

Measurement of Haloacetic Acids in Drinking Water by IC-MS and IC-MS/MS

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ABSTRACT

Haloacetic acids (HAAs) are among disinfection by-products (DBPs) that are produced during chlorination of water containing natural organic matter and bromide. Monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA) are known to be formed from dissolved humic matter during disinfection of water with chlorine. Bromoacetic acids and mixed bromochloroacetic acids including monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), dibromochloroacetic acid (DBCAA) and dichlorobromoacetic acid (DCBAA) may be formed by the reaction of bromide ion with MCAA. In 2005 the U.S. EPA established a maximum contamination level (MCL) of 60 µg/L for the sum of MCAA, MBAA, DCAA, DBAA, and TCAA for Stage 2 disinfectants and disinfectant by-products (Stage 2 DBPR).

Methods used to determine HAAs including EPA Methods 552.1 and 552.2 require tedious derivatization and multiple extraction steps followed by gas chromatography (GC) with electron capture detection (ECD) and mass spectrometry (MS). Ion chromatography-mass spectrometry (IC-MS and IC-MS/MS) offers a sensitive and selective alternative that does not require sample pretreatment. In this method water samples are directly injected into a Dionex ICS 3000 ion chromatography system coupled to an API 2000™ triple quadrupole mass spectrometer. The separation of all nine HAAs addressed in EPA methods is achieved on either a 2 × 250 mm or 1 × 250 mm format of a high-capacity prototype ion-exchange column using a simple hydroxide gradient. Data is collected on the API 2000 using MRM.

All nine haloacetic acids can be separated with excellent peak resolution in a matrix containing up to 250 mg/L each of chloride and sulfate and 30 mg/L of nitrate. Excellent linearity was achieved over a range between 0.4 µg/L and 50 µg/L using ¹³CCl₃COOH as the internal standard. The detection limit is less than 0.51 µg/L for the five regulated HAAs (HAA5) and less than 1 µg/L for the other four HAAs. No significant matrix effects or signal suppression were observed. Recovery of all nine HAAs is greater than 90% in a chloride, sulfate and nitrate matrix in the above concentrations with good reproducibility and robustness. Although the 2 × 250 mm column format can handle higher injection volumes than the 1 × 250 mm format due to its higher total capacity, the separation time can be significantly shortened to less than 40 min using the 1 × 250 mm column.

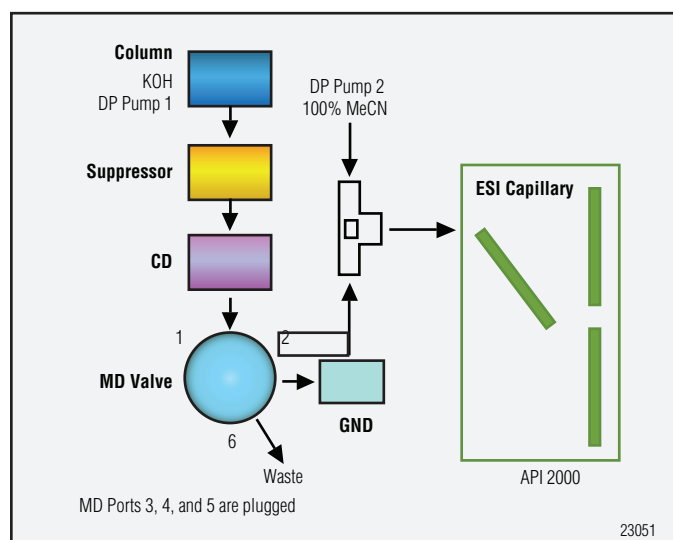
INSTRUMENTATION

Ion Chromatograph: Dionex ICS-3000 composed of AS Auto Sampler, DP Pump module, DC Detector/Chromatography module, EG Eluent Generator module

Triple Quadrupole Mass Spectrometer: MDS Sciex API 2000 Operated in MRM mode
Software: Dionex Chromeleon® DCMS Link and MDS Sciex Analyst 1.4.1

CHROMATOGRAPHIC CONDITIONS

Column: Prototype 250 × 2-mm i.d. or 250 × 1 mm i.d.
Suppressor: ASRS® MS
Eluent generator: KOH gradient; 0.3 mL/min for 2-mm i.d. column, or 0.15 mL/min for 1-mm i.d. column
Matrix diversion/postcolumn solvent addition: 100% MeCN; 0.2 mL/min for 2-mm i.d. column, or 0.25 mL/min for 1-mm i.d. column



DP Pump 1 pumps DI water through the EG Eluent generator.

KOH is generated and pumped through the column and then suppressed by the suppressor.

The suppressor is cation-exchange device which replaces the potassium ion with a hydronium ion which neutralizes the hydroxide and transforms the analytes into the acid form before they are detected by the conductivity detector (CD) and the mass spectrometer.

DP Pump 2 delivers MeCN to the MS/MS continuously; the matrix diversion valve is used to divert sample matrix to waste and then send the analytical stream to the API 2000; the analytical stream is mixed with solvent in a high-efficiency static-mixing tee before entering the API 2000.

Table 1. API 2000 Instrument Parameters for Measured Haloacetic Acids						
Analyte	MRM Transitions	DP (volts)	FP (volts)	EP (volts)	CE (volts)	CXP (volts)
Chloroacetic acid	93/35	-20	-300	-10	-14	-6
Dichloroacetic acid	127/83	-11	-350	-7	-12	-14
Bromoacetic acid	136.8/78.8	-11	-350	-7	-12	-14
Trichloroacetic acid	161/117	-6	-290	-4	-6	-8
Bromochloroacetic acid	171/79	-16	-300	-6	-28	-8
Dibromoacetic acid	215/79	-11	-340	-4.5	-12	-10
Tribromoacetic acid	250.6/79	-11	-350	-5	-32	-12
Bromodichloroacetic acid	79/79	-12	-300	-1.5	-6	-14
Dichlorobromoacetic acid	207/79	-11	-310	-5	-20	-6

All nine haloacetic acids addressed in EPA methods are measured with negative polarity using the API 2000 in the MRM mode. Table 1. shows the MRM transitions, declustering potential (DP), focusing potential (FP), entrance potential (EP), collision energy (CE) and cell exit potential (CXP) for the nine measured haloacetic acids. These values are obtained by manual optimization of the instrument. The collision gas was set at a value of 5 which corresponds to a vacuum of 2.5×10^{-5} torr.

Table 2. Recovery of MCAA Acid in the Presence of 10 ppb ¹³ C-MCAA	
MCAA Concentration (ppb)	% Recovery
0.5	97.2
1.0	95.7
4.0	103.2
8.0	98.5
12.0	99.6

Table 3. Recovery of ¹³ C-MCAA Acid in the Presence of 10 ppb MCAA	
MCAA Concentration (ppb)	% Recovery
0.5	96.4
1.0	105.6
4.0	101.1
8.0	99.2
12.0	99.1

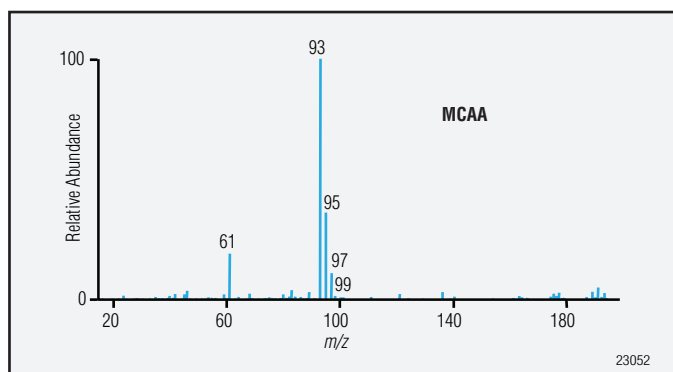


Figure 1. Mass Spectrum of monochloroacetic acid.

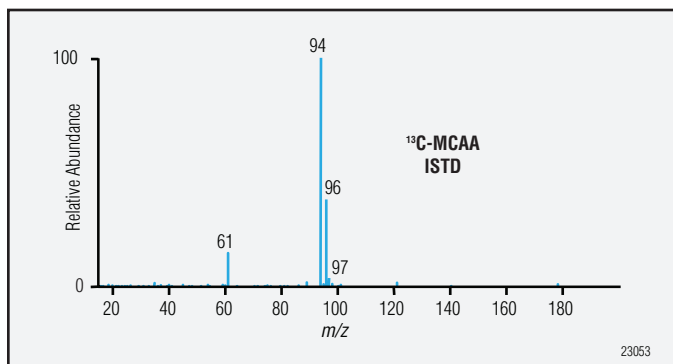


Figure 2. Mass Spectrum of ¹³C- monochloroacetic acid.

¹³C- monochloroacetic acid was used as the internal standard. The spectra of both the analyte and the internal standard are shown in Figure 1 and 2, respectively. The internal standard is monitored at MRM of 94/35 while the analyte at 93/35.

No significant signal suppression of either the analyte or the internal standard was observed due to their coelution. Table 2 shows the recovery of MCAA at different concentrations in the presence of 10 ppb of the internal standard. Table 3 shows the recovery of the internal standard at different concentrations in the presence of 10 ppb of MCAA. Neither MCAA nor the internal standard signal is affected by coelution and the recovery values are larger than 95%.

EFFECT OF MATRIX ON SEPARATION AND RECOVERY

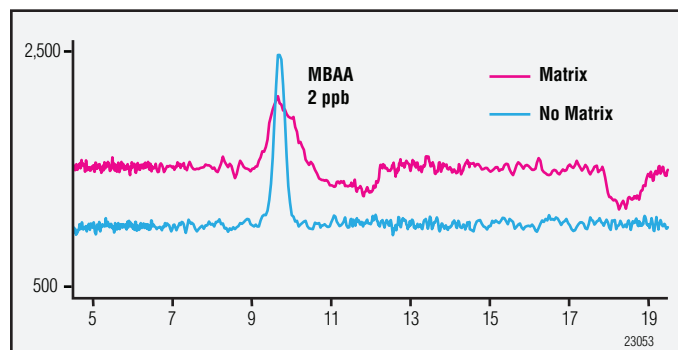


Figure 3. Effect of matrix on peak shape using Dionex IonPac® AS20 250 × 2-mm column for separation.

While the separation of haloacetic acid in DI water is acceptable on columns such as Dionex IonPac AS20 and AS19, the presence of a high matrix in the sample complicates the separation and affects both the recovery and detection limit. The nature of the problem is observed in Figure 3. The chromatograms shown provide examples of what happens to the analyte peaks, in this case monobromoacetic acid, in the presence of matrix ions.

The chromatogram shows MBAA peak in DI water and in a simulated matrix made up of 100 ppm sulfate 10 ppm nitrate 50 ppm chloride and 100 ppm ammonium chloride. In the presence of matrix, the peak gets smeared and distorted by the matrix although there is no coelution of the analyte with the matrix ions. This effect on peak shapes is more prominent at low concentration of the analytes, and has a significant effect on MDL and recovery values.

Table 4. Recovery of HAA5 in the Presence of 100 ppm Sulfate, 10 ppm Nitrate, 50 ppm Chloride and 100 ppm Ammonium Chloride Using Dionex AS20 250 × 2 mm Column for Separation

Analyte	% Recovery			
	2 ppb	4 ppb	8 ppb	16 ppb
MCAA	95.4	93.2	94.9	97.9
DCAA	86.7	76.6	95.4	103.3
MBAA	Below Det.	77.1	82.4	93.8
TCAA	Below Det.	89.9	98.8	100.9
DBAA	90.1	83.8	96.3	99.3

Table 4 shows the recovery values of HAA5 in the presence of 100 ppm sulfate, 10 ppm nitrate, 50 ppm chloride, and 100 ppm ammonium chloride. Although the matrix level is considered intermediate for drinking water, the recovery of all HAAs decreases to unacceptable levels. Also, both MBAA and TCAA become undetectable at 2.0 ppb.

Columns with significantly higher capacity are required to handle the matrix without significant effects on recovery and detection limits

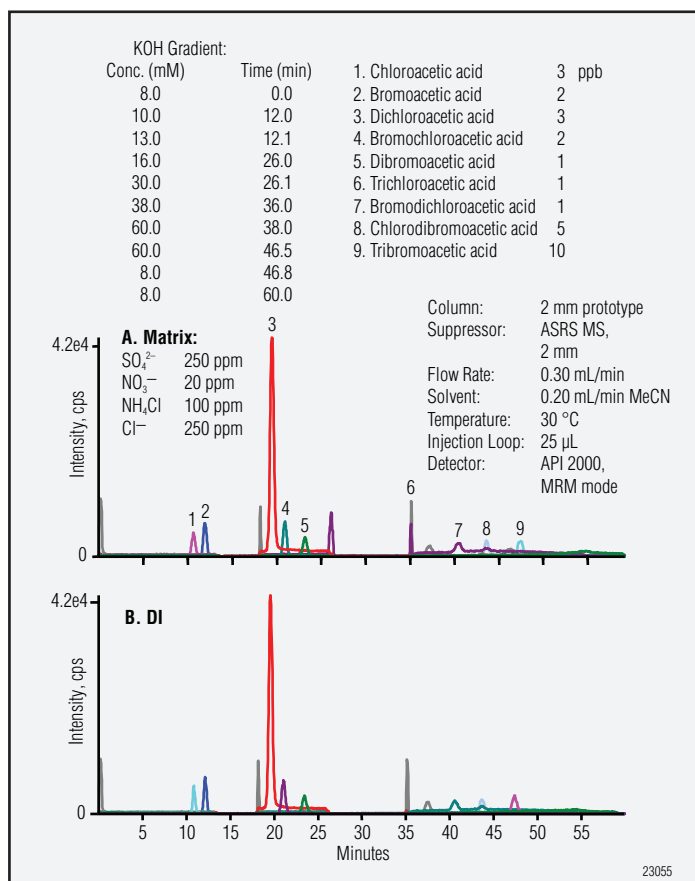


Figure 4. Separation of nine haloacetic acids in (A) simulated high matrix and (B) DI water using a 250 × 2-mm prototype column.

Figure 4A shows the separation of all nine measured haloacetic acids in the presence of 250 ppm sulfate, 20 ppm nitrate, 250 ppm chloride and 100 ppm ammonium chloride using a prototype high capacity 250 x 2 mm anion-exchange column. All nine analytes are well separated from each other and from the matrix ions. Such a matrix is considered high because 97% of U.S. drinking water has less than 250 ppm sulfate.

Figure 4B shows the same separation in DI water. Comparing both chromatograms, the matrix presence has not contributed to significant peak distortion due to the presence of a simulated matrix.

Table 5. Recovery and Shifts in Retention Times for All Nine HAAs Using a Prototype 250 × 2 mm Anion-Exchange Column

Analyte	Concentration (µg/L)	Area DI water N = 7	Area Matrix N = 7	% Recovery	R.T. (min) DI water N = 7	R.T. (min) Matrix N = 7	Shift (min)
MCAA	3	1.11E+05	1.16E+05	104.52	10.56	10.48	-0.08
MBAA	2	1.60E+05	1.72E+05	107.76	11.86	11.80	-0.06
DCAA	3	1.26E+06	1.32E+06	105.41	19.26	19.28	0.02
BCAA	2	1.93E+05	2.00E+05	103.42	20.72	20.72	0.00
DBAA	1	1.16E+05	1.20E+05	102.75	23.08	23.10	0.02
TCAA	1	9.15E+04	9.22E+04	100.72	37.16	36.70	-0.46
BDCAA	2	8.96E+04	9.13E+04	101.97	40.18	40.10	-0.08
CDBAA	5	1.48E+05	1.53E+05	103.52	43.34	43.34	0.00
TBAA	10	1.48E+05	1.55E+05	104.58	47.00	47.02	0.02

Table 5 shows the recovery values and shifts in retention time (R.T.) due to the presence of matrix at the above mentioned levels. The 250 × 2-mm column shows excellent recovery values for all measured HAAs with minimal shifts in retention time. Unlike the IonPac AS20 column, this column is able to handle significantly higher concentrations of sulfate, chloride, and nitrate in the matrix.

Due to the significantly higher capacity of this column, the analysis time is about 55 min at 0.3 mL/min. For faster analysis, a 1-mm prototype column was made so that it can be operated at a relatively faster flow velocity.

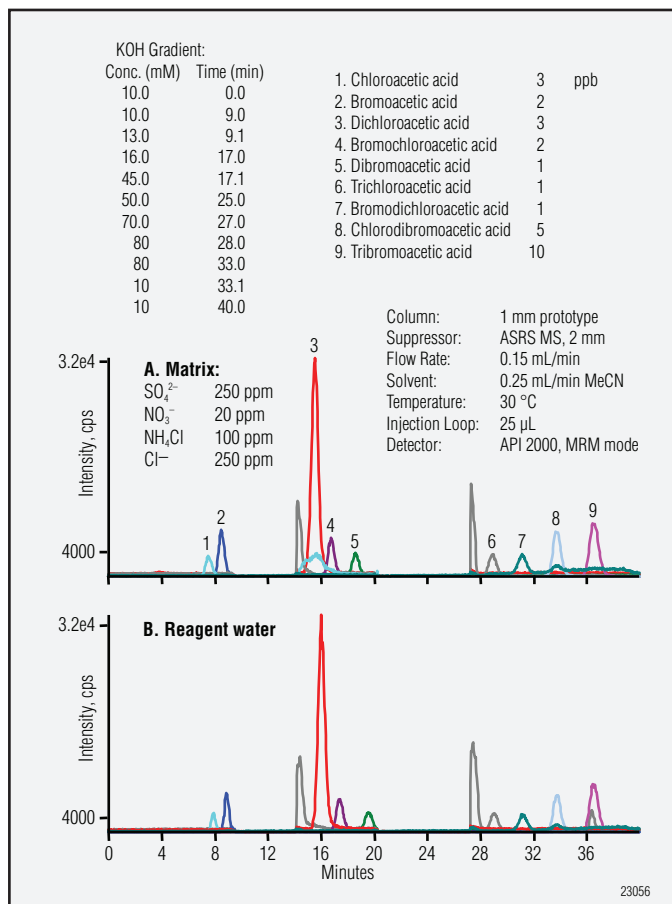


Figure 5. Separation of nine haloacetic acids in (A) simulated high matrix and (B) DI water using a 250 × 1-mm prototype column.

Table 6. Recovery and Shifts in Retention Times for All Nine HAAs Using a Prototype 250 × 1 mm Anion-Exchange Column

Analyte	Concentration (µg/L)	Area DI water N = 10	Area Matrix N = 10	% Recovery	R.T. (min) Matrix N = 7	R.T. (min) Matrix N = 7	Shift (min)
MCAA	3	9.10E+04	9.61E+04	105.58	7.68	7.35	-0.33
MBAA	2	1.61E+05	1.87E+05	116.41	8.70	8.27	-0.43
DCAA	3	1.40E+06	1.18E+06	84.30	15.90	15.27	-0.63
BCAA	2	2.04E+05	1.93E+05	94.42	17.26	16.48	-0.78
DBAA	1	1.25E+05	1.24E+05	99.36	19.47	18.22	-1.25
TCAA	1	1.41E+05	1.45E+05	103.20	28.91	28.71	-0.20
BDCAA	2	1.20E+05	1.31E+05	109.33	31.04	30.93	-0.11
CDBAA	5	2.48E+05	2.75E+05	111.06	33.60	33.50	-0.10
TBAA	10	2.15E+05	2.35E+05	109.39	36.34	36.30	-0.04

Figure 5A and 5B show the separation of all nine measured haloacetic acids in a simulated matrix (250 ppm sulfate, 20 ppm nitrate, 250 ppm chloride, and 100 ppm ammonium chloride) and in DI water, respectively, using a prototype high capacity 250 × 1-mm anion-exchange column. At an operating flow rate of 0.15 mL/min, the analysis time, including column conditioning is about 40 min, that is, about 15 min less than that required by the 250 × 2-mm column format.

Table 6 shows the effect of matrix on recovery and retention time (R.T). The 250 × 1 mm column shows excellent recovery values as well. The shifts in retention times are slightly higher than those observed with the 2 mm column format, but still within a good range.

Table 7. Method Detection Limits for Haloacetic Acids in DI Water and in Simulated Matrix		
Analyte	DI H ₂ O MDL n = 7, ng/L	*Simulated Matrix MDL n = 7, ng/L
MCAA	470	510
DCAA	80	110
MBAA	370	488
TCAA	218	286
BCAA	180	230
DBAA	146	260
DCBAA	408	433
DBCBA	365	480
TBAA	256	423

The detection limits of all nine measured haloacetic acids are shown in Table 7. The first column shows the detection limits in DI water while the second shows those in a simulated matrix made up of 250 ppm sulfate, 20 ppm nitrate, 250 ppm chloride and 100 ppm ammonium chloride.

For all measured acids, the detection limits are less than 0.51 ppb even in sample with a matrix as high as that of the simulated matrix mentioned above.

SUMMARY

- Separation of all nine haloacetic acids and bromate in high matrix concentration
- Simple: No derivatization or sample pretreatment is required, just direct injection
- Fully automated
- MS or MS/MS as a detector:
 - Low MDL: No preconcentration
 - Specific: Limited matrix interference
- MDL < 0.51 ppb for HAA5
- Recovery values > 90%
- Separation in less 40 min

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