

# Determination of low-level haloacetic acids, bromate, and dalapon in drinking water using IC-MS

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## INTRODUCTION

Disinfection treatment is essential to eliminate waterborne disease-causing microorganisms from drinking water. Municipal water authorities most commonly disinfect water using chemical disinfectants such as chlorine, chlorine dioxide, chloramine, and ozone.<sup>1</sup> However, these disinfectants can react with naturally occurring material in the water to form unintended disinfection byproducts (DBPs). These DBPs may pose health risks. For example, long term ingestion of bromate or haloacetic acids may cause cancer.

Dalapon, an herbicide used to control grasses in a wide variety of crops, can be introduced to waterways from runoff. People who for many years drink water containing dalapon above the maximum contaminant level (MCL), the highest level of a contaminant that is allowed in drinking water, could experience minor kidney changes.<sup>2</sup>

To ensure drinking water safety, major regulatory bodies worldwide, including the U.S. Environmental Protection Agency (EPA), European Commission (EC), U.S. Food and Drug Administration (FDA), and World Health Organization (WHO), have set the maximum allowable concentrations for toxic compounds and microorganisms in drinking water.<sup>3-5</sup>

U.S. EPA Method 557 has been validated for the determination of HAAs, bromate, and dalapon. This method uses ion chromatography (IC) coupled with electrospray ionization tandem mass spectrometry (IC-ESI-MS/MS).<sup>6</sup> The new Thermo Scientific™ ISQ™ EC Single Quadrupole Mass Spectrometer was developed for seamless integration with IC and ease of use. This study shows similar performance using a single quad mass spectrometer as that compared to using a triple quad IC-MS/MS method.

Table 1. U.S. EPA regulations for the disinfection byproducts determined by U.S. EPA Method 557

Disinfection byproduct	MCLG	MCL*
Dalapon	0.2 mg/L	0.20 mg/L
Bromate	Zero	0.010 mg/L or 10µg/L
Dichloroacetic acid (DCAA), Trichloroacetic acid (TCAA), Monochloroacetic acid (MCAA), Bromoacetic acid (MBAA), Dibromoacetic acid (DBAA)	Zero, 0.02 mg/L or 20 µg/L, 0.07 mg/L or 70 µg/L	Regulated with this group but has no MCLG
Bromochloroacetic acid (BCAA), Chlorodibromoacetic acid (CDBAA), Bromodichloroacetic acid (BDCAA), Tribromoacetic acid (TBAA)	These four HAAs are not currently regulated, but are on the Unregulated Contaminant Monitoring Rule (UCMR) 4 list for monitoring by public water systems between 2018 and 2020	HAAs are currently regulated at the total level of 60 µg/L (sum of the concentrations of all five haloacetic acids as an annual average)

## MATERIALS AND METHODS

### Sample collection, preservation, and storage

The residential tap drinking water samples were collected from different cities in the San Francisco Bay Area.

### Instrumentation

Thermo Scientific™ ICS-6000 Dual Channel RFIC System including:

- Eluent Generator, Dual Pump, Degasser, Conductivity Detector

Thermo Scientific™ ISQ™ EC single quadrupole mass spectrometer (P/N ISQEC-IC) including Thermo Scientific™ HESI-II probe

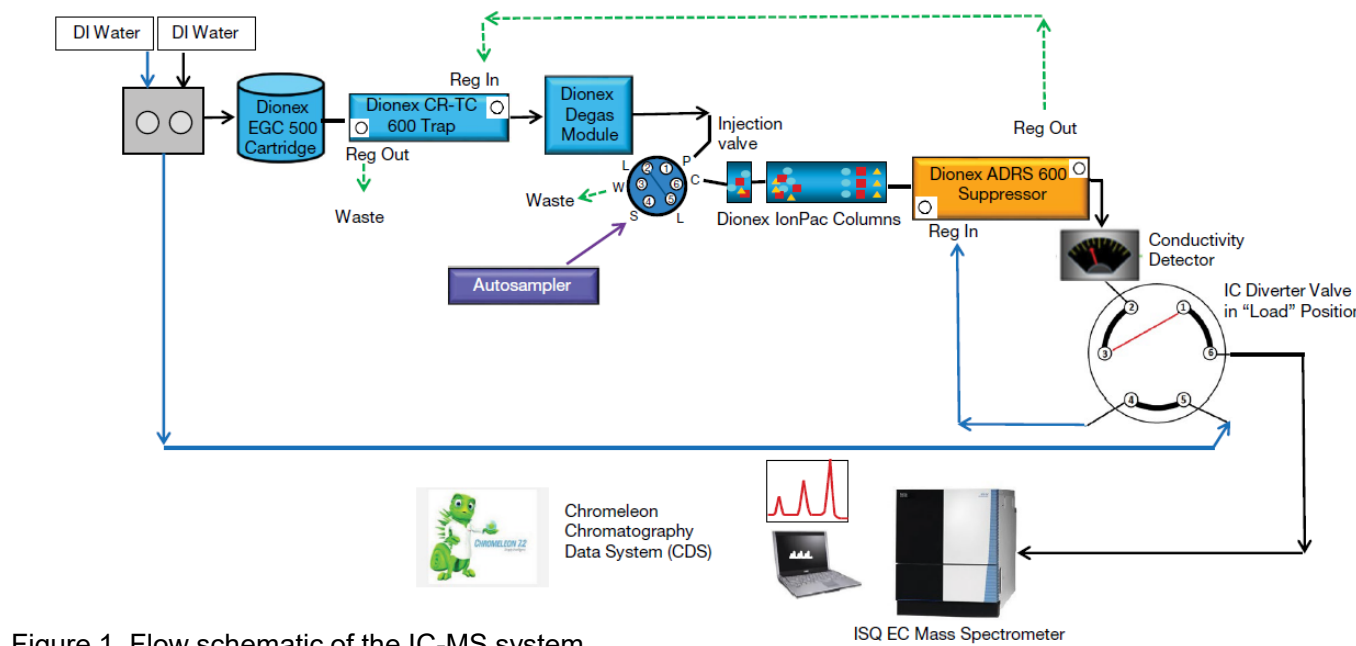


Figure 1. Flow schematic of the IC-MS system

Table 2. Conditions for IC-MS

Parameter	Value
Columns	Dionex IonPac AG31 Guard Column, 2 x 50 mm (P/N 303148) Dionex IonPac AS31 Analytical Column, 2 x 250 mm (P/N 303147)
Eluent	17 mM KOH from -5 to 11.5 min, 17-85 mM KOH from 11.5 to 18 min, 85 mM KOH from 18 to 39 min, 17 mM KOH from 39 to 40 min
Eluent source	Dionex EGC 500 KOH cartridge with Dionex CR-ATC 600
Flow rate	0.3 mL/min
Injection volume	100 µL in Push-Full mode
Column temperature	15 °C
<b>Detection 1, suppressed conductivity</b>	
Suppressor	Dionex ADRS 600 (2 mm) Suppressor, external water mode (flow 0.3 mL/min), legacy mode, 75 mA current
Detection/suppressor compartment temperature	15 °C
Cell temperature	15 °C
Background conductance	<1 µS/cm
System backpressure	~3700 psi
Noise	<1 nS/cm
Run time	40 min
<b>Detection 2, mass spectrometry</b>	
MS detector	ISQ EC single quadrupole MS
Ionization interface	Electrospray ionization (ESI), negative mode
Divertor valve switch time	0-2, 9-11.5, and 20-23 min to waste
Sheath gas pressure	35.0 psi
Aux gas pressure	2.0 psi
Sweep gas pressure	1.0 psi
Foreline pressure	~1.72 Torr
Source voltage	-3528 V
Vaporizer temperature	350 °C
Ion transfer tube temperature	150 °C
Chrom. filter peak width	30 s
Method type	Scan mode (Table 4)

The Dionex ICS-6000 system is equipped with two analytical pumps (DP), eluent generator (EG), autosampler, low temperature microbore column compartment, suppressor, and conductivity detector (CD). DI water is added to the IC system and converted automatically to hydroxide eluent by the EG.

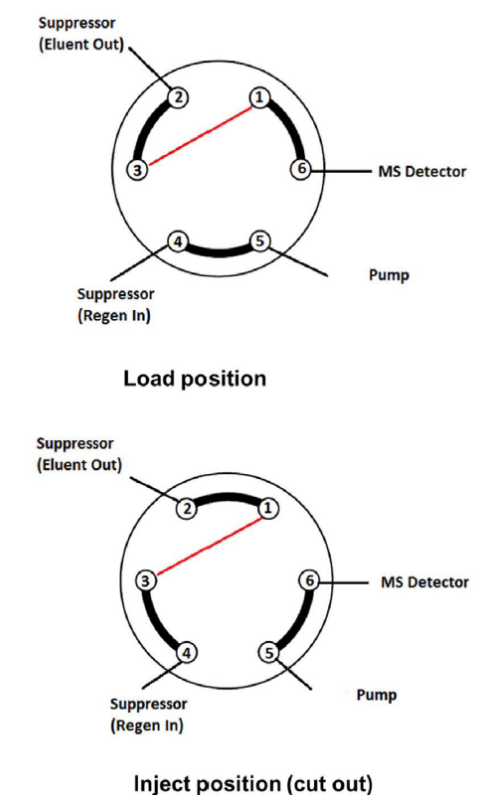


Figure 2. Illustration of the two positions of the 6-port diverter valve

## RESULTS

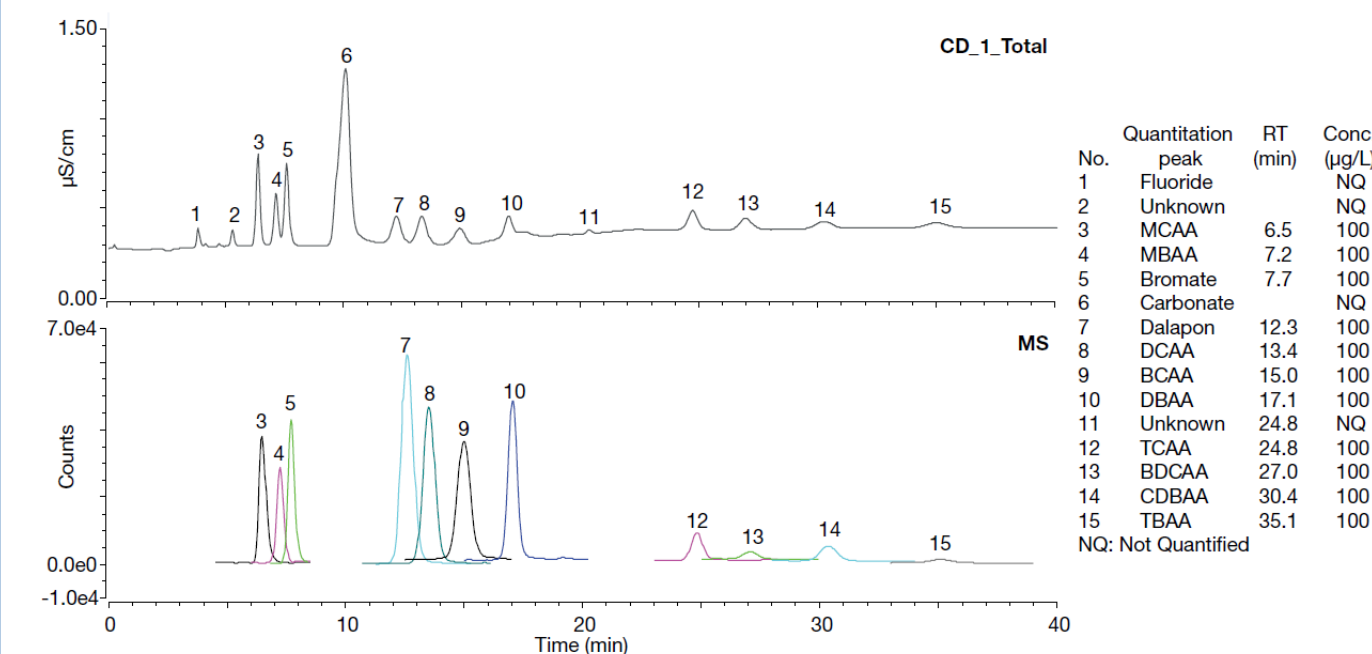


Figure 3. Chromatograms of DI-water spiked with 100 µg/L of nine HAAs, bromate, and dalapon

Table 3. Summary of method performance values and comparison of its MDL to U.S. EPA Method 557

Analyte	Retention time (min)	Internal standard	U.S. EPA Method 557 DL (µg/L)	MDL (µg/L)	Calibration range (µg/L)	r <sup>2</sup> -value
MCAA*	6.5	MCAA-2-13C	0.2	0.1	0.1-100	0.999
MBAA*	7.2	MBAA-1-13C	0.06	0.03	0.1-100	0.998
Bromate	7.7	MBAA-1-13C	0.02	0.12	0.5-100	0.998
Dalapon	12.3	DCAA-2-13C	0.04	0.12	0.5-100	0.999
DCAA*	13.4	DCAA-2-13C	0.06	0.03	0.1-100	0.998
BCAA	15.0	DCAA-2-13C	0.11	0.16	0.5-100	0.998
DBAA*	17.1	DCAA-2-13C	0.02	0.16	0.5-100	0.999
TCAA*	24.8	TCAA-2-13C	0.09	0.67	1-100	0.999
BDCAA	27.0	TCAA-2-13C	0.05	2.79	4-100	0.998
CDBAA	30.4	TCAA-2-13C	0.04	1.04	4-100	1
TBAA	35.1	TCAA-2-13C	0.07	4.55	10-100	1

\*HAA5

### Sample Analysis

The developed method was used to evaluate three residential tap water samples collected from two cities in the San Francisco Bay Area, California. Samples 1 and 2 were from city 1 and sample 3 was from city 2. The results show that although all samples had concentrations lower than the action levels required by the U.S. EPA, each sample had DBPs.

Table 4. Analysis results of drinking water samples

Analyte	Retention time (min)	Water sample 1	RSD range**	Water sample 2	RSD (%)	Water sample 3	RSD range**
MCAA *	6.5	1.5 ± 0.1	3.9-5.0	1.5 ± 0.1	4.0	ND	-
MBAA *	7.2	ND	-	ND	-	ND	-
Bromate	7.7	ND	-	ND	-	0.36 ± 0.03	1.0-25
Dalapon	12.3	ND	-	ND	-	ND	-
DCAA *	13.4	22.1 ± 1.3	0-1.0	22.1 ± 0.2	1.0	21.9 ± 0.9	0-1.0
BCAA	15.0	ND	-	ND	-	4.4 ± 0.3	0.2-8.9
DBAA *	17.1	ND	-	ND	-	0.4 ± 0.1	12-47
TCAA *	24.8	13.8 ± 1.9	1.6-5.8	9.0 ± 0.3	3.5	4.4 ± 0.4	2.9-13.4
BDCAA	27.0	ND	-	ND	-	ND	-
CDBAA	30.4	ND	-	ND	-	ND	-
TBAA	35.1	ND	-	ND	-	ND	-

\*HAA5, \*\*The samples were tested for more than three times over more than three days, n=3/each day.

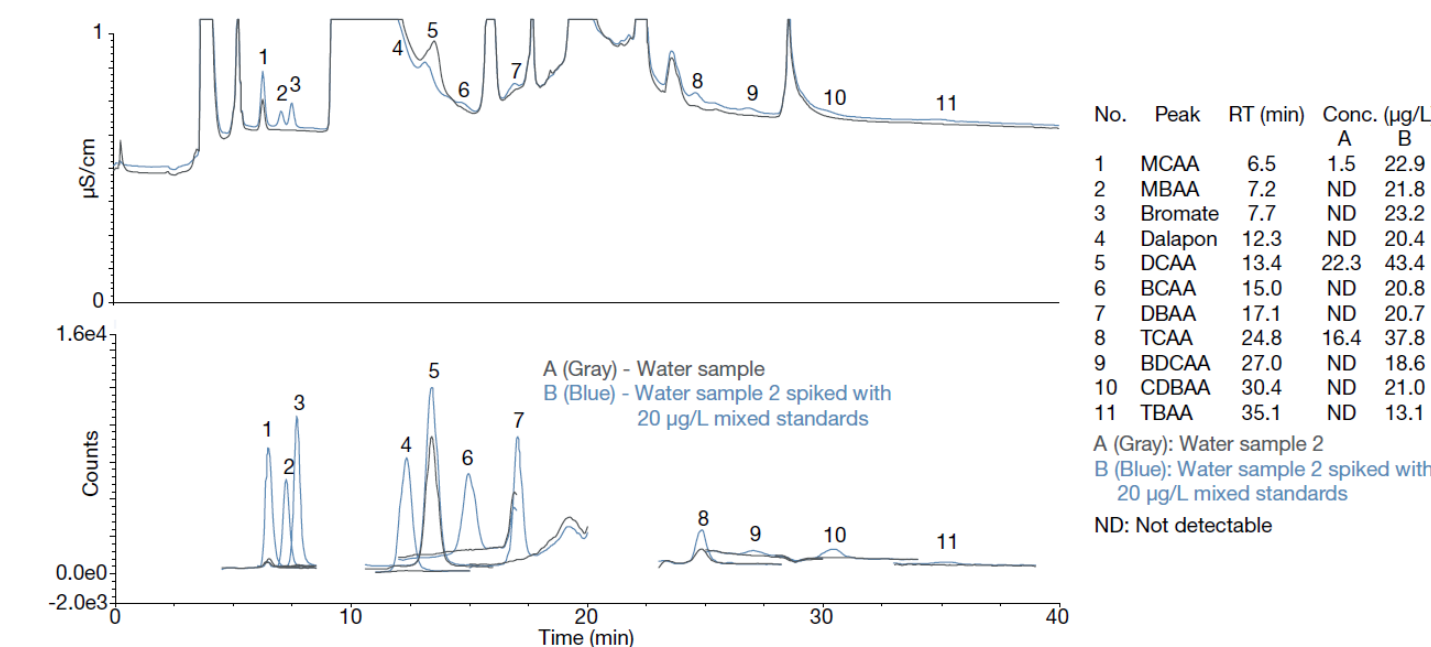


Figure 4. Chromatogram of water sample 2 with and without spiking with 20 µg/L of 9HAAs, bromate, and dalapon

## CONCLUSIONS

This study evaluated an IC-MS method for the determination of all nine haloacetic acids, bromate, and dalapon in drinking water. The method used a Dionex ICS-6000 HPIC system with DP pump and Dionex IonPac AS31 anion-exchange column coupled with suppressed conductivity detection and a single quadrupole mass spectrometer ISQ EC detector. The method is sensitive for the determination of U.S. EPA regulated HAA5 (MCAA (MDL = 0.1 µg/L), MBAA (MDL = 0.03 µg/L), DCAA (MDL = 0.03 µg/L), DBAA (MDL = 0.16 µg/L), and TCAA (MDL = 0.67 µg/L)), bromate (MDL = 0.12 µg/L), and dalapon (MDL = 0.12 µg/L). Plus, the method is sensitive for the determination of not yet regulated HAAs (BCAA (MDL = 0.16 µg/L), BDCAA (MDL = 2.79 µg/L), CDBAA (MDL = 1.04 µg/L), TBAA (MDL = 4.55 µg/L)). The method is accurate for the determination of 10 of 11 analytes in U.S. EPA Method 557 (MCAA, MBAA, bromate, dalapon, DCAA, BCAA, DBAA, TCAA, BDCAA, and CDBAA) with recoveries ranging from 92% to 119% when spiked with 10 µg/L of nine HAAs, bromate, and dalapon in LSSM. The method is precise with retention time precision below 0.1% and internal standard corrected peak area interday precision ranging from 0.7% to 4%.

## REFERENCES

1. Drinking Water Treatment; EPA 810-F-99-013; U.S. Environmental Protection Agency, 1999.
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5. World Health Organization. Disinfectants and Disinfection By-Products; International Program on Chemical Safety-Environmental Health Criteria 216; Geneva, Switzerland, 2000.
6. U.S. Environmental Protection Agency Method 557: "Determination of Haloacetic Acids, Bromate, and Dalapon in Drinking Water by Ion Chromatography Electrospray Ionization Tandem Mass Spectrometry (IC-ESI-MS/MS)" (September 2009).

## TRADEMARKS/LICENSING

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