The Determination of Haloacetic Acids in Real World Samples using IC–ESI-MS–MS

Rosanne Slingsby*, **Charanjit Saini,** and **Christopher Pohl**
Dionex Corp., R&D

Abstract

This paper presents the determination of nine haloacetic acids (HAAs) in high ionic strength, treated effluent waters using an ion chromatography–electrospray ionization-tandem mass spectrometry (IC–ESI-MS–MS) method with internal standards and discussions of each of the method parameters. Data is also provided for these same samples using USEPA Method 552.2. The sample matrices contain up to 170 mg/L chloride and 243 mg/L sulfate. Matrix ions are separated from the analytes using a high capacity anion exchange analytical column and diverted to a waste stream during each analysis to avoid signal suppression and contamination of the detector. No derivatization, offline matrix elimination, or preconcentration is used. Four isotopically-labeled HAAs are used for quantification, and detection limits are in the range of 400–1000 µg/L with R^2 of at least 0.997 over two orders of magnitude for all analytes in matrix. A trichloroacetic acid (TCAA) internal standard with the label on the alpha carbon is found to be more stable than the TCAA-1-^{13}C. Amounts found using IC–MS–MS are 65–130% of amounts found using Method 552.2 for all analytes in the real world treated effluent waters. Detection limits for all nine analytes in matrix are in the range of 100–700 ng/L.

Introduction

Haloacetic acids (HAAs) occur in drinking water as a result of the reaction between chlorine and natural organic material such as humic and fulvic acids during the disinfection process (1,2). When bromide is present in the water, bromoacetic acids and mixed chloro- and bromo-acetic acids can also be found. The iodoacids are much less stable and are usually not included in general analytical methods for haloacetic acids. HAAs have been linked to possible health threats to humans. Monitoring in the U.S. for HAA5, 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 (3), Dec. 16, 1998, with a Contamination Level set at 60 µg/L. Stage II DBP Rule, Jan. 4, 2006, maintained the MCL but also instituted minimum reporting limit requirements of 2 µg/L for MCAA and 1 µg/L for the other HAAs. The remaining four possible HAAs are chlorobromoacetic acid (CBAA), chlorodibromoacetic acid (CDBAA), dichlorobromoacetic acid (DCBAA), and tribromoacetic acid (TBAA), and the entire list is referred to as HAA9.

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 accomplished using a variety of analytical techniques (4). Urbansky (5) provides an early review of a variety of methodologies. USEPA Methods 552.2 and 552.3 (6) use acidic methanol derivatization followed by gas chromatography with electron capture detection. Other papers discuss ion pairing liquid chromatography (LC) (7) and capillary electrophoresis (8). Ion chromatography (IC) using preconcentration and conductivity detection (9), and IC coupled to electrospray (ESI) mass spectrometry (IC–ESI-MS and IC–ESI-MS–MS) (10,11) have been reported. Asami (12) used IC with offline sample pretreatment, external standard calibration, and MS–MS detection for a few haloacetic acids and oxyhalides and internal standard calibration for perchlorate. Bruzzoniti (13) recently discussed use of a cryptand column for the HAA separation and published a table summarizing the existing IC methods for HAAs. Aside from the AS24 column method, however, the methods do not adequately manage high concentrations of common matrix ions.

Stuber and Reemtsma (14) discuss the challenges of quantification using LC–ESI-MS when there are significant matrix effects and provide some guidance for using internal standards.

The work presented in this paper describes the analytical method features and general performance of this IC–ESI-MS–MS method for the determination of HAAs in matrix, using internal standards. Although mass spectrometers are usually expensive, the one chosen for this work is an adequate low-end instrument. The method addresses needs generated by complex matrices and although the overall analysis time is long, samples do not require pre-screening or pre-derivatization. The method can also be shortened if fewer targets are needed or if matrix components are known to be present at low concentration. The analytical column, the chemical properties of the HAA analytes, and the performance of internal standards

* Author to whom correspondence should be addressed.

Reproduction (photocopying) of editorial content of this journal is prohibited without publisher's permission.

are discussed. The importance of proper selection of the labeled carbon in TCAA is shown. This is the first time results from the use of this method for real world samples have been reported. A rigorous statistical comparison of data generated by this method and USEPA Method 552.2 is outside the scope of this paper. Interlaboratory validation of USEPA Method 557 is complete and is now under EPA management review.

Experimental

Instrumentation

A Dionex (Sunnyvale, CA) ICS-3000 IC system is used for this work. The system includes a DP dual pump module, a DC dual zone chromatography module including a CD conductivity detector, an AS autosampler with sample tray cooling, and an EG eluent generator. The eluent generator produces a gradient of potassium hydroxide (KOH) using deionized (DI) water from one of the DP pumps. The second DP pump is used to deliver postcolumn acetonitrile. A Dionex IonPac AS24 hydroxide-selective anion exchange analytical column (250 × 2 mm i.d., 140 µEq/column) and guard column AG24 (50 × 2 mm i.d.) are used for all separations. Electrolytic suppression of the eluent is accomplished with a Dionex ASRS 300 suppressor. DI water from a pressurized reservoir delivers water for electrolytic generation of eluent and suppressor regenerant. Chromatography conditions are provided in Table I.

An ABI-Sciex (Toronto, Canada) API2000 triple quadrupole mass spectrometer with an electrospray interface is coupled to the effluent from the IC after a mixing tee that combines the analytical stream and acetonitrile solvent. Dionex DCMS Link 2.0 software is used to integrate Dionex Chromeleon software (version 6.8) with ABI Sciex Analyst software (version 1.4.2). Data collection/processing and control of the mass spectrometer are accomplished using ABI Sciex Analyst 1.4.2 software. The negative polarity electrospray method is divided into three time periods to insure that the dwell time is sufficient for each analyte. The three time periods are indicated in Figure 1.

Reagents and procedures

Sodium chloride, sodium sulfate, sodium carbonate, and sodium nitrate salts used to prepare stock matrix solutions are all analytical reagent-grade (EM Science, Gibbstown, NJ). All DI water is 18 M-ohm from a Milli-Q system (Millipore, Bedford, MA). Acetonitrile is HPLC grade B&J Brand (Burdick & Jackson, Muskegon, MI) A custom mix standard (1000 µg/mL) of the nine native haloacetic acids, MCAA, MBAA, DCAA, TCAA, DBAA, CBAA, CDBAA, DCBAA, TBAA, is purchased from Ultra Scientific (No. Kingstown, RI, 1000 µg/mL) or Restek (Bellefonte, PA). The internal standards are MCAA-2-^{13}C (1000 µg/mL, Dionex), MBAA-1-^{13}C (1000 µg/mL, Dionex), DCAA-2-^{13}C (1000 µg/mL, Dionex), and TCAA-2-^{13}C (1000 µg/mL, Dionex). These standards are all in methyl t-butyl ether (MtBE). A working standard mixture of the four internal standards is prepared in DI water. All standard solutions are 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, not more than ~0.5% of MtBE is added when making the mixtures, relative to the total water volume.

Table I. Chromatography Conditions*

KOH gradient	Time (Min)	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; matrix diversion (min): 17–22 and 33–41; sample volume: 100 µL loop; column compartment temperature: 15°C; autosampler temperature: 8°C; detection compartment temperature: 30°C; and Column: IonPac AS24 250 × 2 mm I.d., AG24 50 × 2 mm

Results and Discussion

Separation

One of the main features of this method is the ability to quantify the HAA9 in the presence of high ionic matrix. In this work, we initially tried the hydroxide selective anion exchange IonPac AS20 column (250 × 2 mm i.d., 78 µEq/column). We found reduced peak height, lower peak efficiencies, and shifting retention times when the matrix composition was approximately 100 mg/L chloride and sulfate. The IonPac AS24 column (250 × 2 mm i.d., 140 µEq/column) has approximately twice the anion exchange capacity as the AS20 (15) but very similar selectivity. The high anion exchange capacity is necessary for this HAA 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 ion exchange capacity of the column ensures that the ion exchange sites are not consumed with matrix ions during the

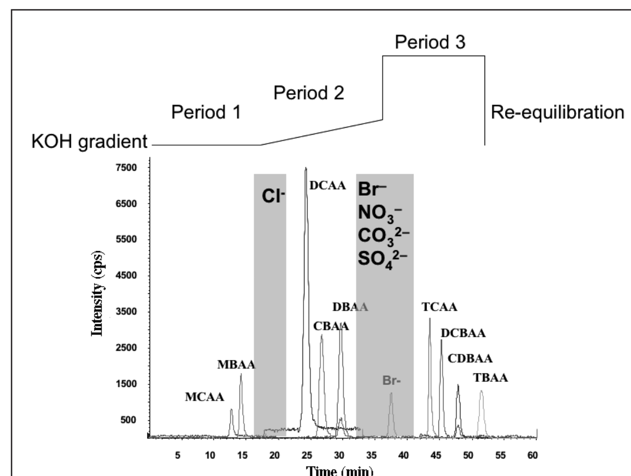

Figure 1. Chromatogram produced by method conditions shown in Table I. The shaded areas show the time windows for matrix diversion to waste and the matrix ions that elute in those windows. The time windows for data collection in periods 1, 2, and 3 are indicated.

separation. Retention time shifts using the AS24 column and this high matrix range from –0.76% for MCAA to –1.2% for TCAA. Peak efficiency in the high matrix for MCAA is 96% of that found in DI water matrix. Figure 1 shows the 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 3-way valve before they can enter the mass spectrometer.

Solvent addition

We found that addition of acetonitrile after the IC suppressor and before the ESI inlet improves sensitivity 3–10× depending on the analyte. We tested various proportions of premixed acetonitrile and water as well as various flow rate combinations with the analytical flow set at 0.3 mL/min. We found that 0.3 mL/min of 100% acetonitrile gave the best signal-to-noise for the HAAs in this method using the API2000 mass spectrometer and is compatible with the desolvation capabilities of the API2000. Optimization of the solvent was conducted by varying concentration and flow-rate during several standard runs and comparing results.

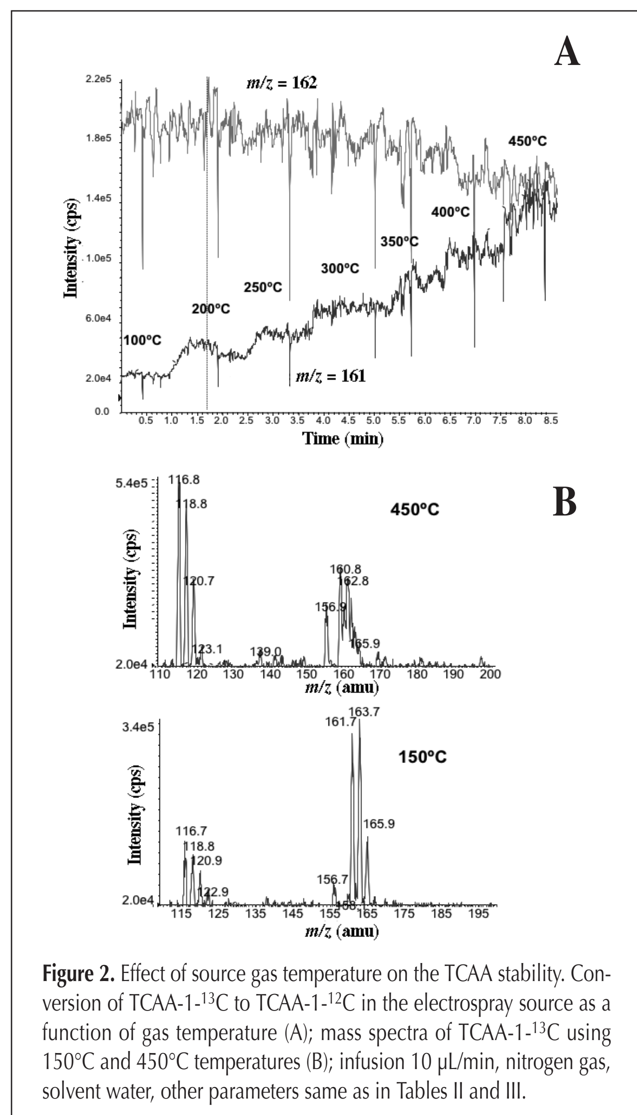

Figure 2. Effect of source gas temperature on the TCAA stability. Conversion of TCAA-1-^{13}C to TCAA-1-^{12}C in the electrospray source as a function of gas temperature (A); mass spectra of TCAA-1-^{13}C using 150°C and 450°C temperatures (B); infusion 10 µL/min, nitrogen gas, solvent water, other parameters same as in Tables II and III.

Temperature

In order to set the times for the matrix diversion windows, we found that it is important to define a definite method temperature because the retention times for the HAAs increase with increasing column temperature. As an example, retention time of MBAA increases 25% using a column compartment temperature of 35°C compared to 15°C. For hydrophobic ions such as HAAs, a decrease in hydration at higher temperatures increases the level of hydrophobic interaction (because both the ion exchange material and the ion are less hydrated), which increases retention. The changes in retention time illustrate the need to control column compartment temperature for good retention time reproducibility. In addition, some of the HAAs, most notably the brominated species, are less stable at higher temperatures and high pH. MBAA was found to have an 85% loss in peak area using a column compartment temperature of 35°C compared to 15°C. This compares to a +6% increase for formate at the same temperatures. The other brominated species show varying losses including CBAA: 0%, DBAA: 0.5%, DCBAA: 4.2%, CDBAA: 25%, and TBAA: 84%. Using the internal standards, the ratio of peak areas for analyte to internal standard is 98% at the same temperature comparison. This data indicates that degradation is minimized at low column compartment temperature and quantification should be accomplished using internal standards. We set the autosampler temperature to 8°C and the column compartment temperature to 15°C in order to maximum analyte and internal standard stability and maximize retention time reproducibility.

The ESI source temperature was optimized for maximum sensitivity of all analytes by running several methods with different temperatures. We found that the tri-substituted HAAs are more susceptible to source temperature and better sensitivity is achieved at the lower end of the necessary range for desolvation in the electrospray interface.

Internal standards

Overall we tested five stable-labeled ^{13}C-HAAs in order to assess their appropriateness as internal standards in this method. As is common, the ratios of peak areas for the analytes and internal standards versus analyte concentration were used to produce the calibration plots. We chose internal standards that elute in each of the three sections of the gradient method because the composition of the background changes over the course of the run. There are several choices for multiple reaction monitoring (MRM) transitions available due to the presence of Cl and Br isotopes. We chose MCAA-2-^{13}C mass-to-charge (*m/z* 94 > *m/z* 35), MBAA-1-^{13}C (*m/z* 138 > *m/z* 79), DCAA-2-^{13}C (*m/z* 128 > *m/z* 84), and TCAA-2-^{13}C (*m/z* 162 > *m/z* 118) because they exhibit low background and good sensitivity and are available. Other transitions may be appropriate, depending on sample matrix and the exact source characteristics of the particular mass spectrometer model.

Referring to Figure 1, period 1 uses 7 mM KOH eluent and the analytes are MCAA and MBAA. Chloride elutes at the end of period 1, so a matrix diversion window separates this first period of the gradient from the second period. The brominated acetic acids, especially MBAA, are known to be susceptible to de-

composition at elevated temperature and pH so the use of the stable-labeled MBAA-1-^{13}C is used for accurate tracking of the MBAA analyte. Because the MBAA is less stable than MCAA, MCAA-2-^{13}C is also used as an internal standard in the first period of the chromatogram for the quantification of MCAA. The stable-labeled internal standard for period 2 of the gradient is DCAA-2-^{13}C. In this section, the KOH concentration ramps to 18 mM, and the analytes are the dihaloacetic acids including DCAA, CBAA, 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, DCBAA, CDBAA, and TBAA elute. The internal standard for this section is TCAA-2-^{13}C.

We originally tested TCAA-1-^{13}C but found that the 1-^{13}C substituted molecule is unstable and converts to the TCAA-^{12}C form, probably through an intermediate with $^{12}CO_2$ present in the interface (16). This reaction is dependent on the temperature of the interface. Figure 2A shows the *m/z* 162 channel and *m/z* 161 channel at interface temperatures ranging from 100°C to 450°C for TCAA-1-^{13}C. Figure 2B shows the *m/z* 162 > *m/z* 118 MRM channel, and the *m/z* 161 > *m/z* 117 MRM at 450ºC and at 150ºC for TCAA-1-^{13}C. Based on this study, we decided to replace TCAA-1-^{13}C with TCAA-2-^{13}C in the study of internal standards for this method. The TCAA-2-^{13}C does not show the exchange from *m/z* 162 to *m/z* 161 over the temperature range of 15ºC to 450ºC. We also studied the stability of MBAA-1-^{13}C over the temperature range of 100ºC to 475ºC using flow injection techniques. We find that the ratio of MBAA-^{12}C to MBAA-^{13}C over this temperature range is stable with variations at less 1.2%.

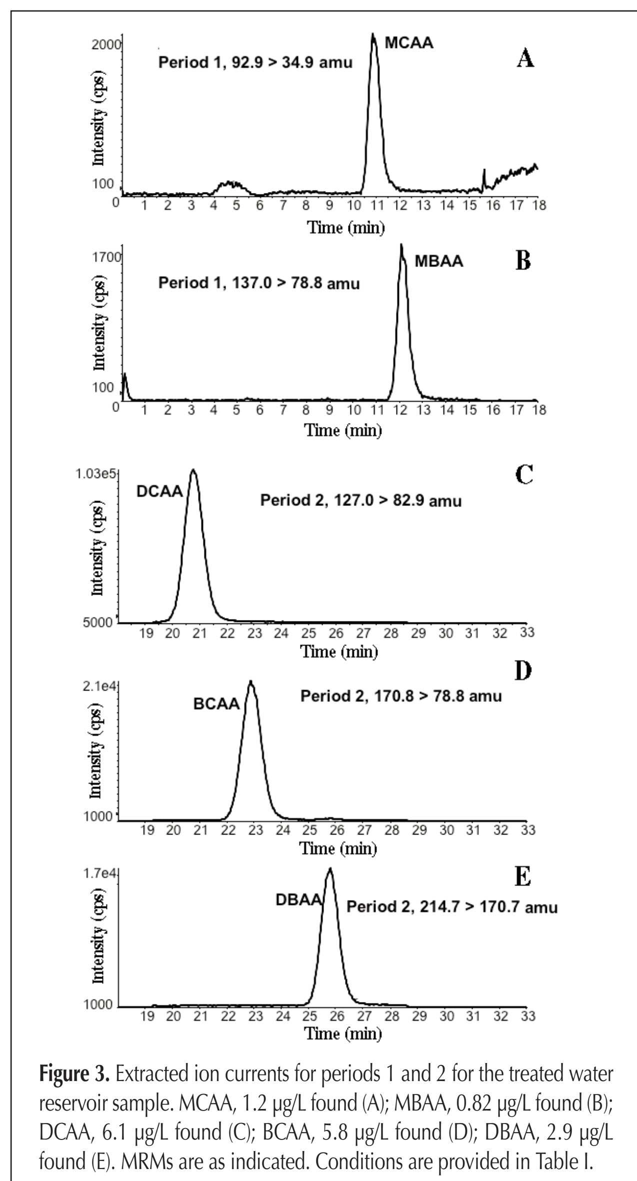

Figure 3. Extracted ion currents for periods 1 and 2 for the treated water reservoir sample. MCAA, 1.2 µg/L found (A); MBAA, 0.82 µg/L found (B); DCAA, 6.1 µg/L found (C); BCAA, 5.8 µg/L found (D); DBAA, 2.9 µg/L found (E). MRMs are as indicated. Conditions are provided in Table I.

Calibration

The system is calibrated using a mixture of nine HAAs at 0.250, 1.0, 2.5, 5.0, 10.0, and 20.0 µg/L with the four isotopically labeled internal standards at 3.0 µg/L added to each sample in DI water or a synthetic ionic matrix. A relative response ratio is generated to produce the calibration plots. We use linear with 1/*x* weighting fits. Correlation coefficients in DI water are at least 0.998. In a future paper, we intend to study these calibrations using weight least squares as necessary to more fully understand the behavior of the cross-calibrations between the five analytes that do not have their own internal standards and close-eluting internal standards.

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 and each was checked for sensitivity. The specific transitions are MCAA (*m/z* 92.9 > *m/z* 34.9), MBAA (*m/z* 137 > *m/z* 78.8), DCAA (*m/z* 127 > *m/z* 82.9), CBAA (*m/z* 170.8 > *m/z* 78.7), DBAA (*m/z* 214.7 > *m/z* 170.7), TCAA (*m/z* 161 > *m/z* 116.9), DCBAA (*m/z* 207 > *m/z* 81 or *m/z* 79 > *m/z* 79), CDBAA (*m/z* 207 > *m/z* 78.8), and TBAA (*m/z* 250.7 > *m/z* 78.8). The trivalent DCBAA and CDBAA are particularly difficult to optimize, and DCBAA often fragments to *m/z* 79 in Q1 so that the best sensitivity can be found at *m/z* 79 > *m/z* 79. Overall, the MS–MS voltages are fairly low, suggesting a general fragility of these analytes. Other parameters include curtain (20 psi), Gas 1 and Gas 2 (50 psi), CAD gas (2 in period 1 and 4 in periods 2 and 3), ionspray voltage (–4500 V), and temperature (475°C).

Analytical results

Table II shows linearity in DI water and a matrix comprised of 250 mg/L chloride, 250 mg/L sulfate, 30 mg/L nitrate, and 150 mg/L bicarbonate. The fitting method is linear with 1/*x* weighting using the Analyst software. We found that at the maximum matrix concentrations, namely a total of 250 mg/L chloride, 250 mg/L sulfate, 150 mg/L bicarbonate ,and 30 mg/L nitrate, the linear range is 0.5–10 µg/L with r^2 = 0.997 or better. The reproducibility on duplicates was 98% or better for all analytes in samples. Minimum detection limits were calculated using the Student's t-test calculation with seven injections. The MDL values were 0.1–1.0 µg/L for the nine HAAs in the high matrix. DCAA showed the best sensitivity and the trivalent mixed acids DCBAA and CDBAA showed the least sensitivity.

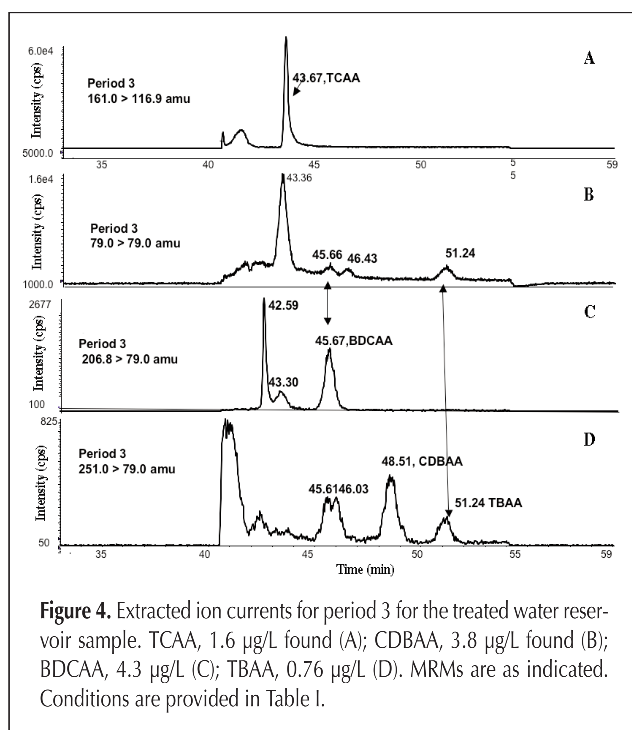

Figure 4. Extracted ion currents for period 3 for the treated water reservoir sample. TCAA, 1.6 µg/L found (A); CDBAA, 3.8 µg/L found (B); BDCAA, 4.3 µg/L (C); TBAA, 0.76 µg/L (D). MRMs are as indicated. Conditions are provided in Table I.

Quality Control (QC) standards were placed in each sequence at approximately every 10 sample injections at the 0.5 and 5.0 µg/L levels and at the end of every sequence. The recovery of the each QC standard was 95–105% in every instance. Each sample was spiked with 2.5 µg/L of the native calibration mixture in order to calculate the % recovery.

Three real world drinking water samples (Treated Reservoir Water, M, and O) with fairly high ionic strengths were analyzed for chloride and sulfate, and the nine HAAs after they were tested at the water treatment facility using US EPA Method 552.2. These samples came from within the pressure zone of a southwest public water utility whose water source is primarily surface water. Chloride and sulfate concentrations were determined in all samples using IC. Recovery spikes at the 2.5 µg/L level were also analyzed. Spikes using the native standard mixture were made into each sample. Samples were not diluted before analysis. The three periods for data collection and the matrix diversion windows are as noted in Table I. Figure 3 shows the EIC for periods 1 and 2 from Sample O, which is representative of the sample set. These are the monosubstituted and disubstituted halogenated analytes. Figure 4 includes the tri-substituted HAAs for Sample O and is fairly complex. These chromatograms were smoothed 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. Of the trisubstituted acids, only TCAA is included in the HAA5 list by the EPA.

Table III provides the calculated amounts of each analyte as determined using the IC–ESI-MS–MS method in our lab. The % recovery in Table III was calculated as (total found / amount found + spike amount) × 100. The data using Method 552.2 at the source lab is provided in Table IV. The % recovery data in Table IV is the calculation (amount found by IC–ESI-MS–MS / amount found using Method 552.2) × 100 and are in the range of 70–130% for most determinations. The exception is the

Table II. Linearity and MDL in DI Water and Matrix

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

Table III. Summary of IC–ESI-MS–MS Analytical Results for Real World Samples

Sample	$Cl^{-}SO_4^{2}$ (mg/L)	MCAA IC–MS–MS (µg/L) %Spike rec	MBAA IC–MS–MS (µg/L) %Spike rec	DCAA IC–MS–MS (µg/L) %Spike rec	BCAA IC–MS–MS (µg/L) %Spike rec	DBAA IC–MS–MS (µg/L) %Spike rec	TCAA IC–MS–MS (µg/L) %Spike rec	BDCAA IC–MS–MS (µg/L) %Spike rec	CDBAA IC–MS–MS (µg/L) %Spike rec	TBAA IC–MS–MS (µg/L) %Spike rec
Treated reservoir water										
	163	1.11	1.08	15.1	8.5	3.72	5.85	7.13	4.75	1.07
	243	93%	103%	72%	76%	84%	80%	104%	92%	106%
Sample M										
	93	2.31	1.16	15.0	9.4	4.40	6.2	7.49	5.12	1.19
	237	118%	106%	56%	65%	80%	70%	99%	72%	125%
Sample O										
	170	1.2	0.82	6.11	5.83	2.93	1.59	4.27	3.85	0.76
	2151	116%	105%	96%	94%	98%	91%	92%	100%	95%

Table IV. Summary of Method 552.2 Results for Real World 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 water reservoir										
	163	1.31	0.95	17.33	10.53	4.7	7.81	7.75	6.39	NF
	243	85%	113%	87%	81%4	78%	75%	104%	74%	
Sample M										
	93	2.12	0.89	16.33	9.86	4.44	7.09	7.03	6.03	NF
	237	109%	130%	92%	95%	100%	87%	106%	85%	
Sample O										
	170	1.33	0.64	6.23	6.54	3.43	2.24	4.32	5.95	NF
	215	91%	128%	98%	89%	85%	71%	99%	65%	

65% recovery for CDBAA in Sample O. Method 552.2 did not report TBAA values for the three samples. The relative standard deviation (RSD) data is the average of two days of seven injections per day. More exhaustive statistical analysis is the subject of another paper.

In Figure 4B, the EIC of *m/z* 79 > *m/z* 79 shows species producing bromide in Q1 from Sample O in period 3. This channel can be the most sensitive for quantification of CDBAA, although with optimized tuning, the Q1 fragmentation is minimized and other transitions including *m/z* 207 > *m/z* 81 and *m/z* 251 > *m/z* 79 can be useful. The *m/z* 207 ion is the nominal mass for DCBAA and the decarboxylated CDBAA. The MRM for TBAA is *m/z* 251 > *m/z* 79, where the *m/z* 251 ion is the result of decarboxylation of the parent ion. There is also some bromide showing at the *m/z* 79 > *m/z* 79 channel which affects the amount found of TBAA at *m/z* 251 > *m/z* 79. In general, as the number of bromide substitutions increases, the parent ion becomes less stable. There is an unknown brominated compound that elutes just prior to TCAA in Sample O that explains the sharp front on the TCAA peak. This probably is the source of the somewhat lower TCAA determination for TCAA in this sample, at 71% of the Method 552.2 value as shown in Table III. Despite the fragility of these analytes the quantification of the analytes as compared to the Method 552.2 results is within 65–130%.

Conclusion

IC coupled to electrospray triple quadrupole MS was applied to the determination of nine HAAs in high ionic strength real world water samples without sample pretreatment or preconcentration. The samples contained several hundred mg/L of chloride and sulfate, and the high capacity separation column allowed sufficient time for matrix cutting so that off-line sample preparation was not necessary. Quantification was produced through the use of four stable-labeled internal standards, and the results are compared with those generated using USEPA Method 552.2.

Acknowledgment

The authors wish to thank Raimund Roehl and Rida AlHorr for their valuable consultation and work on this project.

References

1. H. Weinberg. Disinfection byproducts in drinking water: the analytical challenge. *Anal. Chem. News Features* **71:** 801A–808A (1999).
2. D.A. Reckhow, P.L.S. Rees, and D. Bryan. Watershed sources of disinfection byproduct precursors. *Water Sci. Technol. Water Supply* **4:** 61–69 (2004).
3. http://www.epa.gov/OGWDW/mdbp/dbp1.html.
4. B. Paull and L. Barron. Using ion chromatography to monitor haloacetic acids in drinking water: a review of cuffent technologies. *J. Chromatogr. A* **1046:** 1–9 (2004).
5. E.T. Urbansky. Techniques and methods for the determination of haloacetic acids in potable water. *J. Environ. Monit.* **2:** 285–291 (2000).
6. http://www.epa.gov/safewater/methods/pdfs/met552_3.pdf.
7. R. Loos and D. Barcelo. Determination of haloacetic acids in aqueous environments by solid-phase extraction followed by ion-pair liquid chromatography-electrospray ionization mass spectrometric detection. *J. Chromatogr. A* **938:** 45–55 (2001).
8. D. Martinez, F. Borrull, and M. Caull. Comparative study of a solid-phase extraction system coupled to capillary electrophoresis in the determination of haloacetic compounds in tap water. *J. Chromatogr. A* **827:** 105–112 (1998).
9. Y. Sun and P. Gu. Determination of haloacetic acids in hospital effluent after chlorination by ion chromatography. *J. Environ. Sci.* **19:** 885–891 (2007).
10. R. Roehl, R. Slingsby, N. Avdalovic, and P.E. Jackson. Applications of ion chromatography with electrospray mass spectrometric detection to the determination of environmental contaminants in water. *J. Chromatogr. A* **956:** 245–254 (2002).
11. L. Barron and B. Paull. Simultaneous determination of trace oxyhalides and haloacetic acids using suppressed ion chromatography-electrospray mass spectrometry. *Talanta* **69:** 621–630 (2006).
12. M. Asami, K. Kosaka, Y. Matsuoka, and M. Kamosita. An analytical method for haloacetic acids and oxo halides using ion chromatography coupled with tandem mass spectrometry and detection of perchlorate in environmental and drinking waters. *J. Environ. Chem.* **17:** 363–375 (2007).
13. M.C. Bruzzoniti, R.M. De Carlo, K. Horvath, D. Perrachon, A. Prelle, R. Tofalvi, C. Sarzanini, and P. Hajos. High performance ion chromatography of haloacetic acids on macrocyclic cryptand anion exchanger. *J. Chromatogr. A* **1187:** 188–196 (2008).
14. M. Stuber and T. Reemtsma. Evaluation of three calibration methods to compensate matrix effects in environmental analysis with LC-ESI-MS. *Anal. Bioanal. Chem.* **378:** 910–916 (2004).
15. IonPac AS24 Product Manual, Dionex Corp, June 2007.
16. M. Felipe, J.D. Kubicki, and K.H. Freeman. A mechanism for carbon isotope exchange between aqueous acetic acid and CO[2]/HCO3^{-}: an ab initio study. *Org. Geochem.* **36:** 835–850 (2005).

Manuscript received September 30, 2008;
Revision received December 17, 2008.