

Determination of Haloacetic Acids in Drinking Water Using Matrix Elimination Ion Chromatography

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ABSTRACT

Drinking water in the U.S. is currently monitored for the presence of disinfection byproducts (DBPs), including haloacetic acids (HAAs), to ensure public safety. Of the nine HAAs commonly found, only five are regulated under the U.S. EPA Stage 2 Disinfectants/Disinfection Byproducts Rule. In the recently announced Unregulated Contaminant Monitoring Rule 4 (UCMR4), it was proposed that HAA6Br (brominated HAAs) and HAA9 be monitored in addition to HAAs. This presentation describes the use of matrix elimination ion chromatography (MEIC) to quantitate HAAs at low ppb concentrations. With this direct injection method, recoveries for HAAs ranged from 80–120% and the lowest concentration minimum reporting levels (LCMRL) were sub-ppb, levels that are comparable to those obtained using IC-coupled to tandem mass spectrometry MS/MS (EPA Method 557).

INTRODUCTION

Disinfection byproducts (DBPs) are a class of compounds formed through reaction of organic matter with disinfectants in the treatment process for municipal drinking water. These compounds, which include haloacetic acids (HAAs), are known carcinogens that have been regulated for many years. There are nine HAAs commonly found (HAA9), but only monochloro-, monobromo-, dichloro-, dibromo-, and trichloroacetic acids (HAA5) are regulated under the U.S. EPA Stage 2 Disinfectants/Disinfection Byproducts Rules at a cumulative total concentration of less than 60 ppb annually. In the recently announced Unregulated Contaminant Monitoring Rule 4 (UCMR4)¹, it was proposed that HAA6Br (brominated HAAs) and HAA9 be monitored in addition to HAA5 (Table 1). There are currently two U.S. EPA methods approved for HAA determination, Methods 552.3² and 557³. This work presents an alternative method using matrix elimination ion chromatography (MEIC) in which the first dimension, a 4 mm i.d. column is used to separate matrix components from HAAs, which are then transferred to a concentrator column (Figure 1). The captured HAAs are then separated on a 0.4 mm i.d. column with different selectivity than the first dimension column. The use of columns with different internal diameters yields enhanced sensitivity and the two different chemistries provide additional selectivity, reducing the potential for inaccurate reporting due to co-elution.

Table 1. Haloacetic Acids (HAA5, HAA6Br, and HAA9)

	Acid	HAA	Formula	pK _a
HAA5	Monochloroacetic Acid	MCAA	ClCH ₂ CO ₂ H	2.86
	Dichloroacetic Acid	DCAA	Cl ₂ CHCO ₂ H	1.25
	Trichloroacetic Acid	TCAA	Cl ₃ CCO ₂ H	0.63
HAA9	Monobromoacetic Acid	MBAA	BrCH ₂ CO ₂ H	2.87
	Dibromoacetic Acid	DBAA	Br ₂ CHCO ₂ H	1.47
	Tribromoacetic Acid	TBAA	Br ₃ CCO ₂ H	0.66
HAA6Br	Bromochloroacetic Acid	BCAA	BrClCHCO ₂ H	1.39
	Chlorodibromoacetic Acid	CDBAA	Br ₂ ClCCO ₂ H	1.09
	Bromodichloroacetic Acid	BDCAA	Cl ₂ BrCCO ₂ H	1.09

UCMR 4 (2017-2021, 30 contaminants)

Regulated (EPA)

MATERIALS AND METHODS

Sample Preparation

At time of collection, 100 mg/L NH₄Cl was added to water samples, which were stored at 4 °C until analyzed.

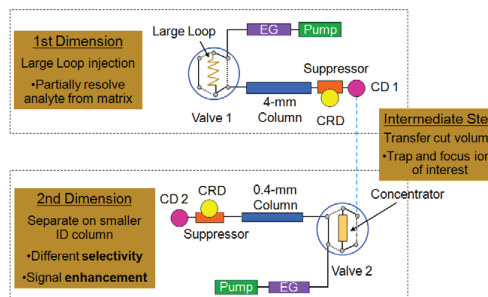
Instrumentation

- Thermo Scientific™ Dionex™ ICS-5000+ HPIC system
- Thermo Scientific™ Dionex™ AS-AP Autosampler
- Thermo Scientific™ Dionex™ AXP Pump

Data Analysis

Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software.

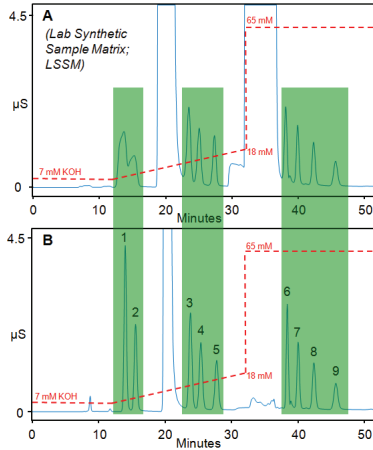
Figure 1. Matrix Elimination IC Setup.



Dionex ICS-5000+ HPIC System

RESULTS

Figure 2. First Dimension Cuts.



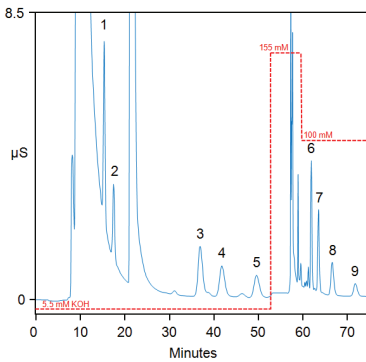
Columns: Thermo Scientific™ Dionex™ IonPac™ AG24A/AS24A, 4 mm
 Flow Rate: 1.0 mL/min
 Eluent: KOH: 7 mM (0–12 min), 7 to 18 mM (12–32 min), Step to 65 mM at 32.1 min
 Eluent Source: Thermo Scientific™ Dionex™ EGC-500 KOH cartridge
 Detection: Suppressed conductivity
 Inj. Volume: 500 µL
 Temp.: 15 °C
 Sample: 1 ppm HAA9 in A. LSSM* B. 100 ppm NH₄Cl

Peaks:

12-17 min	1. MCAA	6. TCAA
	2. MBAA	7. BDCAA
22-29 min	3. DCAA	8. CDBAA
	4. BCAA	9. TBAA
	5. DBAA	
		37-48 min

*LSSM = 250 ppm Cl⁻, 250 ppm, SO₄²⁻, 150 ppm HCO₃⁻, 10 ppm NO₃⁻, 100 ppm NH₄Cl

Figure 3. Second Dimension Chromatography.



Columns: Dionex IonPac AG26/AS26, 0.4 mm
 Flow Rate: 0.012 mL/min
 Eluent: KOH: 5.5 mM (0–50 min), Step to 155 mM at 53 min, Step to 100 mM at 60 min
 Eluent Source: Thermo Scientific Dionex EGC KOH capillary cartridge
 Detection: Suppressed conductivity
 Concentrator: Thermo Scientific™ Dionex™ IonSwift™ MAC-200 column
 Temp.: 15 °C
 Sample: 20 ppb HAA9 in 100 ppm NH₄Cl

Peaks:

1. MCAA	6. TCAA
2. MBAA	7. BDCAA
3. DCAA	8. CDBAA
4. BCAA	9. TBAA
5. DBAA	

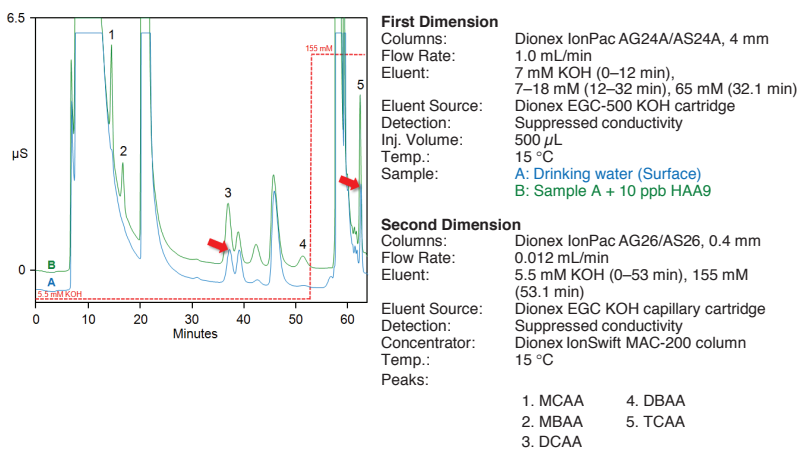
To determine the cut windows for the first dimension, one ppm HAA standard mixture was injected and the cut windows adjusted so that they encompassed all nine HAAs, even in the presence of high salt (LSSM; Figure 2).

For the Lowest Concentration Minimum Reporting Level (LCMRL) determination, data collected from four replicates of eight concentrations of HAAs (0.05–2 µg/L) were entered into the U.S. EPA LCMRL calculator application. The results were comparable to those included in EPA method 557 (Table 2).

Table 2. LCMRL Results Comparing Calculated to EPA Method 557.

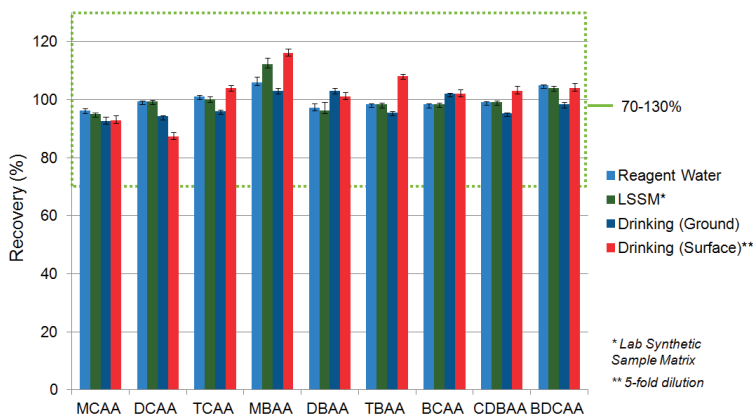
HAA	Calculated LCMRL (µg/L)	U.S. EPA Method 557 (µg/L)
MCAA	0.085	0.58
DCAA	0.41	0.13
TCAA	0.26	0.25
MBAA	0.10	0.19
DBAA	0.090	0.062
TBAA	0.28	0.27
BCAA	0.30	0.16
CDBAA	0.055	0.080
BDCAA	0.29	0.19

Figure 4. HAA5 in Drinking Water (Surface) Before and After Fortification.



All of the HAAs in water samples had levels of HAAs that were within the calibration range (0.5–20 µg/L) except for drinking water that had been derived from a surface source, which had levels for DCAA and TCAA that exceeded 30 µg/L prior to fortification (red arrows in Fig. 4). To ensure that the samples would be in range following HAA addition, surface water was diluted 5-fold prior to determination of accuracy and precision (Figure 5).

Figure 5. HAA Method Accuracy and Precision.



To determine the accuracy (% recovery) and precision of the method, seven replicate solutions containing 10 ppb HAAs in reagent water, LSSM, and drinking water derived from surface and ground water sources were analyzed (Figure 5). The percent recoveries were well within 70–130%, which is a generally accepted range, with relative standard deviations that ranged from 0.2–3.0.

CONCLUSIONS

The matrix elimination IC method for HAAs is a viable alternative to U.S. EPA Methods 552.3 and 557. Advantages include:

- HAAs are directly determined
- No multiple and lengthy derivitization steps
- The method is selective and sensitive
- Designed to reduce matrix interference effects
- Similar to other matrix elimination IC methods that have regulatory acceptance
- Simplified and less costly using a single system, such as the Dionex ICS-5000+ HPIC system with its dual system capabilities and enhanced temperature controls

REFERENCES

1. U.S. Environmental Protection Agency (EPA). Fourth Unregulated Contaminant Monitoring Rule (UCMR4). <https://www.epa.gov/dwucmr/fourth-unregulated-contaminant-monitoring-rule>
2. Domino, M.M.; Pepich, B.V.; Munch, D.J.; Fair, P.S.; and Xie, Y. Method 552.3: Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Microextraction, Derivatization, and Gas Chromatography With Electron Capture Detection. Doc. No. 815-B-03-002. U.S. Environmental Protection Agency, Cincinnati, OH, 2003.
3. Zaffiro, A.D.; Zimmerman, M.; Pepich, B.V.; Slingsby, R.W.; Jack, R. F.; Pohl, C. A.; and Munche, D. J. Method 557: Determination of Haloacetic Acids, Bromate, and Dalapon in Drinking Water by Ion Chromatography Electrospray Ionization Tandem Mass Spectrometry (IC-ESI-MS/MS). Doc. No. 815-B-09-012. U.S. Environmental Protection Agency, Cincinnati, OH, 2009.

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