

# Comparison of EPA Haloacetic Acid Method 552.2 with New EPA Method 557 Using Direct Injection

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## ABSTRACT

Haloacetic acids (HAAs) are disinfection byproducts produced during chlorination of water containing natural organic matter and bromide. Determination of HAAs using EPA Methods 552.1, 552.2, and 552.3 requires 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, 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 nine HAAs and bromate addressed in EPA methods is achieved on the IonPac® AS24 anion-exchange column using a hydroxide gradient. The unique selectivity of this column provides separation of these analytes from common inorganic matrix ions so that the chloride, sulfate, nitrate, and bicarbonate are diverted to waste during the analytical run, avoiding contamination of the ESI-MS/MS instrument.

Excellent peak resolution and linearity are achieved between 0.4 µg/L and at least 20 µg/L in a matrix containing up to 250 mg/L of each of chloride and sulfate, 150 mg/L bicarbonate, and 30 mg/L of nitrate. This matrix also contains 100 mg/L ammonium chloride preservative for a total chloride concentration of 316 mg/L. Four stable-labeled internal standards have been studied and the current regulatory levels (MRLs) of 1 and 2 µg/L for HAA5 are easily achieved. Similar sensitivity is observed for HAA9 targets and bromate. Recoveries of all nine HAAs are greater than 90% in a simulated matrix of the concentrations listed above. This poster presents analytical results to date for this method.

## UNIQUE NEEDS OF IC FOR MASS SPECTROMETRIC DETECTION

- Sensitive low mass detection, e.g., < 100 amu
- Negative polarity ESI
- Typically 100% aqueous eluents
- Quantification, even on a gradient
- Coupling to ion-exchange polymers (separator, suppressors, etc.)
- IC-MS and IC-MS/MS methods that are rugged enough to be official EPA methods
- Internal standards for all methods with diverse matrix requirements

## HALOACETIC ACID IC-MS/MS METHOD OBJECTIVES

### Goals

- No sample pretreatment
- No preconcentration
- Minimize matrix effects
- Good peak efficiency and resolution
- Separate HAAs and common matrix ions
- Achieve MDL of < 0.5 µg/L

### Solution IC-MS or IC-MS/MS

- Anion-exchange separation of all analytes and common matrix ions
- IonPac AS24 column
- Significantly higher capacity than other IC columns
- Good separations
- Good peak shape and retention time stability in high matrix concentration
- Mass spectrometric detection
- Structural information for peak identification
- Sensitive detection
- No preconcentration necessary

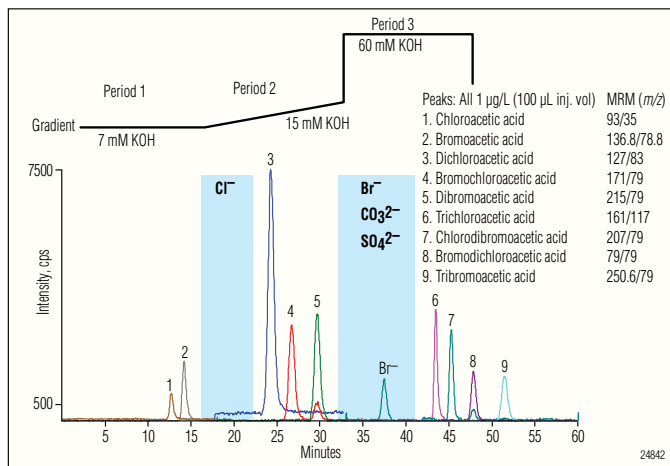


Figure 1. IC-MS-MS MRM channel overlay of nine haloacetic acids using an ICS-3000 ion chromatography system and ABI-Sciex API 2000™ mass spectrometer. The colored boxes show the matrix diversion windows where the analytical flow is diverted to waste during elution of the matrix ions. Peaks 1, 2, 3, and 6 have stable-labeled internal standards. The IC hydroxide gradient is illustrated above the chromatogram overlay. Analytical and solvent flow rates are 0.3 mL/min using the system shown in Figure 2. The column compartment temperature is 15 °C, and the autosampler sample tray is maintained at 8 °C for analyte stability.

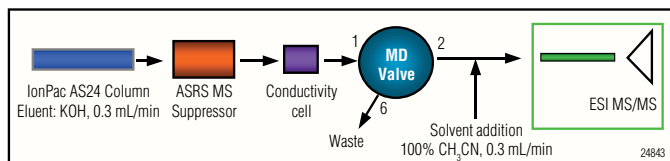


Figure 2. Flow diagram with matrix diversion valve.

In this configuration, acetonitrile is delivered to the mass spectrometer continuously; the matrix diversion valve is used to divert sample matrix to waste and send the analytes to the MS instrument; the analytical stream is mixed with solvent in a mixing tee before entering the mass spectrometer.

## INSTRUMENTATION AND SOFTWARE

Ion Chromatograph: Dionex ICS-3000  
 Mass Spectrometer: MS/MS  
 Software: Dionex DCMS<sup>Link</sup>™ 2.0 and MDS Sciex Analyst<sup>®</sup> 1.4.2 or XCalibur<sup>®</sup> 2.0

## METHOD DETAILS

### Separation

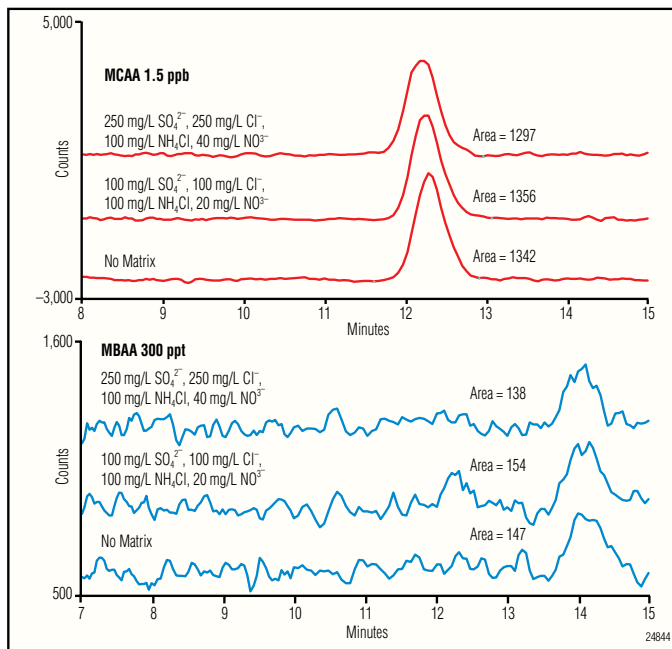


Figure 3. The importance of using a high-capacity anion-exchange column.

With insufficient column capacity, overloading with sample matrix will cause peak broadening and significant shifts in retention times. Reduced peak heights have an adverse effect on detection limits and recoveries, and shifting retention times increase the need for method modifications. When sample lots include several matrix compositions, it can significantly impact the ability to operate in unattended mode. Figure 3 shows stable retention times and peak efficiencies using a high-capacity column in a high-ionic-strength matrix.

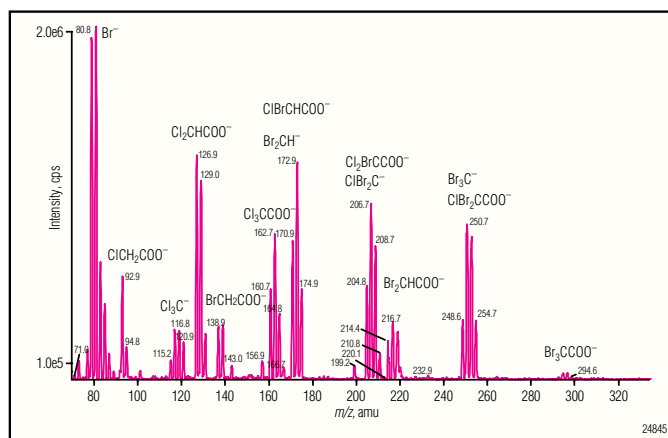


Figure 4. Mass spectra of nine haloacetic acids plus bromide.

## INTERNAL STANDARDS

In this method, the authors used four stable-labeled internal standards for all analytes due to cost and availability issues. Internal standards that elute in each of the three sections of the gradient method were selected because the composition of eluent produces background changes over the course of the run.

In Figure 1, period 1 of the gradient 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- $1-^{13}C$  is used for accurate tracking of the MBAA analyte. MCAA- $1-^{13}C$  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 is DCAA- $2-^{13}C$ . This section ramps the concentration of KOH to 18 mM, and the analytes are the dihaloacetic acids including DCAA, BCAA, DBAA, and dalapon (dichloropropionic acid). The second section ends with the diversion of sulfate, nitrate, and bicarbonate to waste. The concentration of KOH eluent is ramped to 60 mM in Period 3 and the trihaloacetic acids, TCAA, BDCAA, DBCAA, and TBAA elute. All four stable-labeled internal standards are available in ampoules from Dionex as 1000  $\mu\text{g/L}$  solutions in MTBE.

Temp °C	MBAA- $1-^{12}C$	MBAA- $1-^{13}C$	% Ratio
100	2.26E+04	1.88E+06	1.20
100	2.13E+04	1.79E+06	1.19
200	4.12E+04	3.32E+06	1.24
300	5.58E+04	4.49E+06	1.24
400	7.41E+04	5.99E+06	1.24
475	8.92E+04	6.91E+06	1.29

Table 2 shows that MBAA- $1-^{13}C$  is stable over a wide range of interface temperatures in the API2000. The ratio of MBAA- $1-^{13}C$  to MBAA- $1-^{12}C$  is stable.

Figure 5 shows Q1 ions of TCAA- $1-^{13}C$  as a function of source gas temperature. TCAA- $1-^{13}C$  interconverts to TCAA- $1-^{12}C$  through a decarboxylation process in the electrospray source as the temperature of the nitrogen gas is increased. The TCAA- $2-^{13}C$  does not show the exchange from  $m/z$  162 to 161 over the temperature range of 150–450 °C. It was determined that the ratio percentage of  $^{12}C/^{13}C$  for TCAA- $2-^{13}C$  is approximately 1.8 and stable. Based on this information, the authors used TCAA- $2-^{13}C$  as the Period 3 internal standard.

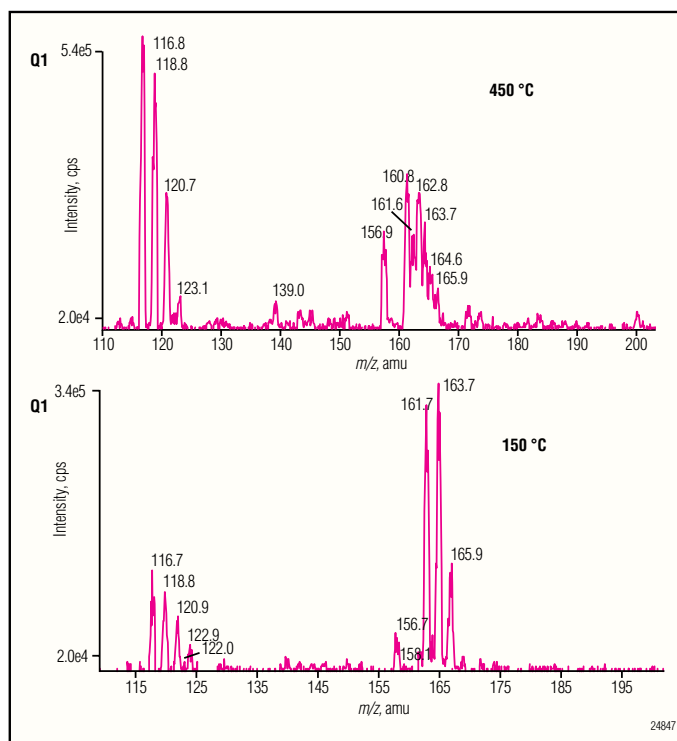


Figure 5. Q1 ions of TCAA- $1-^{13}C$  as a function of source gas temperature.

## LINEARITY, DETECTION LIMITS, AND RECOVERY

Analyte	ISTD 3 or 5 $\mu\text{g/L}$	R <sup>2</sup> (Calibration range 0.250–2 $\mu\text{g/L}$ DIW/Matrix*)	R <sup>2</sup> (Calibration range 0.250–5 $\mu\text{g/L}$ Matrix with NH <sub>4</sub> Cl*)	MDL $\mu\text{g/L}$ / %RSD (n=7, 1 $\mu\text{g/L}$ In Matrix)	Accuracy (%) (at 500 ng/L) DI H <sub>2</sub> O/ HI Matrix with NH <sub>4</sub> Cl
MCAA	MCAA- $1-^{13}C$	0.9997/0.9989	0.9962	0.440/14.7	87.5/81.6
MBAA	MBAA- $1-^{13}C$	0.9999/0.9990	0.9981	0.126/4.2	102/74.
DCAA	DCAA- $2-^{13}C$	0.9999/0.9991	0.9924	0.095/3.3	96.7/73.3
BCAA	DCAA- $2-^{13}C$	0.9999/0.9992	0.9964	0.100/0.8	93.5/88.8
DBAA	DCAA- $2-^{13}C$	0.9999/0.9993	0.9957	0.325/10.8	107.0/79.9
TCAA	TCAA- $2-^{13}C$	0.9999/0.9993	0.9970	0.091/0.3	113.0/87.3
BDCAA 207/81	TCAA- $2-^{13}C$	0.9991/0.9991	0.9963	0.637/18.9	105/89.0
CDBAA	TCAA- $2-^{13}C$	0.9992/0.9994	0.9972	0.521/16.4	128/108.0
TBAA	TCAA- $2-^{13}C$	0.9994/0.9998	0.9954	0.360/9.9	102/95.6

Table 3 provides linearity data for deionized water and high-ionic-strength matrix for this method. Standards in the matrix were used to calculate worst-case minimum detection limits against the DI water calibration. Accuracy for the 500 ppt standard was automatically calculated by the Analyst software for both the DI water data and the matrix data. The high-ionic-strength matrix comprised 315 mg/L chloride, 250 mg/L sulfate, 150 mg/L bicarbonate, and 30 mg/L nitrate. This chloride content includes 250 mg/L sodium chloride salt and 100 mg/L ammonium chloride, which is added as a preservative to each sample. The transition for bromodichloroacetic acid is 207/81. The intensities for this transition are low, leading to the high %RSD and MDL. Better quantification is achieved by monitoring the 79/79 signal for this analyte.

**Table 4. Recovery at Two Analyte Concentrations and Two Matrix Concentrations (Synthetic Matrix)**

Analyte	ISTD	% Recovery <sup>a</sup> 100 matrix <sup>b</sup> 0.5; 2.5 ppb	% Recovery <sup>a</sup> 250 matrix <sup>b</sup> 0.5; 2.5 ppb
MCAA	MCAA	101; 103	103; 101
MBAA	MBAA	102; 110	81; 104
DCAA	DCAA	100; 107	87; 103
BCAA	DCAA	119; 113	103; 111
DBAA	DCAA	114; 124	108; 115
TCAA	TCAA	89; 99	73; 94
BDCAA	TCAA	96; 94	101; 94
CDBAA	TCAA	105; 87	109; 92
TBAA	TCAA	107; 95	109; 91

<sup>a</sup>vs. calibration in DI water

<sup>b</sup>100 matrix = 100 ppm chloride, and sulfate, 60 ppm bicarbonate, 20 ppm nitrate plus 100 ppm ammonium chloride; 250 matrix = 250 ppm chloride and sulfate, 150 ppm bicarbonate, 30 ppm nitrate, plus 100 ppm ammonium chloride

## APPLYING THE METHOD TO PUBLIC WATER UTILITY SAMPLES

The authors obtained three samples from a southwest public water utility whose source is primarily surface water. One sample came from a treated water reservoir and two samples came from the distribution system within the pressure zone. These samples were routinely analyzed using US EPA Method 552.2 before being subjected to the comparative analysis described here. Chloride and sulfate levels were determined using ion chromatography and the samples were not diluted prior to analysis by IC-MS/MS; the samples had already been preserved using ammonium chloride as specified in Method 552.2.

The features of EPA Method 552.2 are provided below along with the achievable detection limits published in the method. Because EPA Method 552.2 is a GC-ECD method, no structural information is produced. This method uses liquid-liquid extraction and methylation of the carboxylic acids before determination by GC-ECD.

- **LLE-GC-ECD**
  - pH-adjust sample
  - Extract with MTBE
  - Methylate
  - Neutralize and back extract
  - Inject into GC-ECD
- **Limitations:**
  - No mass information
  - Requires sample pretreatment
  - Time consuming
  - Labor intensive
  - Subject to multiple procedural errors
- **Advantages:**
  - Good selectivity
  - Low MDLs

Analyte	MDL* (µg/L)
MCAA	0.273
MBAA	0.204
DCAA	0.242
BCAA	0.251
DBAA	0.066
TCAA	0.079
BDCAA	0.091
CDBAA	0.468
TBAA	0.820

\* Student's *t*-value  
3.143, *n*=7; data from  
EPA Method 552.2  
Rev.01

**Table 5A. Comparison of Analytical Results for High-Ionic-Strength Samples**

Sample	Cl <sup>-</sup> SO <sub>4</sub> <sup>2-</sup> (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
<b>Treated Water Reservoir</b>	163 243	1.11 93%	1.08 103%	15.1 72%	8.56 76%	3.72 84%	5.85 80%	7.13 104%	4.75 92%	1.07 106%
<b>System A</b>	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%
<b>System B</b>	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%

Calculated using 79/79

\*Reproducibility on duplicates, 98%; Spike recovery is calculated on a 2.5 µg/L spike.

**Table 5B**

Sample	Cl <sup>-</sup> SO <sub>4</sub> <sup>2-</sup> (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
<b>Treated Water Reservoir</b>	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
<b>System A</b>	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
<b>System B</b>	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

\*Reproducibility on duplicates, 98%; Recovery is 100\*amount found using IC-MS/MS amount found using Method 552.2

Table 5A shows the amounts detected for the nine HAAs using the IC-MS/MS method and recovery calculation for 2.5 µg/L spiked into each undiluted sample. The spike recoveries are 56–125% with most in the 70–120% range. Narrower ranges can be achieved if the samples are diluted 1:2, but this study was designed to test samples without preparation of any kind.

The data shown in Table 5B shows the amount found for the HAAs as determined using EPA Method 552.2 at the water treatment site laboratory. % Rec illustrates the comparison of the amount detected using the IC-MS/MS method to that detected using the Method 552.2. The IC-MS/MS data are 70–130% of the Method 552.2 results for all analytes.

## SUMMARY

The authors have described an IC-MS/MS method for determination of halogenated acetic acids using an anion-exchange separation column with sufficient capacity and selectivity to handle high-ionic-strength matrices without sample preparation. The IC-MS/MS detection provides structural information and sensitive detection without requiring preconcentration. Analytical results show good correlation to data generated using EPA Method 552.2 for high-ionic-strength samples.

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