

# Evaluation of Various Anion-Exchange Chemistries for the Analysis of Haloacetic Acids in Drinking Water Using 2-D Matrix Elimination Ion Chromatography and Suppressed Conductivity Detection

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## Executive Summary

Haloacetic acids (HAAs) are drinking water disinfection byproducts that are regulated due to their potential carcinogenicity. Analysis of trace levels of HAAs in high ionic strength drinking water matrices is challenging. Traditional GC methods require laborious and time-consuming sample preparation and derivatization steps prior to analysis. Direct injection IC-MS-based methods are highly sensitive and selective, and obviate the need for extensive sample pretreatment and derivatization, but ESI-MS instrumentation may not be readily available in routine monitoring laboratories. Two-dimensional matrix elimination IC (MEIC) with suppressed conductivity detection is a simple and cost-effective alternative for sensitive and selective quantitative determination of ppb levels of HAAs in drinking water samples. Optimization of anion-exchange chemistry is critical for maximum method performance.

## Keywords

Haloacetic acids, Water analysis, 2-D ion chromatography, ICS-3000

## Abstract

Disinfecting water is an important step when processing drinking water. However, commonly used disinfectants, such as chlorine, chlorine dioxide, chloramine, and ozone, react with naturally occurring organic and inorganic matter in the source water to form disinfectant byproducts that are potentially harmful to humans. The U.S. EPA has regulated five haloacetic acids referred to as HAA5, which include monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid. Stage 1 Disinfectants/Disinfection Byproducts Rule regulates the HAA5 at 60 µg/L annual average.

U.S. EPA Methods 552.1, 552.2, and 552.3 are presently used for analyzing the HAAs. These methods are labor intensive and require multiple extraction and derivatization steps. Recently, a direct injection IC-MS and IC-MS-MS method that uses a high capacity Thermo Scientific™ Dionex™ IonPac™ AS24 anion-exchange column showed excellent separation of nine HAAs and bromate with greater than 90% recovery in the presence of high concentrations of matrix ions such as chloride and sulfate. In this analysis, we evaluated a direct injection suppressed conductivity detection method for analyzing HAAs. Additionally, we evaluated the use of two-dimensional MEIC in conjunction with various column chemistries such as Dionex IonPac AS11-HC, AS16, AS19, and AS24.

Table 1. What Are HAAs?

Acid	Abbreviation	Chemical Formula	pKa	Boiling Point °C
Monochloroacetic Acid	MCAA*	ClCH <sub>2</sub> CO <sub>2</sub> H	2.86	187.8
Dichloroacetic Acid	DCAA*	Cl <sub>2</sub> CHCO <sub>2</sub> H	1.25	194
Trichloroacetic Acid	TCAA*	Cl <sub>3</sub> CCO <sub>2</sub> H	0.63	197.5
Monobromoacetic Acid	MBAA*	BrCH <sub>2</sub> CO <sub>2</sub> H	2.87	208
Dibromoacetic Acid	DBAA*	Br <sub>2</sub> CHCO <sub>2</sub> H	N/A	195
Tribromoacetic Acid	TBAA	Br <sub>3</sub> CCO <sub>2</sub> H	0.66	245
Bromochloroacetic Acid	BCAA	BrClCHCO <sub>2</sub> H	N/A	103.5
Dibromochloroacetic Acid	DBCBA	Br <sub>2</sub> ClCCO <sub>2</sub> H	N/A	N/A
Dichlorobromoacetic Acid	DCBAA	Cl <sub>2</sub> ClCCO <sub>2</sub> H	N/A	N/A

\* MCAA, DCAA, TCAA, MBAA, and DBAA are collectively referred to as HAA5.

## U.S. EPA Regulation

### Current: Stage 2 Disinfection Byproducts Rule (DBPR)

- Monitoring of HAA5 at all plants that disinfect with chlorine
  - Total MCAA, MBAA, DCAA, DBAA, and TCAA
  - Maximum contamination level (MCL) = 60 µg/L annual average
- Maximum contamination level goal (MCLG)
  - DCAA should not be present
  - TCAA less than 30 µg/L
- Bromate
  - MCL = 10 µg/L
  - MCLG = not present

### Drinking Water Matrix

Sulfate in drinking water currently has a secondary maximum contaminant level (SMCL) of 250 mg/L, based on aesthetic effects (i.e., taste and odor). This regulation is not a federally enforceable standard, but is provided as a guideline for states and public water systems. U.S. EPA estimates that about 3% of the public drinking water systems in the country may have sulfate levels of 250 mg/L or greater.

- Chloride 250 mg/L
- Nitrate 20 mg/L
- Ammonium chloride 100 mg/L

### Current Methods

- U.S. EPA 552.1, 552.2, and 552.3  
Liquid-liquid microextraction, derivatization, and gas chromatography with:
  - (a) Electron capture detection
  - (b) Mass spectrometry detection
- Suppressed ion chromatography with MS or MS-MS detection:
  - Direct injection method
  - Matrix diversion setup
  - No need for liquid-liquid extraction or sample pretreatment
  - No need for derivatization
  - Fully automated
  - Coelution not an issue since MS is a selective detector
  - Recovery >90%

Table 2. Column chemistry details.

Column	Functionality	Capacity µeqv/ Column	Hydrophobicity
Dionex IonPac AS16, 4 × 250 mm	Alkanol quaternary ammonium	170	Ultralow
Dionex IonPac AS19, 4 × 250 mm	Alkanol quaternary ammonium	240	Low
Dionex IonPac AS20, 4 × 250 mm	Alkanol quaternary ammonium	310	Low
Dionex IonPac AS24, 2 × 250 mm	Alkanol quaternary ammonium	140	Ultralow

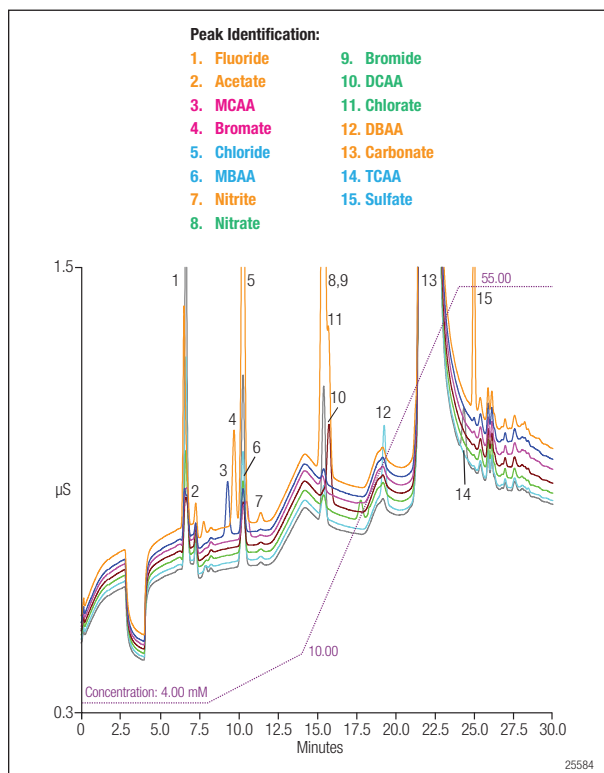


Figure 1. Analysis of HAA5 in the presence of inorganic matrix ions using a Dionex IonPac AS16 column at 30 °C. HAA5 is poorly resolved or coelutes with matrix ions as shown above (colored labels).

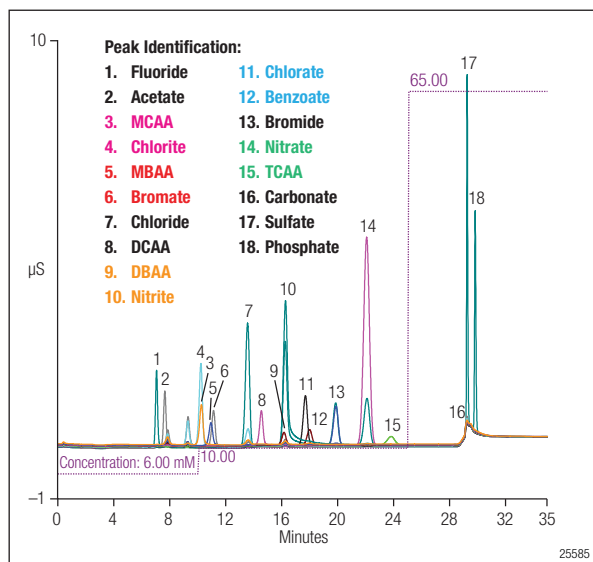


Figure 2. Analysis of HAA5 in the presence of inorganic matrix ions using a Dionex IonPac AS19 column at 15 °C. HAA5 is poorly resolved or coelutes with matrix ions as shown above (colored labels).

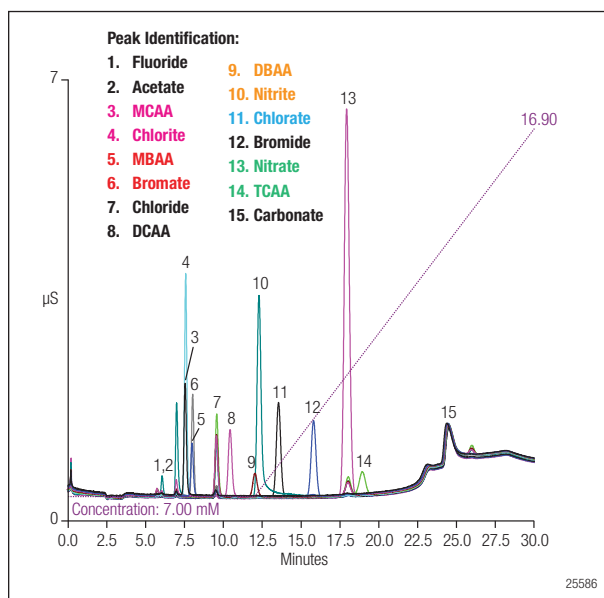


Figure 3. Analysis of HAA5 in the presence of inorganic matrix ions using a Dionex IonPac AS20 column at 15 °C. HAA5 is poorly resolved or coelutes with matrix ions as shown above (colored labels).

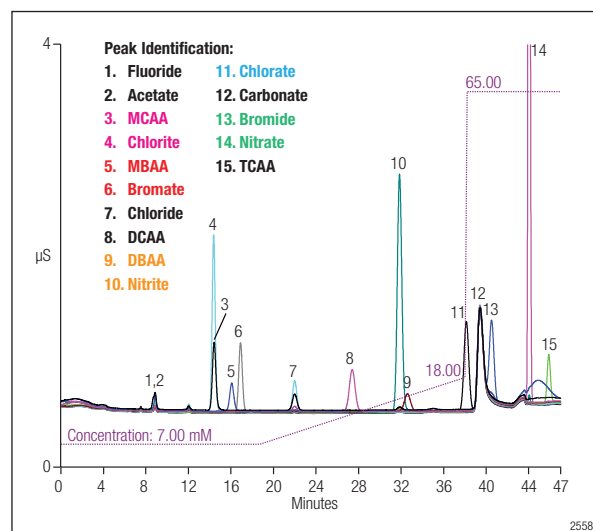


Figure 4. Analysis of HAA5 in the presence of inorganic matrix ions using a Dionex IonPac AS24 column at 15 °C. HAA5 is poorly resolved or coelutes with matrix ions as shown above (colored labels).

## Matrix Elimination Ion Chromatography

### Features

- Allows for large loop injection in the first dimension (4 mm column):
  - Possible to inject a larger loop than the standard approach since the capacity and selectivity of the analytical column in the first dimension dictates the recovery, and the analyte of interest is analyzed in the second dimension
- Focus the ions of interest in a concentrator column after suppression in the first dimension:
  - Hydroxide eluent suppressed to deionized (DI) water, thus providing an ideal environment for focusing or concentrating the ions of interest
- Pursue analysis in the second dimension using a smaller column format with a smaller cross-sectional area, leading to sensitivity enhancement that is proportional to the flow rate ratio:
  - For example, for a 4 mm column operated in the first dimension at 1 mL/min and a 1 mm column operated in the second dimension at 0.05 mL/min, the enhancement factor is 20
- Pursue analysis in the second dimension using a different chemistry:
  - Enhanced selectivity
- Easy implementation on the Thermo Scientific Dionex ICS-3000 system

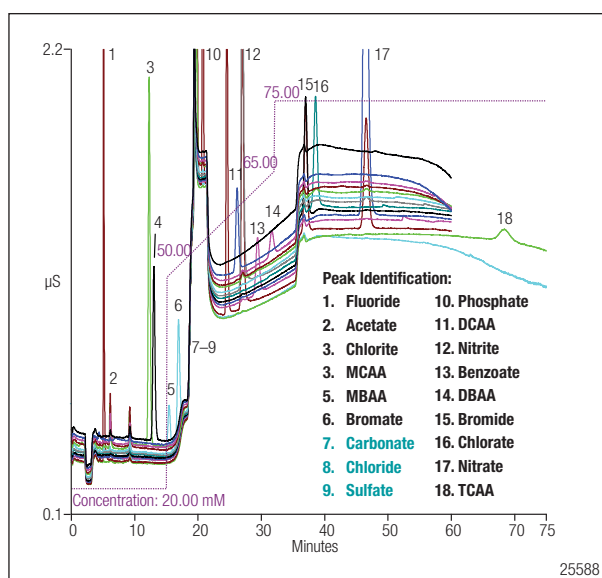


Figure 5. Analysis of HAA5 in the presence of inorganic matrix ions using a new prototype anion-exchange chemistry at 15 °C. Excellent resolution of all HAA5 was achieved in the presence of matrix ions.

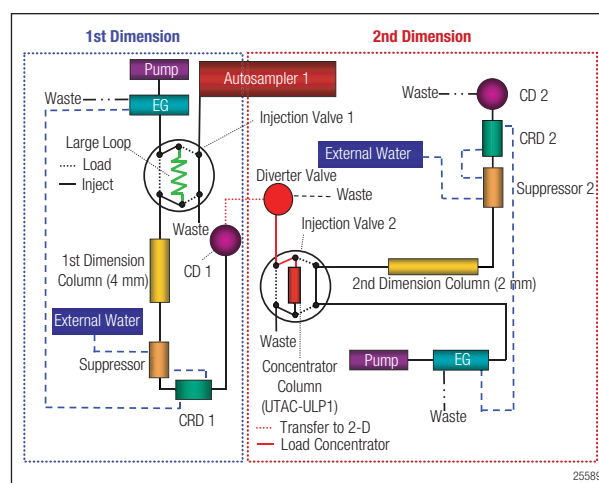


Figure 6. Diagram of an MEIC 2-D system setup.

Figure 7 shows analysis of HAA5 in reagent water (DI water). The top chromatogram shows the analysis in the first dimension of the MEIC setup using a 4 mm Dionex IonPac AS19 column. Excellent resolution of HAA5 can be inferred. The bottom chromatogram shows the analysis in the second dimension of the MEIC setup using a 2 mm Dionex IonPac AS19 column.

In Figure 8, conditions are similar to Figure 7, except the sample is high-ionic-strength water (HIW). Under these conditions, the matrix ions overwhelm the analytes, as shown in the top chromatogram. The bottom chromatogram shows the analysis in the second dimension using the MEIC setup. Performance is similar to what was shown in Figure 7B. The above example demonstrates the utility of the MEIC methodology for this work.

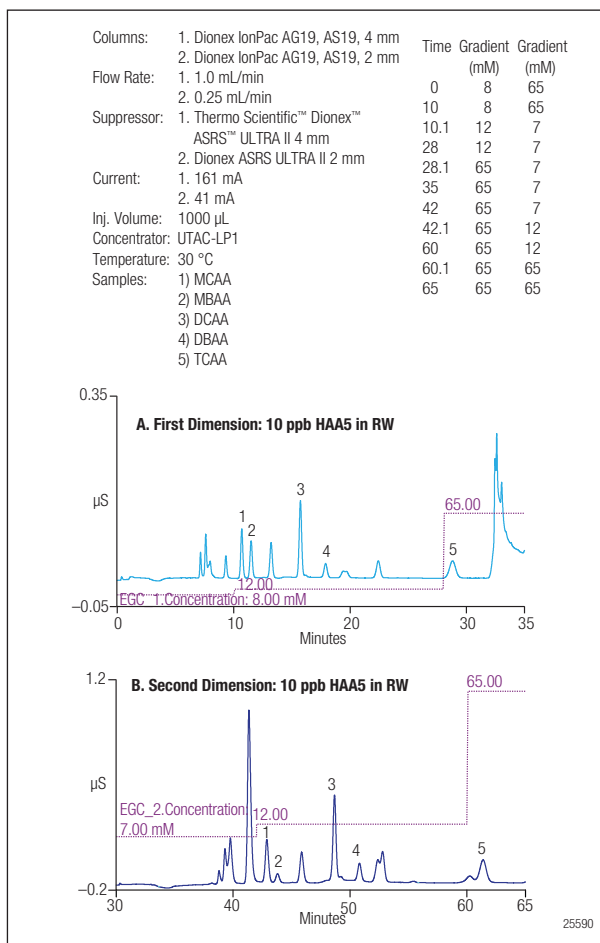


Figure 7. MEIC analysis of HAA5 in reagent water (deionized water).

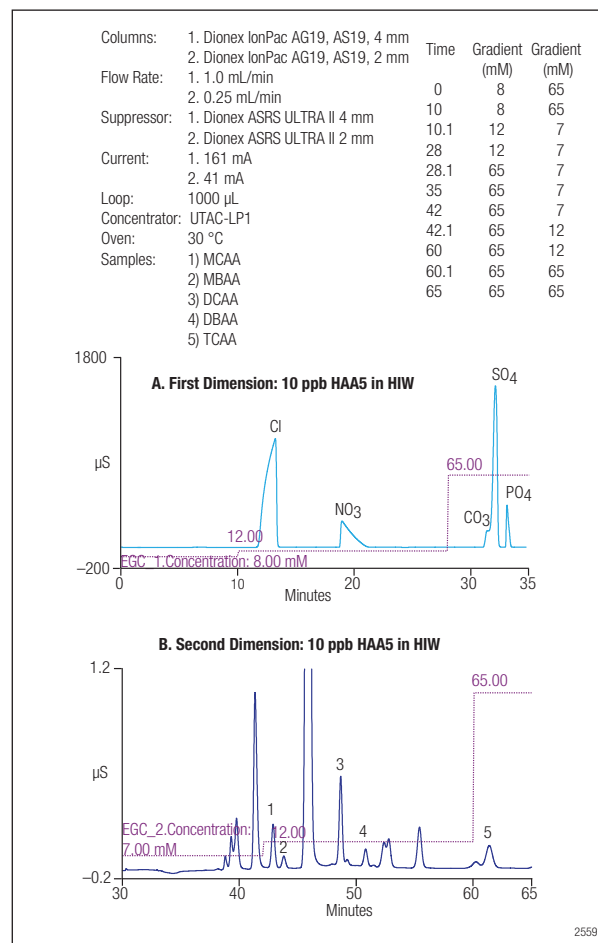


Figure 8. MEIC analysis of HAA5 in HIW (high ionic strength water).

## Conclusion

An MEIC method was developed for the analysis of HAAs in drinking water matrices. HAA5 were detected at low ppb levels in reagent water and in high-ionic-strength water. Several column chemistries were evaluated and a new high capacity stationary phase was found to optimize separation selectivity and method performance. MEIC is a (potentially) simple and economical alternative to current GC- and IC-MS techniques for routine monitoring of HAAs in drinking water.

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