

Two-Dimensional Matrix-Elimination Ion Chromatography for Trace Ion Analysis

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ABSTRACT

Purpose: To improve the detection of trace amounts of analytes in the presence of a large amount of matrix ions in water samples.

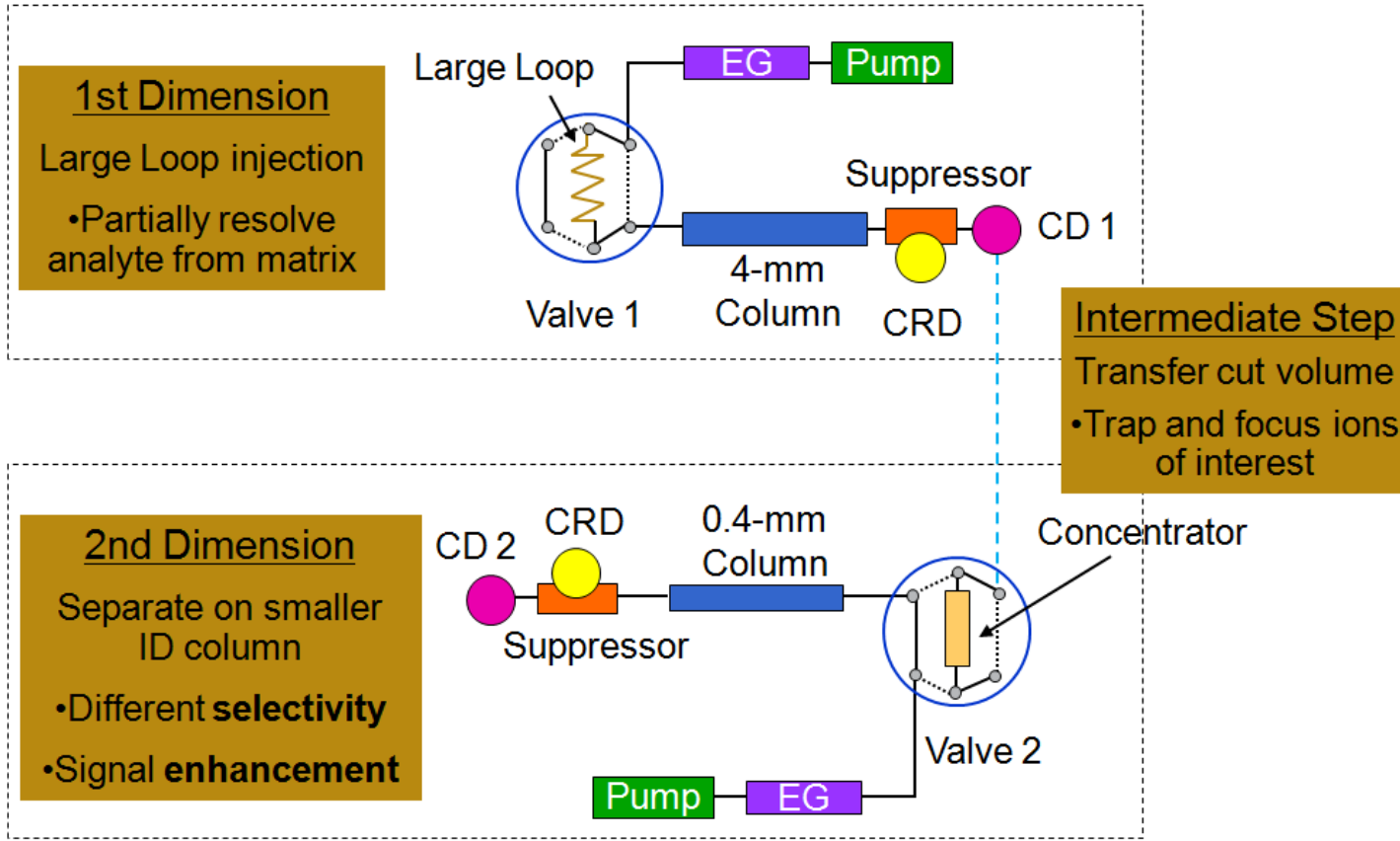
Methods: Two-dimensional matrix-elimination ion chromatography was developed for the trace analysis. The matrix ions were eliminated in the first dimension, while the ions of interest would be analyzed in the second dimension.

Results: The method was applied successfully for the analysis of perchlorate, bromate, and haloacetic acids in drinking water samples and showed excellent recovery and detection limits.

INTRODUCTION

Ion chromatography with suppressed conductivity detection has been used routinely for ion analysis. To achieve lower detection limits, a large volume of sample needs to be preconcentrated onto a concentrator column before analysis. The presence of matrix ions will shift the retention time and distort the peak shapes of peaks of interest, leading to poor quantitation. To address this issue, a two-dimensional matrix elimination ion chromatography has been developed. This approach utilizes a large-format column in the first dimension to separate the matrix ions from the analytes of interest. After the suppression of the eluent in the first dimension, the cell effluent becomes essentially deionized water and can be enriched onto a concentrator column to focus the ion of interest. The trace ion of interest can subsequently be analyzed in the second dimension by using a small-format column to provide enhanced sensitivity with a concentration-sensitive detector, such as a conductivity detector. For example, if a 4 mm column format is used for the first dimension and a 2 mm column is used for the second dimension, it will result in a four-fold enhancement in sensitivity. The first and second dimension column chemistry can also be optimized to provide enhanced selectivity.

Figure 1. Two-Dimensional Matrix Elimination Ion Chromatography Schematic



MATERIALS AND METHODS

Sample Preparation

For bromate analysis, 50 mg/L EDA was added to water samples at time of collection.

For haloacetic acid analysis, 100 mg/L NH₄Cl was added to water samples at time of collection and the samples were stored at 4 °C until analyzed.

Instrumentations

Thermo Scientific™ Dionex™ ICS-5000+ HPLC™ system

Thermo Scientific™ Dionex™ AS-AP Autosampler

Thermo Scientific™ Dionex™ AXP Pump

Data Analysis

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

RESULTS

Perchlorate Analysis

Figure 2. 0.5 µg/L perchlorate spiked in high ionic strength water; A: First dimension analysis; B: Second dimension analysis.

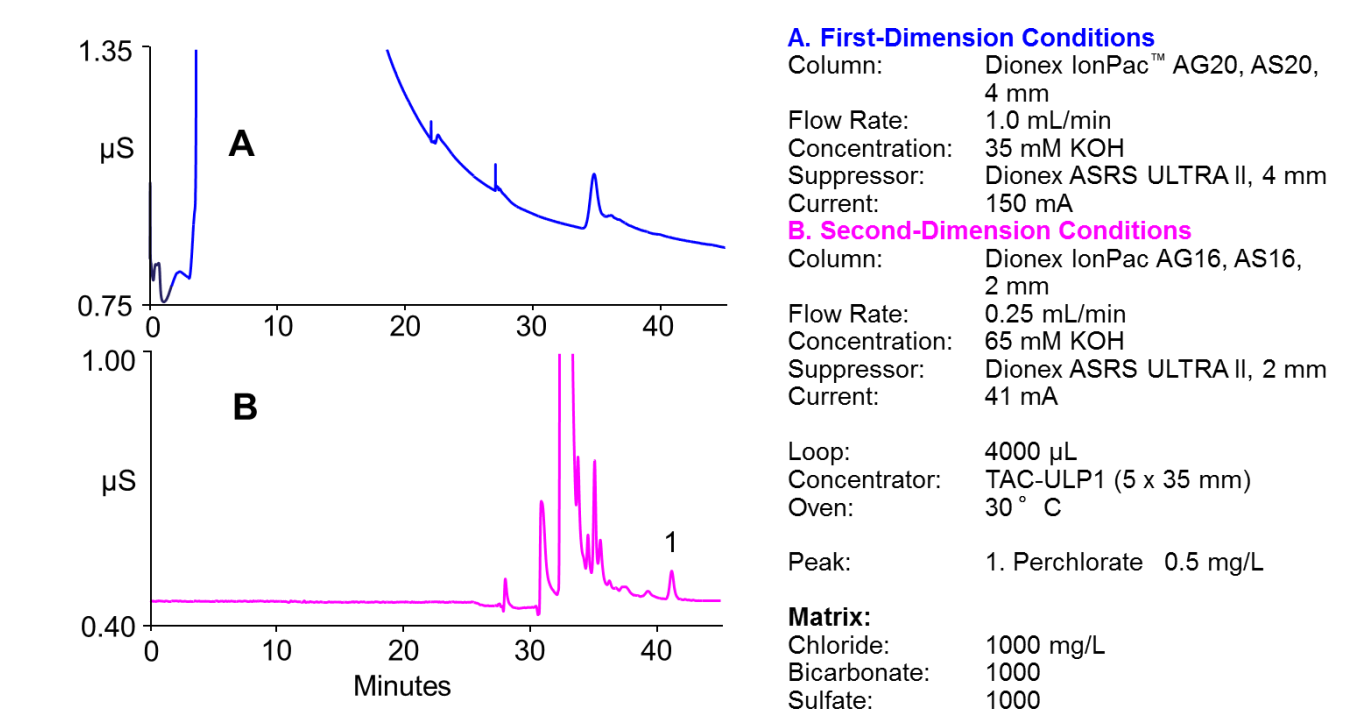


Table 1. Linearity and Method Detection Limits.

Method	Range (mg/L)	Linearity* (r ²)	MDL ^b (mg/L)	Retention Time Precision (%RSD ^a)	Peak Area Precision (%RSD)
2D ClO ₄ ⁻	0.3–10	0.9998	0.016	0.02	2.66
Primary (Method 314.1)	0.5–10	0.9999	0.023	0.06	5.15
Confirmatory (Method 314.1)	0.5–10	0.9999	0.026	0.10	5.64

Table 2. Precision and accuracy for perchlorate analysis in different water samples

Matrix	Spiked Perchlorate (µg/L)	MEIC %	Primary Method (314.1) %	Confirm. Method (314.1) %	MEIC	Primary Method (314.1)	Confirm. Method (314.1)
HIW	0.5	2.07	4.24	4.10	95.8	93.3	95.7
	5.0	0.21	2.22	2.22	99.7	106.4	101.8
Sunnyvale Tap Water	0.5	1.40	3.30	N/A	95.9	106.6	N/A
	5.0	0.74	1.42	5.96	98.9	97.4	120.1
San Jose Tap Water	0.5	1.77	3.40	2.28	102.0	98.8	103.8
	5.0	0.94	2.60	2.21	99.0	108.8	108.7
Scotts Valley Tap Water	0.5	1.53	4.00	N/A	97.1	107.8	N/A
	5.0	0.99	2.24	4.95	100.9	112.0	107.3
Palo Alto Tap Water	0.5	1.54	—	—	100.8	—	—
	5.0	0.98	—	—	100.9	—	—

Bromate Analysis

Bromate is a disinfection byproduct typically encountered when water is disinfected with ozone during the water treatment process. It has been shown that bromate is a possible carcinogen and long-term exposure to bromate can pose significant health risks. The U.S. EPA regulates bromate at a maximum contamination level (MCL) of 10 µg/L and a maximum contamination level goal (MCLG) of 0 µg/L.

Figure 3. First dimension for bromate analysis.

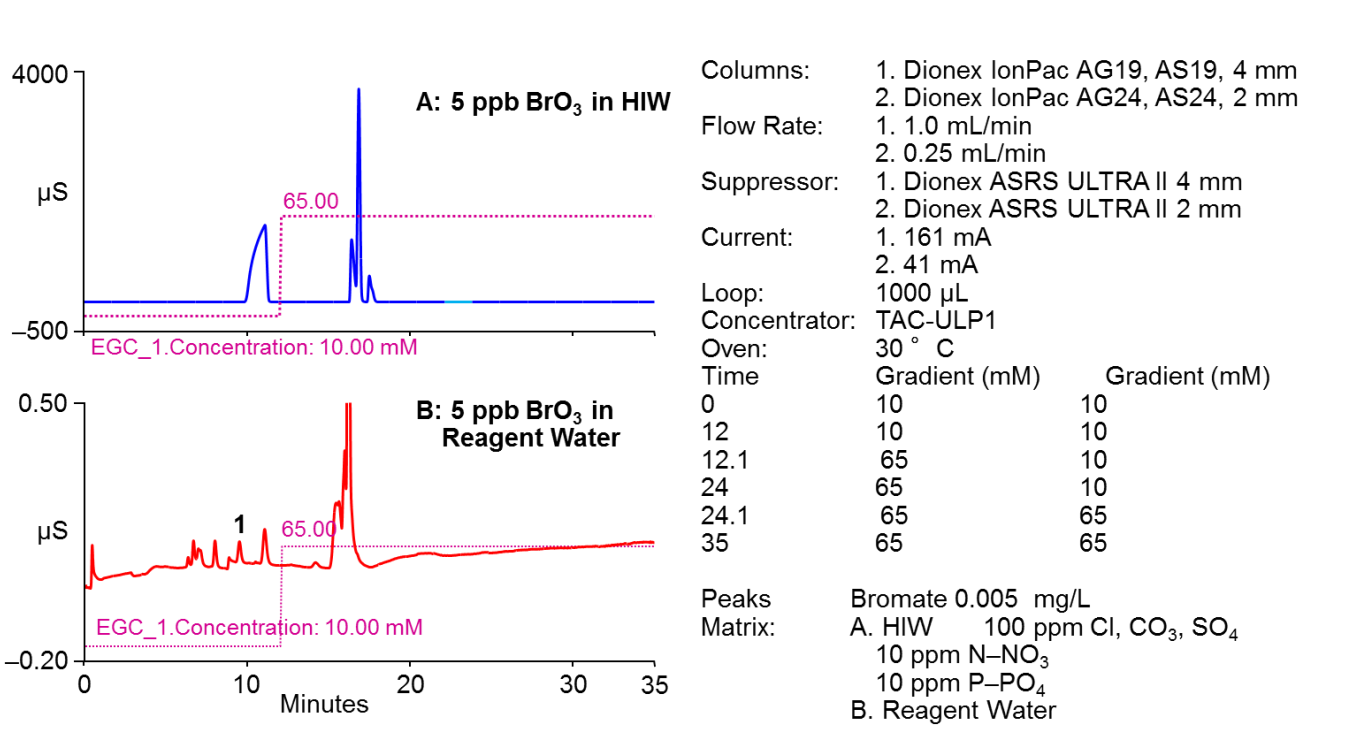


Figure 4. Second dimension for bromate analysis.

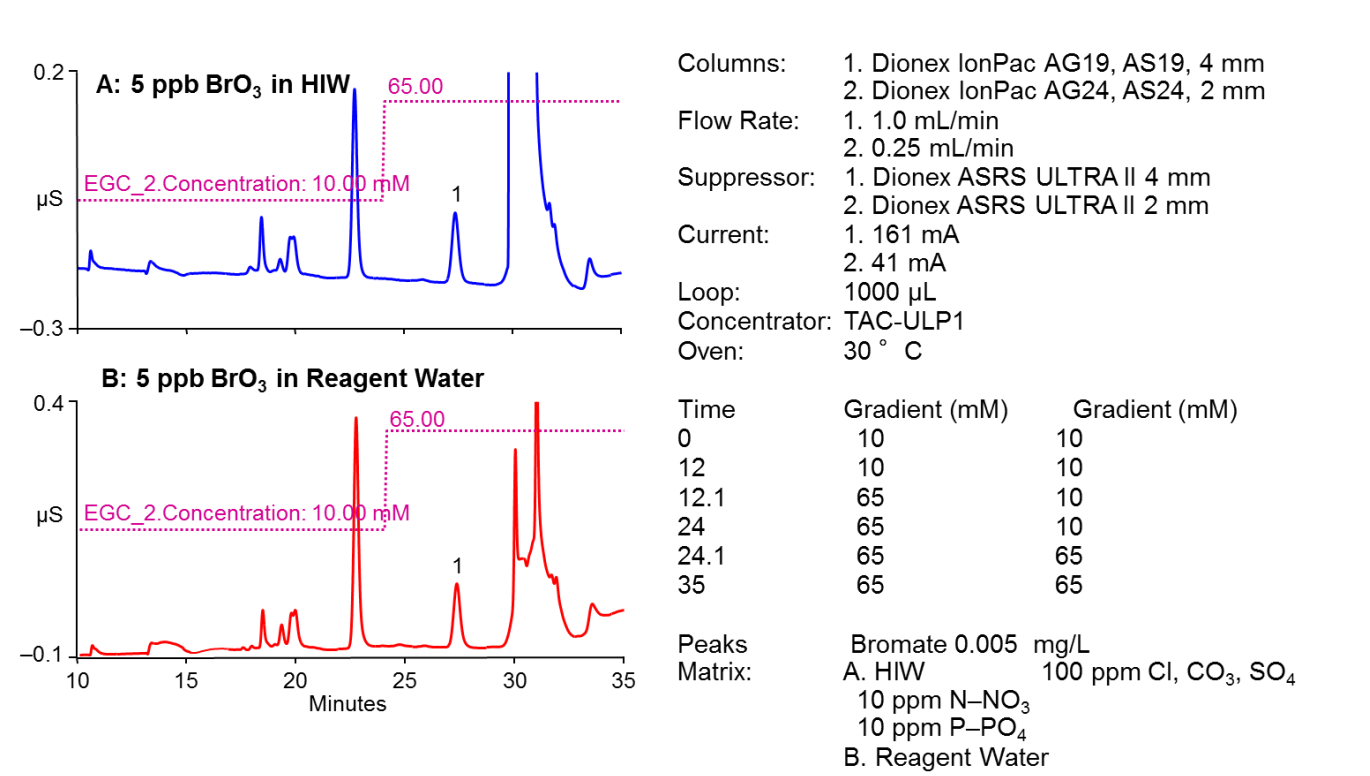


Table 3. Precision and accuracy for bromate analysis in different water samples.

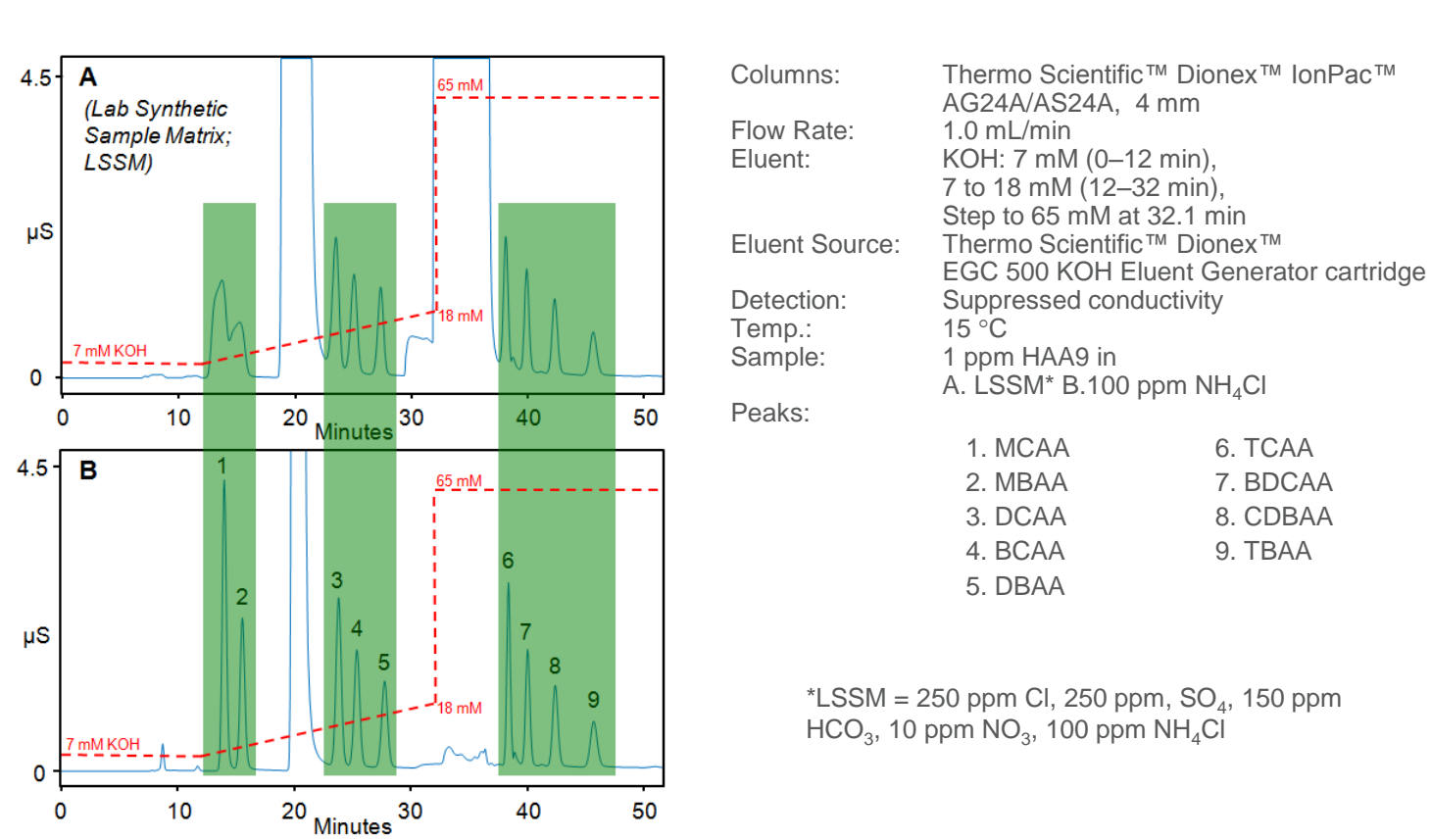
Matrix/Location	Bromate Found (mg/L)	Spiked Bromate (mg/L)	Peak Area Precision (RSD)	Recovery (%)
Reagent Water	—	0.5	4.36	96.6
		5.0	1.17	99.4
HIW	—	0.5	3.39	96.9
		5.0	1.48	101.2
Lebanon	0.41	0.5	1.77	103.7
		5.0	1.75	100.5
Fort Mitchell	0.99	0.5	3.60	108.5
		5.0	2.70	101.9
Cincinnati	<MDL	0.5	4.40	79.8
		5.0	0.89	102.9
Celine	0.23	0.5	5.27	96.1
		5.0	0.80	101.2

Haloacetic Acid Analysis

Haloacetic acids are a group of disinfection byproducts resulting from the reaction of naturally occurring organic matter and bromide in drinking water with chemical disinfectants, used in processing drinking water, such as chlorine and chloramine. Long-term exposure to these haloacetic acids is known to have adverse effects on human health. There are nine haloacetic acid congeners, commonly referred to as HAA9: 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). Out of these nine haloacetic acids, five (MCAA, MBAA, DCAA, DBAA and TCAA) are currently regulated by the U.S. EPA. Under the Stage 2

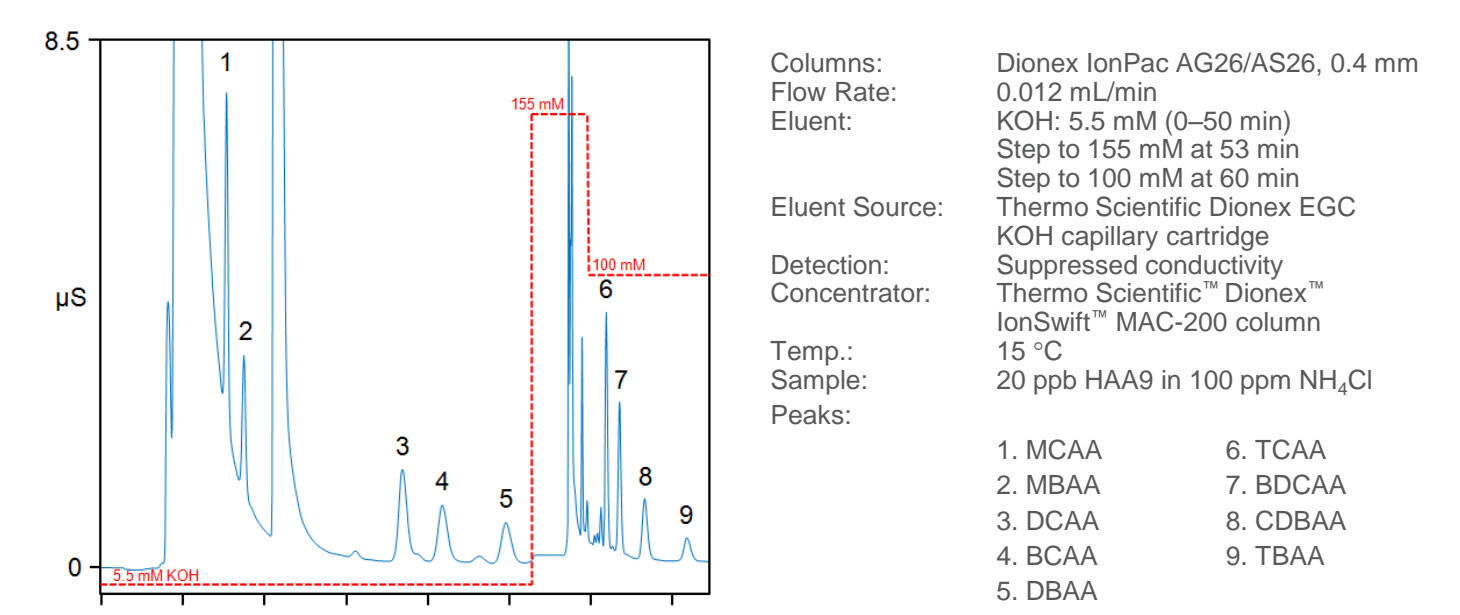
Disinfectants and Disinfection Byproducts rules set by the U.S. EPA, the maximum contamination level (MCL) for these five haloacetic acids (HAA5) is set at 60 µg/L. In the recently announced Unregulated Contaminant Monitoring Rule 4 (UCMR4)1, it was proposed that HAA6Br (brominated HAAs) and HAA9 be monitored in addition to HAA5.

Figure 5. First dimension cuts.



To determine the cut windows for the first dimension, 1 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 5).

Figure 6. Second dimension analysis of haloacetic acids.



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 4).

Table 4. Method detection limit.

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 7. Precision and accuracy for haloacetic acid analysis in different water samples.



CONCLUSIONS

The two-dimensional matrix-elimination ion chromatography methods show:

- Enhanced sensitivity for selected analytes (bromate, perchlorate, and HAA9) using suppressed conductivity detection.
- Enhanced selectivity due to two different column chemistries, resulting in minimal interference from matrix ions.
- Direct injection method, no sophisticated sample preparation and easy automation.

Overall, this is a simpler analytical method when compared to post-column reaction methods.

TRADEMARKS/LICENSING

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