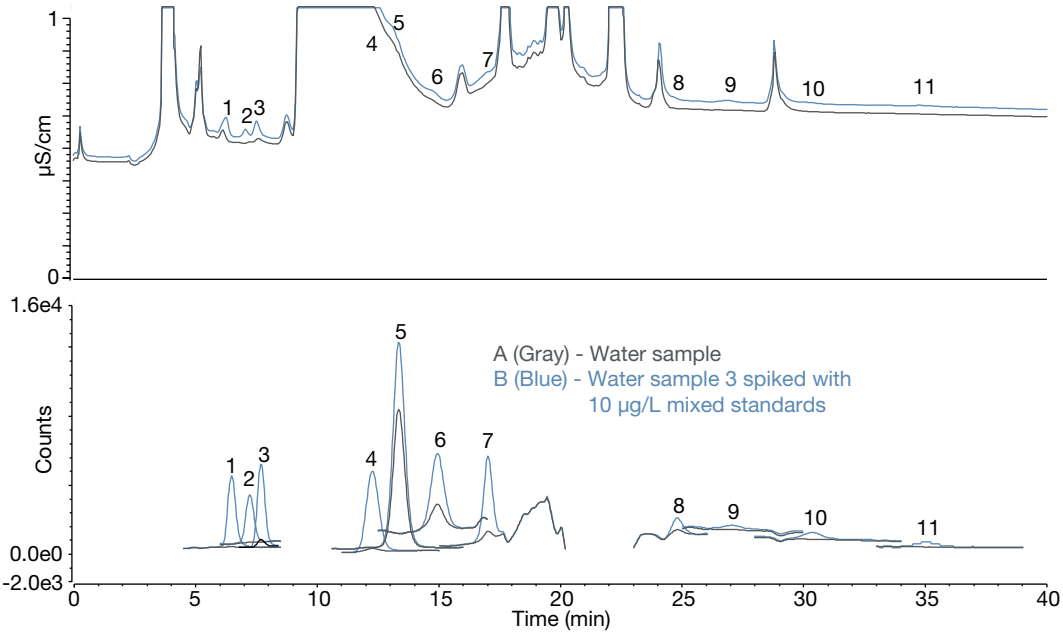


No.	Peak	RT (min)	Conc. (µg/L) A	Conc. (µg/L) B
1	MCAA	6.5	1.5	22.9
2	MBAA	7.2	ND	21.8
3	Bromate	7.7	ND	23.2
4	Dalapon	12.3	ND	20.4
5	DCAA	13.4	22.3	43.4
6	BCAA	15.0	ND	20.8
7	DBAA	17.1	ND	20.7
8	TCAA	24.8	16.4	37.8
9	BDCAA	27.0	ND	18.6
10	CDBAA	30.4	ND	21.0
11	TBAA	35.1	ND	13.1

A (Gray): Water sample 2
B (Blue): Water sample 2 spiked with 20 µg/L mixed standards

ND: Not detectable

Figure 9. Chromatogram of water sample 2 with and without spiking with 20 µg/L of 9HAAs, bromate, and dalapon



No.	Peak	RT (min)	Conc. (µg/L) A	Conc. (µg/L) B
1	MCAA	6.5	ND	10.7
2	MBAA	7.2	ND	11.1
3	Bromate	7.7	0.33	12.3
4	Dalapon	12.3	ND	10.4
5	DCAA	13.4	21.8	33.7
6	BCAA	15.0	4.9	14.7
7	DBAA	17.1	0.4	9.5
8	TCAA	24.8	4.7	16.5
9	BDCAA	27.0	ND	9.9
10	CDBAA	30.4	ND	10.3
11	TBAA	35.1	ND	8.8

A (Gray): Water sample 3
B (Blue): Water sample 3 spiked with 10 µg/L mixed standards

ND: Not detectable

Figure 10. Chromatogram of water sample 3 with and without spiking with 10 µg/L of nine HAAs, bromate, and dalapon

Method accuracy

Method accuracy was evaluated through spike-recovery of 10 µg/L of nine HAAs, bromate, and dalapon in drinking water samples and the LSSM. Table 9 shows the results. The method is accurate and sensitive for the determination of 10 analytes (MCAA, MBAA, bromate, dalapon, DCAA, BCAA, DBAA, TCAA, BDCAA, and CDBAA) including U.S. EPA regulated HAA5 at this level with recoveries ranging from 92% to 119% in the LSSM. The recoveries from samples ranged from 91% to 129%. The recoveries of TBAA are not accurate at 10 µg/L as this is close to its limit of quantification (MDL=4.55 µg/L). U.S. EPA Method 557 requires the average percent recovery of the replicate analyses must be within ±30% of the true value. Therefore, this method with a single quadrupole mass spectrometer is suitable for the determination of 10 out of the 11 analytes in U.S. EPA Method 557 that uses a triple quadrupole mass spectrometer.

Precision

The precision of the method was determined by seven replicate analyses of 10 µg/L of nine HAAs, bromate, and dalapon in the LSSM over three separate days. As shown in Table 10, the retention times are very stable with precision ranges from 0 to 0.1% for all analytes. The high precision of this method is consistent with results typically found with an RFIC system. The MS peak areas are not as stable. However, the addition of the internal standards corrects the variability of peak area due to instrument and sample matrix. The RSD of the corrected peak areas (ISTD area) ranged from 0.7 to 4% for 10 of the analytes. This passes the requirement of U.S. EPA Method 557 (must be ≤20% for all method analytes). Again, this method is suitable for the determination of 10 out of the 11 analytes in U.S. EPA Method 557.

Table 9. Recoveries of 10 µg/L of nine HAAs, bromate, and dalapon in drinking water samples and in the LSSM

	Water sample 2[a]		Water sample 3[a]		LSSM[b]	
Analyte	Recovery (%)	RSD	Recovery (%)	RSD	Recovery (%)	RSD
MCAA*	110	1.6	109	2.2	99–100	1.6–2.7
MBAA*	114	1.3	113	2.6	105–112	1.6–5.4
Bromate	128	2.1	121	1.8	97–99	0.9–2.5
Dalapon	107	1.3	104	0.6	110–112	1.0–1.5
DCAA*	119	1.5	121	0.6	101–102	0.5–1.9
BCAA	102	1.6	110	1.8	92–98	1.5–3.7
DBAA*	106	0.8	91	1.1	99–109	1.2–2.8
TCAA*	129	3.9	119	2.5	109–119	5.2–7.5
BDCAA	121	22.9	112	11	106–117	13–27
CDBAA	96	3.1	111	12.3	105–110	5–10
TBAA	62	17	88	16.4	132–231	10–77

*HAA5; [a]n=3; [b]n=7, over 3 days

Table 10. Relative standard deviation (RSD) of retention time and peak area

Analyte	Retention time		Area		ISTD area
	Intraday	Interday	Intraday	Interday	Interday
MCAA*	0–0.1	0.01	1.4–2.2	9.5	0.7
MBAA*	0–0.1	0	1.4–5.1	7.0	1.0
Bromate	0	0	0.9–2.3	8.6	0.8
Dalapon	0	0	0.9–2.0	5.6	0.8
DCAA*	0	0	1.6–2.0	6.0	0.7
BCAA	0–0.1	0.1	1.3–3.3	4.8	1.8
DBAA*	0	0	0.9–3.0	3.7	1.9
TCAA*	0	0	4.1–7.0	3.5	0.8
BDCAA	0	0	6.5–23.5	4	4
CDBAA	0	0	2.6–9.1	4.6	1.8
TBAA	0.3–0.4	0.1	10.4–22.2	29.1	25.7

*HAA5

Precautions

There are critical IC system conditions that are important for successful implementation of this application:

Autosampler and IC system compartment temperature

Some HAAs (e.g., MBAA, CDBAA, and TBAA) are not thermally stable and degrade in aqueous solutions, especially readily at high pH values. To minimize these degradations, samples should be held at low temperature (4 °C) until they can be injected for analysis (i.e., a temperature-controlled autosampler is required). Additionally, because a high pH eluent is used for the separation, the ability of the IC system to precisely and consistently maintain the columns at 15 °C is critical for HAA determinations. At 15 °C, degradation in the column eluent is minimized and the concentrations of HAAs are determined correctly (i.e., a Low Temperature Detector/ Chromatography Module (DC) with column cooling is required).

Divert windows

Analyte retention times may vary from column to column and may slowly shift toward lower values as the column ages. Because this method employs multiple divert windows, the analyst must monitor peak locations to ensure that each analyte peak elutes entirely within the MS elution windows.

Conductivity background

The analyst should observe the background conductivity before starting an analysis sequence each day. Excessive background conductivity will cause MS signal suppression and result in method sensitivity decrease. Figure 11 shows the chromatograms of a mixed standard (40 µg/L of nine HAAs, bromate, and dalapon in DI water with preservative) with a normal and a malfunctioning (aged) CR-ATC. When an aged (about one year) CR-ATC was installed in the IC system, the CD background (~2–3 µS/cm) increased slightly. However, higher MS noise, higher MS background, and lower MS peak areas were observed compared to historical values when the background conductivity was lower (~0.5 µS/cm). The method sensitivity also decreased dramatically.

To ensure the IC system is optimal for MS analysis, low conductivity (<0.5 to 1.5 µS/cm) is recommended. If total conductivity is too high, troubleshoot as follow:

1. Make sure DI water is clean (conductivity <18 MΩ·cm).

2. Check that the CR-ATC and suppressor are connected and working. If the CR-ATC is approximately a year old or older, replace it.

3. Flush the IC system (including columns, suppressor, and detector) at the highest eluent concentration in the gradient (i.e., 85 mM KOH) for more than one hour.

4. Increase the suppressor current from the recommended 64 mA to 70 mA and stabilize the IC system until the background is at an acceptable value.

5. Replace the consumables (i.e., CR-ATC and suppressor).

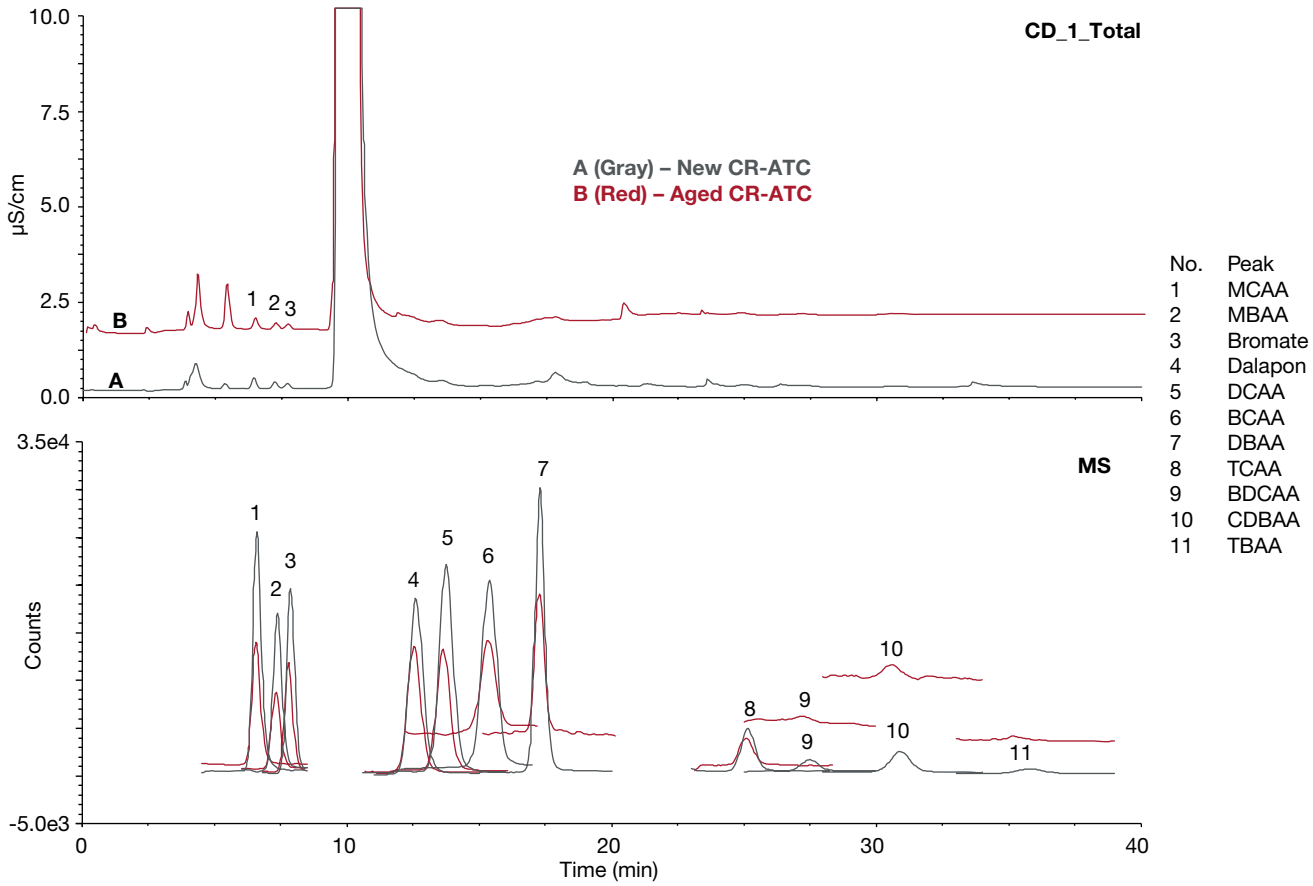


Figure 11. Chromatograms of a mixed standard with a normal and a malfunctioning CR-ATC

Conclusion

This study evaluated an IC-MS method for the determination of all nine haloacetic acids, bromate, and dalapon in drinking water. The method used a Dionex ICS-6000 HPIC system with DP pump and Dionex IonPac AS31 anion-exchange column coupled with suppressed conductivity detection and a single quadrupole mass spectrometer ISQ EC detector.

We found that the IC-MS method is fast (40 min vs. 60 min in U.S. EPA Method 557) and linear over the established analytical range for the 11 analytes with an r^2 value range of 0.998 to 1. The method is sensitive for the determination of U.S. EPA regulated HAA5 (MCAA (MDL = 0.1 µg/L), MBAA (MDL = 0.03 µg/L), DCAA (MDL = 0.03 µg/L, DBAA (MDL = 0.16 µg/L), and TCAA (MDL = 0.67 µg/L)), bromate (MDL = 0.12 µg/L), and dalapon (MDL = 0.12 µg/L). Plus, the method is sensitive for the determination of not yet regulated HAAs (BCAA (MDL = 0.16 µg/L), BDCAA (MDL = 2.79 µg/L), CDBAA (MDL = 1.04 µg/L), TBAA (MDL = 4.55 µg/L). The method is accurate for the determination of 10 of 11 analytes in U.S. EPA Method 557 (MCAA, MBAA, bromate, dalapon, DCAA, BCAA, DBAA, TCAA, BDCAA, and CDBAA) with recoveries ranging from 92% to 119% when spiked with 10 µg/L of nine HAAs, bromate, and dalapon in LSSM. The method is precise with retention time precision below 0.1% and internal standard corrected peak area interday precision ranging from 0.7% to 4%.

We also observed that there are critical IC system conditions important for successfully running this application:

1. Low autosampler and IC system compartment temperature

2. Correct divert windows

3. Low conductivity background.

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In conclusion, the single quad IC-MS method meets the guidelines in U.S. EPA Method 557 and can be used for the determination of U.S. EPA regulated HAA5, bromate, and dalapon. The single quadrupole MS provides sufficient selectivity and limits of detection for the purpose of screening for HAA5. For more selective detection of HAAs and their quantitation at lower limits of detection required by most regulatory entities, an ion chromatograph coupled to either a triple quadrupole (IC-MS/MS) or high-resolution accurate mass (IC-HRAM-MS) mass spectrometer are recommended.

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