

Development of a New Column for the Measurement of Halocetic Acids in Drinking Water by IC-MS and IC-MS/MS

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ABSTRACT

Haloacetic acids (HAAs) are among the disinfection by-products produced during chlorination of water containing natural organic matter and bromide. EPA Methods 552.1 and 552.2 used to determine HAAs 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. Water samples are directly injected into an ion chromatograph coupled to a triple quadrupole mass spectrometer. The separation of all 9 HAAs addressed in EPA methods is achieved on either a 2 × 250 mm or 1 × 250 mm high-capacity ion-exchange column using simple hydroxide gradients.

Excellent peak resolution and linearity are achieved between 0.4 µg/L and 100 µg/L in a matrix containing up to 250 mg/L each of chloride and sulfate and 30 mg/L of nitrate. Using $^{13}\text{C}_2\text{H}_2\text{COOH}$ as an internal standard, the detection limit is less than 0.4 µg/L for each of the five regulated haloacetic acids (HAA5) and less than 1 µg/L for the other four. No significant matrix effects are observed. Recoveries of all nine HAAs are greater than 90% in a simulated matrix of the above concentrations.

INSTRUMENTATION

Ion Chromatograph: Thermo Scientific™ Dionex™ ICS-3000 composed of:
AS Autosampler, DP Dual Pump module, DC Detector/Chromatography module, and EG Eluent Generator module

Triple Quadrupole Mass Spectrometer: MS/MS operated in MRM mode

Software: Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System, DCMS^{Link}™, and MDS Sciex Analyst® 1.4.1

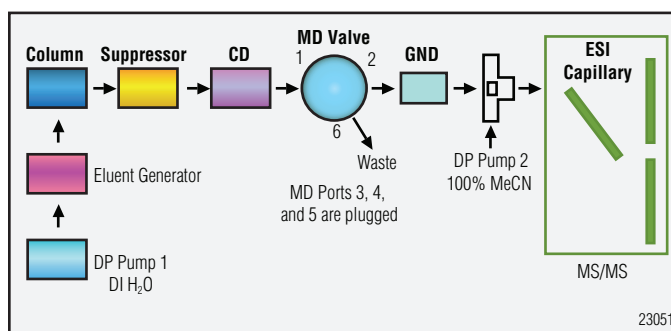
CHROMATOGRAPHIC CONDITIONS

Column: Thermo Scientific™ Dionex™ IonPac™ AS24, 2 × 250 mm

Suppressor: Thermo Scientific™ Dionex™ ASRS™ MS

Eluent generator: Thermo Scientific™ Dionex™ EluGen™ EGC II KOH cartridge, gradient; 0.3 mL/min

Matrix diversion/post column solvent addition: 100% acetonitrile; 0.2 mL/min



- DP Pump 1 pumps deionized (DI) water through the EG Eluent Generator.
- KOH is generated electrolytically and pumped through the column and subsequently suppressed by the suppressor.
- The matrix diversion valve is used to divert sample matrix to waste and then send the analytical stream to the MS/MS.
- DP Pump 2 delivers acetonitrile to the MS/MS continuously. The analytical stream is mixed with solvent in a high-efficiency static-mixing tee before entering the MS/MS.

MS/MS EXPERIMENTAL CONDITIONS

	ESI Settings
Curtain Gas:	20
Collision Gas:	5
Temperature:	475 °C
Ion Source Gas 1 (GS1):	75
Ion Source Gas 2 (GS2):	85

Table 1. MS/MS Instrument Parameters Recommended for Haloacetic Acids Detection

Analyte	MRM Transitions	DP (volts)	FP (volts)	EP (volts)	CE (volts)	CXP (volts)
Chloroacetic acid (MCAA)	93/35	-20	-300	-10	-14	-6
Dichloroacetic acid (DCAA)	127/83	-11	-350	-7	-12	-14
Bromoacetic acid (MBAA)	136.8/78.8	-11	-350	-7	-12	-14
Trichloroacetic acid (TCAA)	161/117	-6	-290	-4	-6	-8
Bromochloroacetic acid (BCAA)	171/79	-16	-300	-6	-28	-8
Dibromoacetic acid (DBAA)	215/79	-11	-340	-4.5	-12	-10
Tribromoacetic acid (TBAA)	250.6/79	-11	-350	-5	-32	-12
Bromodichloroacetic acid (BDCAA)	79/79	-12	-300	-1.5	-6	-14
Chlorodibromoacetic acid (CDBAA)	207/79	-11	-310	-5	-20	-6

All nine haloacetic acids addressed in EPA methods are measured with negative polarity using the MS/MS in the MRM mode. Table 1 shows the multiple reaction monitoring (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.

Current IC Columns: Why Sample Prep is Needed

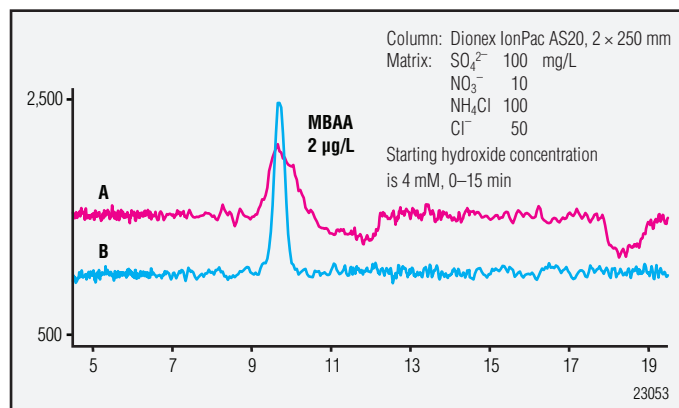


Figure 1. Effect of matrix on peak shape using Dionex IonPac AS20 2 × 250 mm column for separation. (A) Sample without preparation. (B) Sample after matrix removal.

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

Analyte	% Recovery			
	2 µg/L	4 µg/L	8 µg/L	16 µg/L
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

Columns Investigated

Dionex IonPac AS19 and AS20:

- Poor recovery and poor sensitivity in the presence of matrix ions
- Narrow window for matrix diversion

New Dionex IonPac AS24 column:

- Significantly high capacity
- Improved time window for matrix diversion
 - Allows resolution of analytes in the presence of 250 mg/L chloride
 - Baseline resolution of SO_4^{2-} , TCAA, and DBCAA
 - Able to separate nine HAAs

INTERNAL STANDARD & CALIBRATION

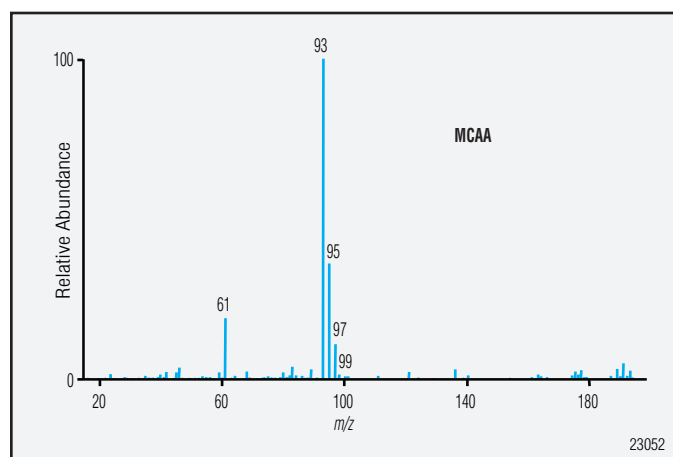


Figure 2. Mass spectrum of monochloroacetic acid.

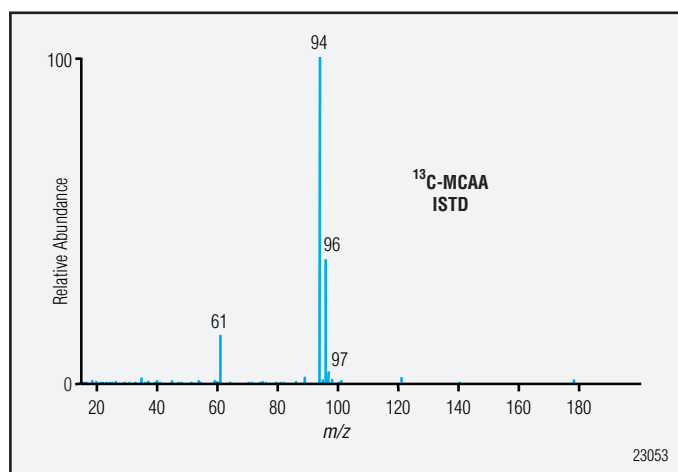


Figure 3. Mass spectrum of ^{13}C -monochloroacetic acid.

Table 3. Recovery of MCAA Acid in the Presence of 10 $\mu\text{g/L}$ ^{13}C -MCAA	
MCAA Concentration ($\mu\text{g/L}$)	% Recovery
0.5	97.2
1.0	95.7
4.0	103.2
8.0	98.5
12.0	99.6

Table 4. Recovery of ^{13}C -MCAA Acid in the Presence of 10 $\mu\text{g/L}$ MCAA	
MCAA Concentration ($\mu\text{g/L}$)	% Recovery
0.5	96.4
1.0	105.6
4.0	101.1
8.0	99.2
12.0	99.1

^{13}C -monochloroacetic acid was used as the internal standard. The spectra of both the analyte and the internal standard are shown in Figures 2 and 3, respectively. The internal standard is monitored at MRM of 94/35 and the analyte at m/z 93/35.

No significant signal suppression of either the analyte or the internal standard was observed due to coelution. Table 3 shows the recovery of MCAA at different concentrations in the presence of 10 $\mu\text{g/L}$ of the internal standard. Table 4 shows the recovery of the internal standard at different concentrations in the presence of 10 $\mu\text{g/L}$ of MCAA. Neither the MCAA nor the internal standard signal is affected by coelution and the recovery values are greater than 95%.

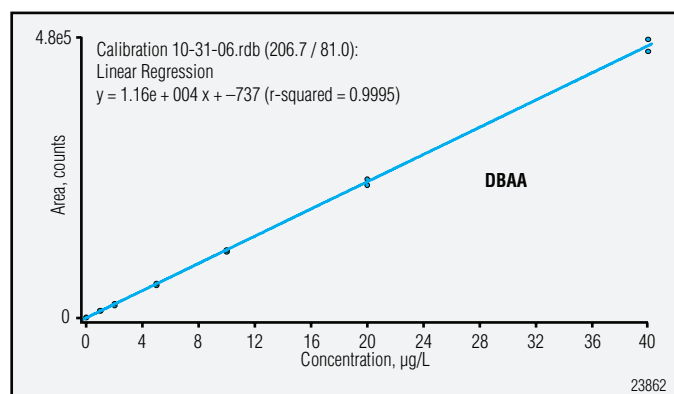


Figure 4. Example of internal calibration curve for DBAA.

Performance Benefits

- Excellent Linearity
- Wide Linear Range
- Good Recovery

Table 5. R-squared Values for Linear Calibration of 9 HAAs	
Analyte	R-squared
MCAA	0.9985
MBAA	0.9993
DCAA	0.9983
BCAA	0.9997
DBAA	0.9995
TCAA	0.9995
CDBAA	0.9999
BDCAA	0.9995
TBAA	0.9991

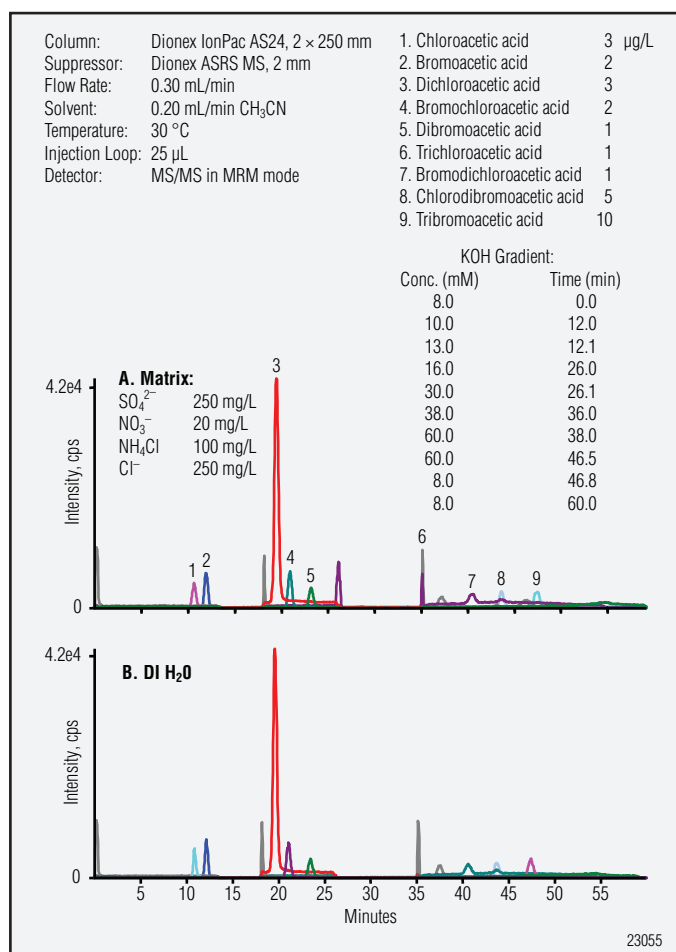


Figure 5. Separation of nine haloacetic acids in simulated high-ionic-strength matrix (A) and DI water (B) using Dionex IonPac AS24, 2 × 250 mm column.

Table 6. Recovery and Shifts in Retention Times for All Nine HAAs Using a AS24, 250 × 2 mm Anion-Exchange Column							
Analyte	Concentration (µg/L)	Area 1 (counts)	Area 2 (counts)	% Recovery	R.T. 1 (min)	R.T. 2 (min)	Shift (min)
MCAA	3	1.11E+05	1.16E+05	104	10.56	10.48	-0.08
MBAA	2	1.60E+05	1.72E+05	107	11.86	11.80	-0.06
DCAA	3	1.26E+06	1.32E+06	105	19.26	19.28	0.02
BCAA	2	1.93E+05	2.00E+05	103	20.72	20.72	0.00
DBAA	1	1.16E+05	1.20E+05	102	23.08	23.10	0.02
TCAA	1	9.15E+04	9.22E+04	100	37.16	36.70	-0.46
BDCAA	2	8.96E+04	9.13E+04	101	40.18	40.10	-0.08
CDBAA	5	1.48E+05	1.53E+05	103	43.34	43.34	0.00
TBAA	10	1.48E+05	1.55E+05	104	47.00	47.02	0.02

N = 7 replicates
 1 = DI water
 2 = Matrix

Table 6 shows the recovery values and shifts in retention time (RT) due to the presence of matrix ions at the above mentioned levels. The Dionex IonPac AS24 column showed excellent recovery values for all measured HAAs with minimal shifts in retention time. Unlike the Dionex IonPac AS20 column, the AS24 is able to handle significantly higher concentrations of sulfate, chloride, and nitrate in the matrix.

The method detection limits (MDLs) 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 <0.51 ppb even in samples with a high-ionic-strength matrix.

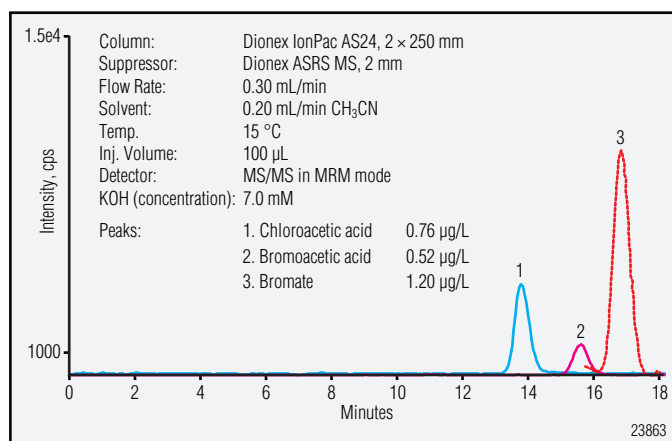


Figure 6. Separation of MCAA, MBAA, and bromate in a drinking water sample using the Dionex IonPac AS24 column.

Table 7. Method Detection Limits for Haloacetic Acids in DI Water and in Simulated Matrix		
Analyte	DI H ₂ O MDL, ng/L	Matrix MDL, 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

N = 7 replicates

SUMMARY

- New HAA method with a new Dionex IonPac AS24 column:
 - Separation of all nine haloacetic acids and bromate was achieved in drinking water with a high ionic strength matrix
 - Separation was completed in less than 50 minutes
 - Simple: no derivatization or sample pretreatment is required—direct injection
 - Fully automated
 - MDL <0.5 ppb for HAA5 and bromate; <1 ppb for all other non-regulated HAAs
 - Recovery values >90%
- MS or MS/MS as a detector:
 - High sensitivity
 - Specific (m/z)

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