

EPA Method 557:

Determination of Haloacetic Acids, Bromate, and Dalapon in Drinking Water by IC-MS/MS

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Overview

All drinking water plants in the United States must determine the concentration of disinfection by products in drinking water prior to release. This IC-MS/MS method follows the current guidelines outlined in EPA Method 557, and was found to be sensitive and reproducible for the quantitation of low-level haloacetic acids, bromate, and dalapon in drinking and surface waters.¹⁻²

Introduction

We rely on municipalities to clean drinking water for the prevention of bacterial illness. However, when by-products from the disinfection process are formed in our drinking water, we may experience unexpected health risks. For instance, when chlorine used to disinfect water reacts with organic decaying vegetation, haloacetic acids (HAAs) form. Bromate is formed when disinfecting ozone reacts with naturally occurring bromide. Long term ingestion of bromate or haloacetic acids may cause cancer.³

Another mechanism for the contamination of drinking water is introduction through runoff. Dalapon, an herbicide used to control grasses in a wide variety of crops, can be introduced to waterways from runoff when used on rights of way. People who drink water containing dalapon in excess of the maximum contaminant level (MCL) for many years could experience minor kidney changes.⁴

Haloacetic acids are a family of organic compounds based on the acetic acid molecule (CH_3COOH), where one or more hydrogen atoms attached to carbon atoms are replaced by a halogen (chlorine or bromine). There are nine species of HAAs: monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetic acid (TCAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), and tribromoacetic acid (TBAA), however only five acids (MCAA, MBAA, DCAA, DBAA, and TCAA) are regulated with a cumulative legal limit of 60 $\mu\text{g/L}$ in drinking water. The MCL for bromate is 10 $\mu\text{g/L}$, while dalapon is 0.2 mg/L .²⁻³



Typical approaches to the detection of these compounds require derivatization and multiple extraction steps followed by gas chromatography with electron capture detection. Using ion chromatography as a separation technique prior to detection with tandem mass spectrometry (IC-MS/MS) with the API 3200™ system, we achieve a sensitive direct injection method for the detection and quantitation of nine haloacetic acids, dalapon, and bromide without time consuming derivatization steps.

Experimental

Chemicals

Deionized water (18M Ω) was produced in house.

Acetonitrile was purchased from JT Baker.

Haloacetic acid and dalapon standards were purchased from Sigma-Aldrich.

Bromate and internal standards of: MCAA-2-¹³C, MBAA-2-¹³C, DCAA-2-¹³C, and TCAA-2-¹³C were purchased from Dionex.

IC

A Dionex ICS3000 system equipped with a Dionex IonPac AG24 2.1 x 50 mm and AS24 2.1 x 250 mm performed the separation with a column temperature of 15°C. The potassium hydroxide gradient was made online via online eluent generation; a one hour gradient (Table 1) separated the nine haloacetic acids, bromate, and dalapon from typical matrix ions such as chloride, sulfate, nitrate, and carbonate.

Table 1. Ion chromatography gradient

Time	[KOH]
0	7
16.8	7
34.2	18
34.4	60
51.2	60
51.4	7

The potassium hydroxide mobile phase was passed through a suppressor prior to its introduction into the mass spectrometer. The suppressor exchanged the potassium counter ion of the mobile phase with hydronium, making the IC effluent into the mass spectrometer predominantly water. Acetonitrile was added post-column at 200 µL/min to assist in desolvation, and to provide a makeup flow during periods of diversion.

Internal standards of monochloroacetic acid 2-¹³C, monobromoacetic acid 2-¹³C, and trichloroacetic acid 2-¹³C were added for a final concentration of 4 ng/mL.

The injection volume was 100 µL.

MS/MS

An AB SCIEX API 3200™ system with Turbo V™ source operated in negative Electrospray Ionization (ESI) mode was used. During periods of matrix elution, the switching valve on the API 3200™ system diverted column effluent from the source.

The Turbo V™ source is equipped with a static grounding union. Traditionally this union is installed with a two-port (in/out flow through) piece. In order to introduce acetonitrile to the sample stream, this two-port piece was replaced with the three-port (tee) piece. Operating in this fashion, the eluent composition entering the source is 60% aqueous / 40% organic, which assists in desolvation. During periods of matrix diversion, the acetonitrile

flow through the tee acts as a make-up flow to the Turbo V™ source.

The mass spectrometer was operated in Multiple Reaction Monitoring (MRM) mode. Analyte detection was separated into four periods, with temperature and gas settings optimized for compound detection (Table 2 and 3).

Table 2. MRM Transitions used for analysis

	Analyte	Q1	Q3
Period 1	MCAA	93	35
	MBAA	137	79
	Bromate	127	111
	MCAA-ISTD	94	35
	MBAA-ISTD	138	79
Period 2	DCAA	127	83
	Dalapon	141	97
	BCAA	173	129
	DBAA	217	173
	DCAA-ISTD	128	84
Period 3	TCAA 1	161	117
	TCAA 2	163	119
	TCAA-ISTD	162	118
Period 4	TBAA	251	79
	BDCAA	163	81
	CBDA	207	79

Table 3. Temperature and ion spray voltage by period

	IS (V)	TEM (°C)
Period 1	-4500	400
Period 2	-3500	550
Period 3	-4500	250
Period 4	-4500	350

Results and Discussion

A method for quantitation and identification of nine haloacetic acids, bromate, and dalapon was examined to screen drinking and surface water samples. The method followed the guidelines and met the requirements of EPA method 557 (Figure 1).

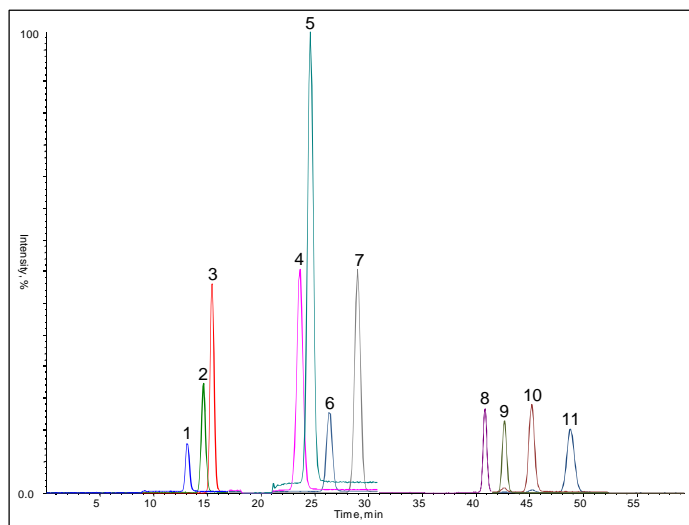


Figure 1. Chromatogram of a 10 µg/L standard, with the following order of elution: (1) MCAA (2) MBAA (3) bromate (4) dalapon (5) DCAA (6) BCAA (7) DBAA (8) TCAA (9) BDCAA (10) CDBAA (11) TBAA

The periods of detection had to be optimized for maximum sensitivity of the analytes, as the response of haloacetic acids in the mass spectrometer is very sensitive to temperature and ion spray voltage. For instance, a third period had to be defined specifically for temperature sensitive TCAA, whereas other analytes in the method had much better performance at higher temperatures (Table 3).

All analytes showed good linearity with $r > 0.998$ over two and a half orders of magnitude in reagent water (Table 5). The detection limit (DL) was calculated from the formula:

$$DL = S \times t_{(n-1, 1-\alpha = 0.99)}$$

where $t_{(n-1, 1-\alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom (for seven replicate injections, the Student's t value is 3.143 at a 99% confidence level)

n = number of replicates, and
S = standard deviation of replicate analyses.¹

DLs were found between 0.025 µg/L and 0.25 µg/L (Table 5). These detection levels are well below the EPA MCL of 60 µg/L and the maximum contaminant level goals (MCLG) established in the National Primary Drinking Water Regulations Stage 1 and Stage 2 for Disinfectants and Disinfection Byproducts Rule. The low DLs allow dilution of real water samples before analysis to reduce possible matrix effects and interferences (i.e. retention time shifts).

Precision, accuracy and robustness were demonstrated by injecting all analytes at 1 µg/L in reagent water and fortified into the EPA defined laboratory synthetic sample matrix of 20 mg/L nitrate, 150 mg/L bicarbonate, 250 mg/L chloride, 250 mg/L sulfate and 100 mg/L ammonium chloride.

Relative standard deviation (RSD) and recovery (REC) were calculated from the formulae:

$$\%RSD = \frac{\text{Standard deviation of measured conc.}}{\text{Average concentration}} \times 100$$

$$\%REC = \frac{\text{Average measured concentration}}{\text{Fortified concentration}} \times 100^1$$

Method robustness in reagent water was examined for 24 hours; the RSD was less than 0.06% for all analytes.

Samples were fortified into the synthetic sample matrix. During periods of the matrix elution, column effluent was diverted from the mass spectrometer (Figure 2). The peak shape of the haloacetic acids was altered in the presence of the matrix ions. However, recoveries of all nine haloacetic acids, bromate, and dalapon were within 15% of the expected concentration at 1 µg/L (Table 4).

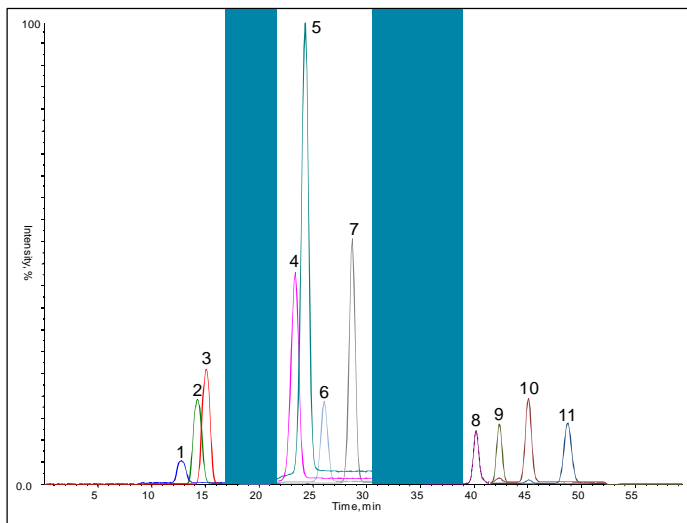


Figure 2. 5 µg/L standard fortified into a synthetic sample matrix of 20 mg/L nitrate, 150 mg/L bicarbonate, 250 mg/L chloride, 250 mg/L sulfate and 100 mg/L ammonium chloride. Periods shaded blue were those of matrix elution, and diverted from the mass spectrometer source. Order of elution: (1) MCAA (2) MBAA (3) bromate (4) dalapon (5) DCAA (6) BCAA (7) DBAA (8) TCAA (9) BDCAA (10) CDBAA (11) TBAA

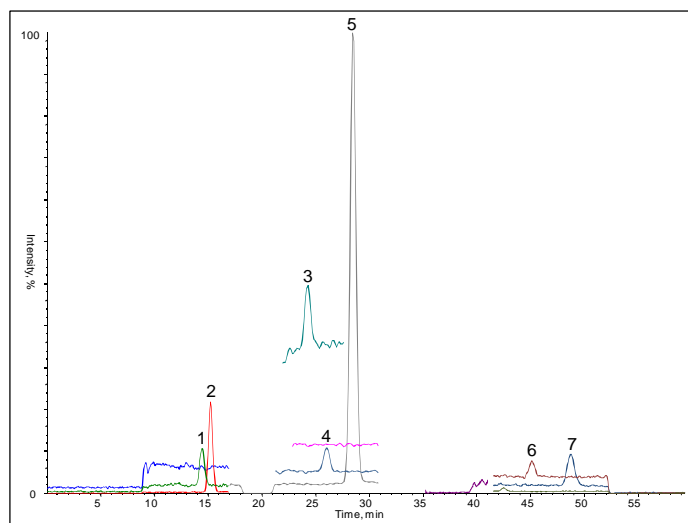


Figure 3. Sample of urban drinking water shows the presence of: (1) MBAA, (2) bromate, (3) DCAA, (4) BCAA, (5) DBAA, (6) CDBAA, and (7) TBAA. The concentrations reflected in this sample do not exceed the regulatory requirement of 60 µg/L

Table 4. Reproducibility of a 1 µg/L sample in synthetic sample matrix over 24 hours of injections. The table shows relative standard deviation for retention time and peak area (RSD), and recovery (REC).

Analyte	RSD RT (%)	RSD Area (%)	REC (%)
MCAA	0.36	1.5	102
MBAA	0.40	4.6	104
Bromate	0.28	2.7	105
Dalapon	0.00	2.5	90
DCAA	0.00	6.1	100
DBAA	0.00	2.8	101
BCAA	0.00	3.7	95
TCAA	0.13	2.7	102
BDCAA	0.05	7.7	114
CDBAA	0.05	7.0	113
TBAA	0.09	6.8	106

The developed method was used to evaluate two types of drinking water samples: urban drinking water that has been processed through traditional drinking water treatment, and well water samples, where the samples were not treated to disinfectants. The results (Figures 3 and 4) show that in the urban water sample, haloacetic acids and bromate are present, although at concentrations lower than the action levels required by the US EPA. No dalapon was detected in this sample.

With the sample obtained from a rural well, neither haloacetic acids nor bromide were detected. However, there was a small amount of dalapon detected. Most likely this herbicide entered the sample from runoff.

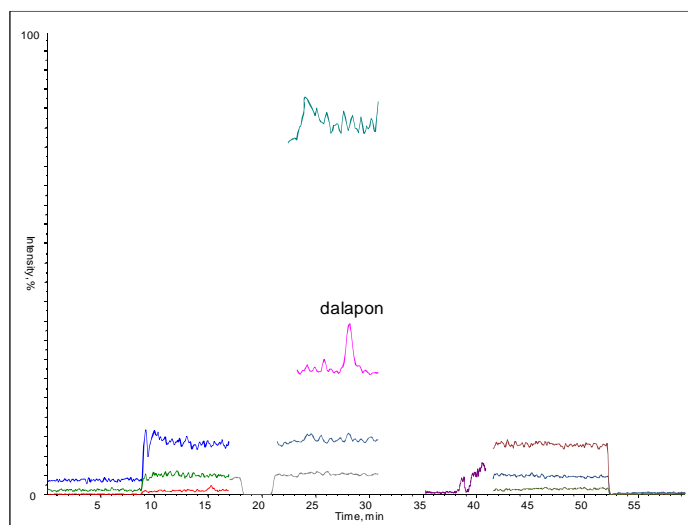


Figure 4. Drinking water sample from a rural well does not have any detectable haloacetic acids. However, dalapon is detected, with a concentration less than the action level of 0.2 mg/L

Table 5. Obtained method performance values

Analyte	Retention Time (min)	Internal Standard	Method 557 DL (µg/L)	DL (µg/L)	Calibration Range (µg/L)	r value
MCAA	13.1	MCAA-2- ¹³ C	0.20	0.25	0.25-50	0.9990
MBAA	14.6	MBAA-2- ¹³ C	0.06	0.03	0.25-50	0.9991
Bromate	15.4	MBAA-2- ¹³ C	0.02	0.04	0.25-50	0.9989
Dalapon	23.5	DCAA-2- ¹³ C	0.04	0.03	0.025-50	0.9992
DCAA	24.5	DCAA-2- ¹³ C	0.06	0.03	0.025-50	0.9997
BCAA	26.3	DCAA-2- ¹³ C	0.11	0.05	0.05-50	0.9994
DBAA	28.9	DCAA-2- ¹³ C	0.02	0.04	0.05-50	0.9996
TCAA	40.9	TCAA-2- ¹³ C	0.09	0.03	0.05-50	0.9998
BDCAA	42.6	TCAA-2- ¹³ C	0.05	0.06	0.05-50	0.9997
CDBAA	45.1	TCAA-2- ¹³ C	0.04	0.06	0.05-50	0.9996
TBAA	48.7	TCAA-2- ¹³ C	0.07	0.05	0.05-50	0.9996

Summary

When disinfecting agents react with naturally organic or inorganic matter in the water, harmful byproducts may form. A robust and reliable analysis for the detection of haloacetic acids, bromate, and dalapon in drinking water was performed. Following the guidelines of EPA Method 557, a direct injection of drinking water into an ion chromatography system coupled to an API 3200™ system allowed for the quantitation of nine haloacetic acids, bromate, and dalapon. Running the analysis by this methodology spares the analyst from derivatization required by gas chromatography methodology. Method robustness over the course of several hours is a key component to this method, and this method was found to be robust over 24 hours.

References

- ¹ US Environmental Protection Agency Method 557: 'Determination of Haloacetic Acids, Bromate, and Dalapon in Drinking Water by Ion Chromatography Electrospray Ionization Tandem Mass Spectrometry' (September 2009)
- ² <http://water.epa.gov/scitech/drinkingwater/labcert/upload/met557.pdf>
- ³ <http://water.epa.gov/drink/contaminants/basicinformation/disinfectionbyproducts.cfm>
- ⁴ <http://water.epa.gov/drink/contaminants/basicinformation/dalapon.cfm>

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