

Determination of Haloacetic Acids in Water Using IC-ESI-MS/MS

INTRODUCTION

This method allows separation and detection of sub- $\mu\text{g/L}$ levels of nine haloacetic acids (HAAs) in high-ionic strength matrices. Using this method, the analytes are separated from chloride, sulfate, nitrate, bromide and bicarbonate, and detected using a triple quadrupole mass spectrometer with an electrospray interface. Quantification is achieved using internal standards.

Haloacetic acids occur in drinking water during the disinfection process, as a result of the reaction between chlorine and natural organic materials, such as humic and fulvic acids.^{1,2} The iodoacids (e.g. iodoacetic acid) are much less stable and are not included in this analysis. When bromide is present in the water, bromoacetic acids and mixed chloro- and bromoacetic acids can also be generated. Haloacetic acids have been linked to possible health threats to human health. Monitoring for monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA) and dibromoacetic acid (DBAA) has been in effect since they were first regulated under the Stage I Disinfection Byproducts (DBP) Rule, Dec. 16, 1998, with a Minimum Contamination Level (MCL) set at 60 $\mu\text{g/L}$. Stage II DBP Rule, Jan. 4, 2006, maintained the MCL, but also instituted minimum reporting limits (MRL) requirements of 2 $\mu\text{g/L}$ for MCAA and 1 $\mu\text{g/L}$ for the other HAAs. The remaining four HAAs that may be present in drinking water are: chlorobromoacetic acid (CBAA), chlorodibromoacetic acid (CDBAA), dichlorobromoacetic acid (DCBAA), and tribromoacetic acid (TBAA).

The determination of the chloro-, bromo-, and mixed haloacetic acids in waters destined for human consumption, including drinking water and swimming pool water, has been reported using a variety of analytical techniques.³ USEPA Methods 552.2 and 552.3 use acidic methanol derivatization followed by gas chromatography with electron capture detection.⁴ This method is both labor-intensive and time-consuming. Bruzzoniti⁵ recently published a table summarizing the existing IC columns and methods used for HAAs analysis, including this method, which uses the IonPac[®] AS24 column. Asami⁶ used offline sample pretreatment with external standard calibration and MS/MS detection for calibration of haloacetic acids and oxyhalides, using perchlorate as an internal standard. Only the method using the IonPac AS24 method addresses the issue of high-ionic strength matrices. All the IC methods take advantage of the low pKa values of HAAs ($\sim 0.7\text{--}2.8$) by using anion-exchange separation mode. Hydroxide-based eluents are used in conjunction with chemical suppression, so the background signal entering the mass spectrometer is as low as that of water. When mass spectrometric detection is used, the matrix ions are typically diverted to waste during the analytical run to avoid contamination of the detector. USEPA Method, 332.0⁷ uses the same configuration as discussed in this paper for the determination of perchlorate in drinking water; namely, ion chromatography with matrix diversion and detection using suppressed conductivity followed by electrospray mass spectrometry. The selectivity of the analytical column in a method using

matrix diversion must be designed such that the matrix ions are sufficiently resolved from target analytes.

Four internal standards are used in our method for the nine target analytes. These were chosen because they elute throughout the chromatographic run, thus allowing easy tracking of close-eluting analytes. Stuber and Reemtsma⁸ discuss the challenges of quantification using LC-ESI-MS in the presence of significant matrix effects, and provide some guidance for using internal standards. Most of the currently published work describing various analytical approaches for determination of HAAs, however, does not adequately address the challenges of very high-ionic strength matrices, or the need for internal standards to obtain accurate and precise quantification.

Figure 1 shows the chromatogram of the nine standards, the two matrix diversion windows, and the general form of the KOH gradient. The three periods noted in the figure correspond to three periods for data collection in the Analyst method program. Figure 2 shows the general instrumentation schematic.

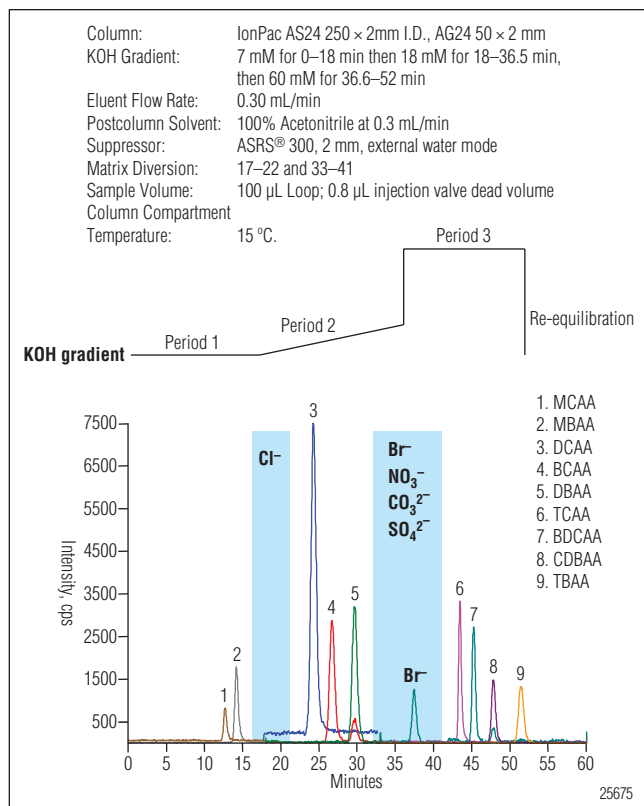


Figure 1. Chromatogram produced by chromatography conditions and mass spectrometer conditions provided in Table 1. The shaded areas show the time windows for matrix diversion to waste and the matrix ions that elute in those windows. The time windows for data collection in Periods 1, 2, and 3 are indicated.

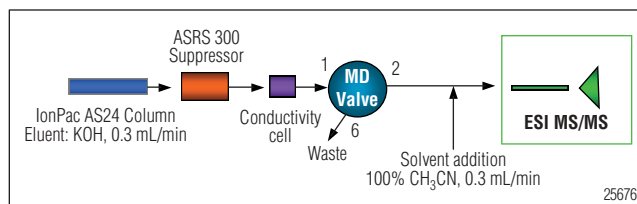


Figure 2. ICS-3000 system schematic, showing matrix diversion and mass spectrometric detection.

RECOMMENDED EQUIPMENT

ICS3000 Chromatography System

DP Dual Pump module (or SP and an AXP)

DP1 Analytical Pump

DP2 pump is used to deliver post-suppressor acetonitrile

DC Dual-Zone Chromatography Module

CD Conductivity Detector

AS Autosampler with sample tray cooling

EG Eluent Generator

Mixing Tee (Upchurch, part number U-466)

Mass Spectrometer

ABI-Sciex (Toronto, Canada) API2000™ Triple

Quadrupole Mass Spectrometer with electrospray interface capable of negative ion detection, or equivalent

Nitrogen and Zero Air supplies as specified by MS manufacturer

25-pin relay cable connecting mass spectrometer to DP pump module; pins 19 (red) and 7 (black) in the DP connector

Software

Dionex DCMSLink™ 2.0 software or higher

ABI Sciex Analyst software (version 1.4.2 or higher)
XCalibur 2.0 or higher

Standards

Deionized water: 18 MΩ or better

Acetonitrile (HPLC grade)

Analyte standard mix (1000 μg/mL) of the nine native HAAs; monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), dibromoacetic acid (DBAA), chlorobromoacetic acid (CBAA), chlorodibromoacetic acid (CDBAA),

dichlorobromoacetic acid (DCBAA), and tribromoacetic acid (TBAA) purchased from Restek (P/N31896).

The internal standards from Dionex are: monochloroacetic acid-2-13C (1000 µg/mL, P/N 069406), monobromoacetic acid-1-13C (1000 µg/mL, P/N 069407), dichloroacetic acid-2-13C (1000 µg/mL, P/N 069408), and trichloroacetic acid-2-13C (1000 µg/mL, P/N 069409). Standards are dissolved in methyl tert-butyl ether (MtBE). A working standard mixture of the four internal standards was prepared in deionized water. All standard solutions were kept refrigerated at 4 °C when not in use. Standards in the 2-5 µg/L range are stable for 14 days when stored at 4 °C with PTFE/silicone septa. Because the standards are purchased in MtBE, which has limited solubility in water (~ 5%), not more than ~ 0.5% of MtBE is added when making the mixtures, relative to the total water volume.

Sample Preparation

Samples were collected in amber glass bottles with PTFE-lined screw caps. Crystalline or granular ammonium chloride is added to the sample containers to produce a final concentration of 100 mg/L of ammonium chloride. The preservation requirements are exactly the same as those described in EPA Method 552.3.

CONDITIONS

Chromatography Conditions

Column:	IonPac AS24 250 × 2mm I.D., IonPac AG24 50 × 2mm	
KOH Gradient:	Time	KOH (mM)
	-7.0	7
	0.0	7
	18.0	7
	36.5	18
	36.6	60
	52.0	60
Eluent Flow Rate:	0.30 mL/min	
Postcolumn Solvent:	100% Acetonitrile at 0.3 mL/min	
Suppressor:	ASRS 300 (2 mm) External water mode	
Anion Trap:	CR-ATC (2-mm)	
Matrix Diversion:	17-22 and 33-41	
Sample Volume:	100 µL sample loop	
Column Compartment Temperature:	15 °C	
Autosampler Temperature:	8 °C	
Detector Compartment Temperature:	30 °C	
Mass Spectrometric Conditions:	Tables 1-5	

Table 1. API2000 Conditions

Analyte	KOH Gradient	Transition	Source-Dependent Parameters	Declustering Potential (V)	Focusing Potential (v)	Collision Energy (eV)	Entrance Potential (V)	Collision Cell Entrance Potential (V)	Collision Cell Exit Potential (V)	Dwell Time (mSec)
MCAA MCAA-21-13C	7 mM 0 – 18 min	92.9/34.9 93/34.9	Curtain 20 CAD 2 Ionspray -4500 Temp 475 °C	-20	-300	-12	-10	-12	-6	600 each
MBAA MBAA-1-13C		137/78.8 138/78.8		-11	-350	-12	-7	-10	-14	600 each
Dalapon	18 mM 18 – 36.5 min.	141/97	Curtain 25 CAD 4 Ionspray -4500 Temp 475 °C GS1/GS2 90/90	-13	-350	-11	-8	-13	-6	500
DCAA DCAA-2-13C		127/82.9 128/84		-11	-320	-12	-6.5	-12	-6	500 each
BCAA		170.8/78.8		-16	-300	-28	-6	-14	-8	500
DBAA		214.7/170.7		-11	-350	-12	-4.5	-15	-10	500
TCAA TCAA-2-13C	60 mM 36.6 – 52 min	161/116.9 162/118	Curtain 25 CAD 4 Ionspray -4500 Temp 475 °C GS1/GS2 90/90	-6	-290	-7	-7	-13.7	-13.7	400 each
BDCAA		207/81 or 79/79		-12	-300	-6	-4	-15	-14	400
CDBAA		207/78.8		-11	-300	-20	-4	-15	-6	400
TBAA		250.75/78.8		15	-350	-28	-5	-12	-12	400

Table 2. API3200 Conditions

Analyte	KOH Gradient	Transition	Source-Dependent Parameters	Declustering Potential (V)	Collision Energy (eV)	Entrance Potential (V)	Collision Cell Entrance Potential (V)	Collision Cell Exit Potential (V)	Dwell Time (mSec)
MCAA MCAA-2-13C	7 mM 0 – 18 min	92.9/34.9	Curtain 30 CAD 2 Ionspray -4500 Temp 500 °C	-15	-3	-5	-17	-5	600 each
MBAA MBAA-1-13C		137/78.8		-14	-7	-8	-20	-1.5	600 each
Dalapon	18 mM 18 – 36.5 min.	141/97	Curtain 30 CAD 3 Ionspray -4500 Temp 500 °C GS1/GS2 70/70	-17	-5	-5	-11	-1	500
DCAA DCAA-2-13C		127/82.9		-15	-3	-5	-17	-1	500 each
BCAA		170.8/78.8		-26	-4	-8	-32	-1.5	500
DBAA		214.7/170.7		-22	-3.5	-22.8	-18	-1.5	500
TCAA TCAA-2-13C	60 mM 36.6 – 52 min	161/116.9	Curtain 30 CAD 3 Ionspray -4500 Temp 250 °C GS1/GS2 70/70	-12	-3	-6	-19	-1	400 each
BDCAA		207/81 or 79/79		-85	-4	-15.1	-10	-1.5	400
CDBAA		207/78.8		-12	-3	-16.8	-6	-14	400
TBAA		250.75/78.8		-13	-2.5	-13	-32	-1.5	400

Table 3. API4000 Conditions

Analyte	KOH Gradient	Transition	Source-Dependent Parameters	Declustering Potential (V)	Collision Energy (eV)	Entrance Potential (V)	Collision Cell Exit Potential (V)	Dwell Time (mSec)
MCAA MCAA-2-13C	7 mM 0 – 18 min	92.9/34.9	Curtain 20 CAD 2 Ionspray -4000 Temp 500 °C	-25	-15	-2	-3	600 each
MBAA MBAA-1-13C		137/78.8		-25	-15	-2	-3	600 each
Dalapon	18 mM 18 – 36.5 min.	141/97	Curtain 20 CAD 8 Ionspray -4300 Temp 500 °C GS1/GS2 50/50	-33	-15	-4	-13	500
DCAA DCAA-2-13C		127/82.9		-43	-31	-5	-2	500 each
BCAA		170.8/78.8		-31	-17	-5	-9	500
DBAA		214.7/170.7		-21	-11	-4	-5	500
TCAA TCAA-2-13C	60 mM 36.6 – 52 min	161/116.9	Curtain 20 CAD 10 Ionspray -4200 Temp 250 °C GS1/GS2 50/50	-35	-22	-4.5	-12	400 each
BDCAA		206.8/81		-35	-22	-4.5	-12	400
CDBAA		206.8/81		-35	-22	-4.5	-12	400
TBAA		250.9/78.8		-30	-34	-4	-12	400

Table 4. Thermo Quantum Access Conditions

Analyte	Q1/Q3	CE	Tube Lens	Cap Temp (°C)	Sheath Gas/Aux Gas	Ion Sweep	Skimmer Offset (V)	Scan Time/Section (s)
MCAA MCAA-2-13C	93/35.6 94/35.6	10	26	270	40/15	0.1	0	1.25
MBAA MBAA-1-13C	137/79.1 138/79.1	12	33	270	40/15	0.1	0	1.25
DCAA DCAA-2-13C	127/83.2 128/84	11	26	270	40/15	0.1	0	1.25
DBAA	214.8/79.2	24	33	270	40/15	0.1	0	1.25
BCAA	171/79.2	35	44	270	40/15	0.1	0	1.25
TCAA TCAA-2-13C	161.1/117.1 162/118	10	69	270	40/15	0.1	0	1.6
BDCAA	79/79	15	30	270	40/15	0.1	0	1.6
CDBAA	206.7/79.1	15	30	270	40/15	0.1	0	2.5
TBAA	250.7/79.1	25	26	270	40/15	0.1	0	2.5

Table 5. Waters Quattro Premier Parameters

Analyte	Transition	Dwell (sec)	Cone, V	Extractor/RF Lens/Source Block Temp (V/V/oC)	Collision Energy, V
MCAA MCAA-2-13C	92/35 93/93	1.0 0.5	15	-3/-0.5/120	8
MBAA MBAA-1-13C	136.9/78.9	0.5	15	-3/-0.5/120	10
DAL	140.9/97	0.5	18	-3/-0.5/120	8
DCAA DCAA-2-13C	126.9/83	0.5	17	-3/-0.5/120	10
BCAA	172.9/128.9	0.5	17	-3/-0.5/120	10
DBAA	216.8/172.84	0.5	18	-3/-0.5/120	12
TCAA TCAA-2-13C	160.9/116.9 162.9/118.9	0.5 0.5	16	-3/-0.5/120	8
BDCAA	162.9/80.9	1.0	25	-3/-0.5/120	10
CDBAA	206.8/78.9	1.0	28	-3/-0.5/120	10
TBAA	250.8/78.9	1.0	28	-3/-0.5/120	12

Other Conditions:

Desolvation Gas: 350 °C @ 940 L/hr

Capillary: -2.8V

Collision Pressure: 5.5×10^{-3} (0.15 flow @ 7 psig)

Cone Flow: 100 L/hr,

ACN Flow Rate: 0.2 mL/min

RESULTS AND DISCUSSION OF THE METHOD Separation

One of the most important features of this method is the ability to quantify the HAAs in the presence of matrices of high-ionic strength. Initially, the separation was achieved using the IonPac AS20 (250 × 2 mm I.D., 78 μEq/column). Reduced peak height, lower peak efficiencies, and shifting retention times were observed when the matrix composition exceeded 100 mg/L chloride and sulfate. The IonPac AS24 column (250 × 2 mm I.D.) 140 μEq/column provides approximately twice the anion-exchange capacity as the AS20.⁹ This improved capacity is required for this application, where the concentration of common matrix ions can be as high as 250 mg/L chloride, 250 mg/L sulfate, 150 mg/L bicarbonate, and 30 mg/L nitrate. The high capacity of the column insures that the ion-exchange sites are not consumed with matrix ions during the separation.

Figure 1 shows separation of nine HAA standards and the time windows for the common matrix ions. The common ions shown are separated from the HAAs, and this separation allows time for the diversion of these ions to waste using a three-way valve before they can enter the mass spectrometer.

Solvent Addition

Addition of 0.3 mL/min of 100% acetonitrile after the IC suppressor and before the ESI inlet improves sensitivity from twofold to 10-fold depending on the analyte and condition of the mass spectrometer. The flow of solvent to the mass spectrometer continues during matrix diversion for stability of the electrospray.

Temperature

The retention times for the HAAs increase as column temperature increases. In addition, some of the HAAs—most notably the brominated species—are less stable at higher temperatures and high pH. The autosampler temperature was set to 8 °C and the column compartment temperature to 15 °C to maximize analyte and internal standard stability and retention time reproducibility. In addition, stable retention times are critical to maintain the times for the matrix diversion windows.

The ESI source temperature was optimized for maximum sensitivity of all analytes. With this method, trisubstituted HAAs are more susceptible to source temperature changes, and the best sensitivity was achieved at the minimum temperature needed for desolvation in the electrospray interface.

Matrix Diversion

The IonPac AS24 column manual contains a procedure for setting the correct matrix diversion window times and method parameters.

Internal Standards and Calibration

As is common, the ratios of peak areas for analytes and internal standards versus analyte concentration are used to produce the calibration plots. Internal standards were chosen that elute in each of the three sections of the gradient method due to changes in the background and eluent composition over the course of the run. Several choices for Multiple Reaction Monitoring (MRM) transitions were available due to the presence of Cl and Br isotopes. MCAA-2-13C (m/z 94 > 35), MBAA-1-13C (m/z 138 > 79), DCAA-2-13C¹ (m/z 128 > 84), and TCAA-2-13C¹³C (m/z 162 > 118) were chosen because they exhibited low background and good sensitivity. Other choices may be appropriate depending on sample matrix.

Referring to Figure 1, Period 1 uses 7 mM KOH eluent and the analytes are MCAA and MBAA. Chloride elutes at the end of this region, so a matrix diversion window separates this first section of the gradient from the second section. The brominated acetic acids—especially MBAA—are known to be susceptible to decomposition at elevated temperature and pH, so stable-labeled MBAA-1-13C is used for accurate tracking of the MBAA analyte. MCAA-2-13C is also used as an internal standard in the first section of the chromatogram for the quantification of MCAA. The stable-labeled internal standard for Period 2 of the gradient is DCAA-2-13C. In this section, the KOH concentration ramps to 18 mM and the analytes are the dihaloacetic acids, including DCAA, BCAA, and DBAA. Period 2 ends with the diversion of sulfate, nitrate, bromide, and bicarbonate to waste. The concentration of KOH eluent is increased to 60 mM in Period 3 of the gradient and the trihaloacetic acids TCAA, BDCAA, DBCAA and TBAA elute. The internal standard for this section is TCAA-2-13C.

The system was calibrated using a mixture of nine haloacetic acids at levels of 0.25, 1.0, 2.5, 5.0, 10.0, and 20.0 $\mu\text{g/L}$, with the four isotopically labeled internal standards at 3.0 $\mu\text{g/L}$ added to each sample and standard. A relative response ratio was generated to produce the calibration plots. A linear fit was used with 1/x weighting. Correlation coefficients in deionized water were 0.998 or better

Precursor and Product Ions

Precursor ions are generally the result of deprotonation (M-H)⁻ of the organic acid. Because the target species all have halide substituents, there are multiple choices for possible transitions. The specific transitions are: MCAA (92.9 > 34.9), MBAA (137 > 78.8), DCAA (127 > 82.9), BCAA (170.8 > 78.7), DBAA (214.7 > 170.7), TCAA (161 > 116.9), BDCAA (207 > 81 or 79 > 79), CDBAA (207 > 78.8), and TBAA (250.7 > 78.8). The trivalent compounds BDCAA and CDBAA are difficult to optimize, and BDCAA often fragments to m/z 79 in Q1, so the best sensitivity can usually be found at 79 > 79, although other transitions can be used if they provide adequate sensitivity. The MS/MS voltages are relatively low, suggesting the general fragility of these analytes. Tables 1–5 provide working conditions for five different mass spectrometers tested with this method.

Analytical Results

Table 6 shows linearity in deionized water and a matrix composed of 250 mg/L chloride, 250 mg/L sulfate, 30 mg/L nitrate, and 150 mg/L bicarbonate. The fitting method was linear with 1/x weighting using Analyst software. At the maximum matrix concentrations (250 mg/L chloride, 250 mg/L sulfate, 150 mg/L bicarbonate and 30 mg/L nitrate) linear range is 0.5–10 $\mu\text{g/L}$ with $r^2 = 0.997$ or better. Minimum detection limits (MDLs) were calculated using the Student's *t*-test calculation with seven injections. The MDL values were 0.1–1.0 $\mu\text{g/L}$ for the nine HAAs in the high-level matrix. DCAA showed the highest sensitivity, and the trivalent mixed acids BDCAA and CDBAA showed the least sensitivity.

Calibration check standards (CCS) were placed in each sequence at approximately every 10 sample injections at levels of 0.5 and 5.0 $\mu\text{g/L}$, and at the end of every sequence. The recovery of each CCS was 95–105% in every instance. In addition, the sample was spiked with 2.5 $\mu\text{g/L}$ of the native calibration mixture to calculate percent recovery.

Figure 3 shows the extracted ion currents for Periods 1 and 2, and Figure 4 shows the extracted ion current for Period 3 from a water sample with high-ionic strength. This sample is from within the pressure zone of a southwest public water utility whose source is primarily surface water. The chloride concentration of the sample was 170 mg/L and the sulfate concentration was 215 mg/L. Concentrations were determined by

ion chromatography, and the sample was not diluted before analysis. The monosubstituted and disubstituted halogenated analytes found in Period 1 and 2 are: MCAA (1.2 $\mu\text{g/L}$), MBAA (0.8 $\mu\text{g/L}$), DCAA (6.1 $\mu\text{g/L}$), BCAA (5.8 $\mu\text{g/L}$), and DBAA (2.9 $\mu\text{g/L}$). Figure 4 includes the trisubstituted HAAs for the sample. The analytes found in this sample are: TCAA (1.6 $\mu\text{g/L}$), BDCAA (4.3 $\mu\text{g/L}$), CDBAA (3.8 $\mu\text{g/L}$), and TBAA (0.7 $\mu\text{g/L}$) (See Table 7). These chromatograms were processed using Gaussian smoothing for 10 cycles. Some analytes can be found at several MRM transitions. Analytes that are seen on two MRM transitions used in the method are indicated with arrows. These results were compared to amounts quantified using Method 552.2 and amounts range from 65–130% of that method. (See Table 8).

Figure 4B shows the brominated species in the sample which experienced some degradation in Q1. An unidentified brominated compound elutes just prior to TCAA in the sample; this explains the sharp front on the TCAA peak. The 251 > 79 transition is the most sensitive for quantification of CDBAA, although, with optimized tuning, monitoring mass 79 (79 > 79) and transition m/z 207 > 81 was useful. The m/z 207 ion is the nominal mass for BDCAA and the decarboxylated CDBAA. As the number of bromide substitutions increases, the parent ion becomes less stable. The MRM for TBAA is m/z 251 > 79 where the m/z 251 ion is the result of decarboxylation of the parent ion. With the isotopes and the presence of the multiple halogens, there are several possibilities for MRM transitions.

Table 6. Linearity and MDL in Deionized Water and Matrix

Analyte	ISTD 5 $\mu\text{g/L}$	R ² (Calibration Range 0.250-20 $\mu\text{g/L}$) DIW/Matrix	MDL $\mu\text{g/L}/\%RSD$ (n=7, 1 $\mu\text{g/L}$)	DI water MDL $\mu\text{g/L}/\%RSD$ (n=7, 1 $\mu\text{g/L}$) In Matrix
MCAA	MCAA-1-13C	0.9997/0.9989	0.51/3.5	0.44/14.7
MBAA	MBAA-1-13C	0.9999/0.9990	0.08/3.6	0.13/4.2
DCAA	DCAA-2-13C	0.9999/0.9991	0.39/2.0	0.10/3.3
BCAA	DCAA-2-13C	0.9999/0.9992	0.20/0.8	0.10/0.8
DBAA	DCAA-2-13C	0.9999/0.9993	0.16/5.5	0.33/10.8
TCAA	TCAA-2-13C	0.9999/0.9993	0.24/0.5	0.09/0.3
BDCAA	TCAA-2-13C	0.9991/0.9991	0.26/5.0	0.64/18.9
CDBAA	TCAA-2-13C	0.9992/0.9994	0.38/5.5	0.52/16.4
TBAA	TCAA-2-13C	0.9994/0.9998	0.26/9.2	0.36/9.9

Table 7. Summary of IC-ESI-MS/MS Analytical Results for Real Samples										
Sample	Cl ⁻ -SO ₄ ²⁻ (mg/L)	MCAA IC/MSMS (µg/L) %Spike Rec	MBAA IC/MSMS (µg/L) %Spike Rec	DCAA IC/MSMS (µg/L) %Spike Rec	BCAA IC/MSMS (µg/L) %Spike Rec	DBAA IC/MSMS (µg/L) %Spike Rec	TCAA IC/MSMS (µg/L) %Spike Rec	BDCAA* IC/MSMS (µg/L) %Spike Rec	CDBAA IC/MSMS (µg/L) %Spike Rec	TBAA IC/MSMS (µg/L) %Spike Rec
Treated Reservoir Water	163 243	1.11 93%	1.08 103%	15.1 72%	8.5 76%	3.72 84%	5.85 80%	7.13 104%	4.75 92%	1.07 106%
Sample M	93 237	2.31 118%	1.16 106%	15.0 56%	9.4 65%	4.40 80%	6.2 70%	7.49 99%	5.12 72%	1.19 125%
Sample O	170 215	1.21 116%	0.82 105%	6.11 96%	5.83 94%	2.93 98%	1.59 91%	4.27 92%	3.85 100%	0.76 95%

Table 8. Summary of Method 552.2 Results for Real Samples										
Sample	Cl ⁻ -SO ₄ ²⁻ (mg/L)	MCAA (µg/L) 552.2 %Rec	MBAA (µg/L) 552.2 %Rec	DCAA (µg/L) 552.2 %Rec	BCAA (µg/L) 552.2 %Rec	DBAA (µg/L) 552.2 %Rec	TCAA (µg/L) 552.2 %Rec	BDCAA (µg/L) 552.2 %Rec	CDBAA (µg/L) 552.2 %Rec	TBAA (µg/L) 552.2 %Rec
Treated Reservoir Water	163 243	1.31 85%	0.95 113%	17.33 87%	10.53 81%	4.74 78%	7.81 75%	7.75 104%	6.39 74%	Na
Sample M	93 237	2.12 109%	0.89 130%	16.33 92%	9.86 95%	4.44 100%	7.09 87%	7.03 106%	6.03 85%	Na
Sample O	170 215	1.33 91%	0.64 128%	6.23 98%	6.54 89%	3.43 85%	2.24 71%	4.32 99%	5.95 65%	Na

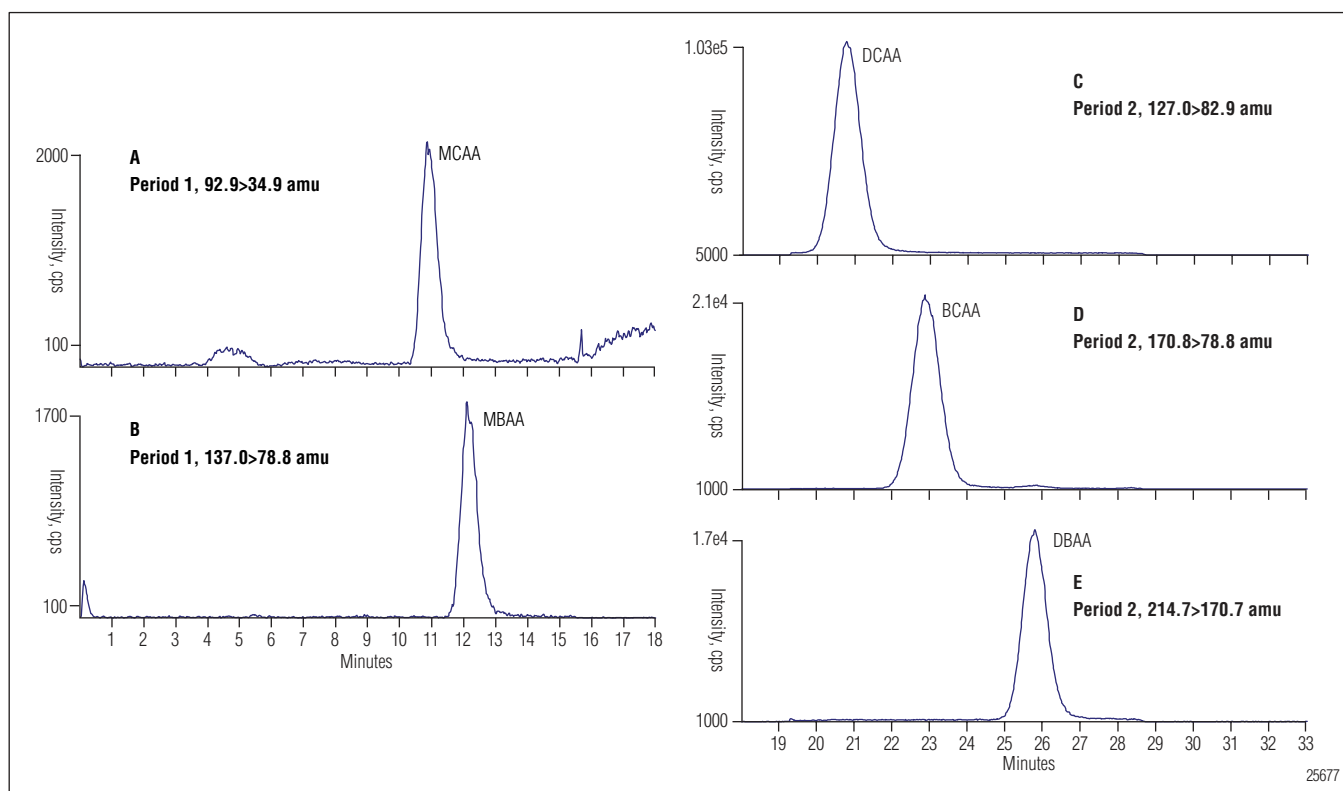


Figure 3. Extracted ion currents for Periods 1 and 2 for the treated water reservoir sample. A, monochloroacetic acid, 1.2 µg/L found; B, monobromoacetic acid, 0.82 µg/L found; C, dichloroacetic acid, 6.1 µg/L found; D, bromochloroacetic acid, 5.8 µg/L found; E, dibromoacetic acid, 2.9 µg/L found. MRMs are as indicated. For conditions, see Figure 1.

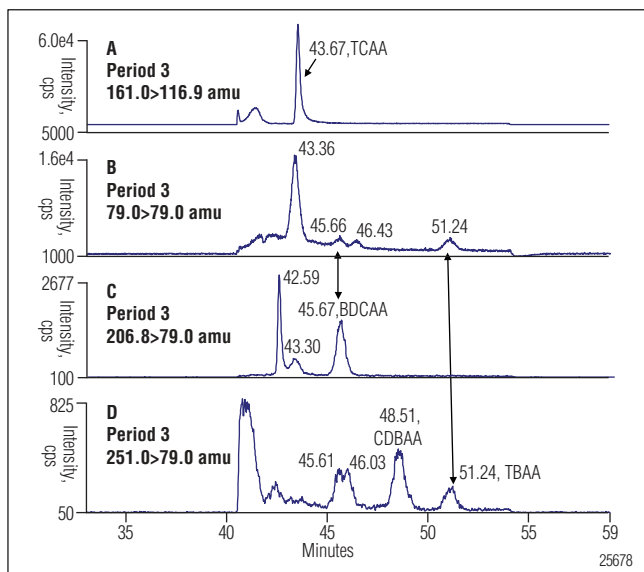


Figure 4 shows the extracted ion chromatograms for the indicated transitions of a water sample with high-ionic strength. A, 1.6 $\mu\text{g/L}$ trichloroacetic acid found; B, bromide fragments; C, 4.3 $\mu\text{g/L}$ bromodichloroacetic acid found; D, 3.8 $\mu\text{g/L}$ chlorodibromoacetic acid and 0.7 $\mu\text{g/L}$ tribromoacetic acid found

Conclusion

This application note describes a method for the determination of haloacetic acids without sample preparation. Using IC-MS/MS with the RFIC™ system and matrix diversion, this method provides sub- $\mu\text{g/L}$ level detection of nine haloacetic acid compounds with direct injection of a sample with high-ionic strength. The parameters used in this method were used in the development of EPA method 557 for determination of haloacetic acids, bromide, and Dalapon, a general-use pesticide.

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