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EPA Method 557 Quantitation of Haloacetic Acids, Bromate, and Dalapon in Drinking Water Using Ion Chromatography and Tandem Mass Spectrometry

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ABSTRACT

Purpose: To demonstrate a simple and sensitive IC-MS/MS method for analyzing haloacetic acids, the pesticide dalapon, and bromate in water using U.S. EPA method 557

Methods: Direct injection of drinking water samples using IC-MS/MS

Results: Quantitive analysis of nine haloacetic acids, bromate, and dalapon at sub-ppb levels

INTRODUCTION

Haloacetic acids (HAAs) are formed as disinfection byproducts when water is chlorinated to remove microbial content. Chlorine reacts with naturally occurring organic and inorganic matter in the water, such as decaying vegetation, to produce disinfection byproducts (DBPs) that include HAAs. Of the nine species of HAAs, five are currently regulated by the U.S. EPA (HAA5): monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA). The remaining four HAAs are currently unregulated: bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA). However, they are also of health concern, and are often analyzed along with the HAA5. This method allows for the analysis of all 9 HAAs, plus bromate and the pesticide dalapon in the same IC-MS/MS run, without sample preparation.

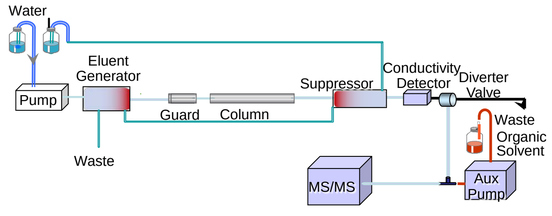
According to the U.S. EPA, there is an increased risk of cancer associated with long-term consumption of water containing levels of HAAs that exceed 0.06 mg/L.[1] EPA Methods 552.1, 552.2, and 552.3 are used to determine nine HAAs in drinking water[2,3,4] using derivatization and multiple extraction steps followed by gas chromatography (GC) with electron capture detection (ECD). By comparison to conventional EPA methods using GC-ECD, the combination of IC-MS and IC-MS/MS offers sensitive and rapid detection without the need for sample pretreatment. In order to develop a simple, easy-to-use direct injection method, the U.S. EPA promulgated method 557[5] for the analysis of HAAs, bromate, and dalapon in drinking water by IC-MS/MS.

MATERIALS AND METHODS

Sample Preparation

NH_4Cl was added as a preservative at 100 mg/L to all drinking water samples. No further sample preparation was performed prior to injection.

Figure 1. Schematic diagram of the flow path of the IC-MS/MS system



Ion Chromatography

IC analysis was performed on a Thermo Scientific™ Dionex™ ICS-5000⁺ system. Samples were directly injected and no sample pre-treatment was required. The IC conditions used are shown in Table 1. The sample is injected without cleanup or concentration onto a Thermo Scientific™ Dionex™ IonPac™ AS24 column specifically designed to separate method analytes from the following common anions (matrix components) in drinking water: chloride, carbonate, sulfate, and nitrate.

Mass Spectrometry

MS analysis was carried out on a Thermo Scientific™ TSQ Endura™ triple quadrupole mass spectrometer with a heated electrospray ionization (H-ESI-II) probe. The MS conditions used are shown in Table 3. Individual standards were infused into the mass spectrometer to determine optimum RF lens settings and collision energies for the product ions. Table 4 describes the MS conditions for specific HAAs, dalapon, bromate, and internal standards.

Data Analysis

Data acquisition and processing were carried out using Thermo Scientific™ TraceFinder™ software version 3.2.

Table 1. Ion chromatography system conditions.

Column	Dionex IonPac AG24 (2 × 50 mm), IonPac AS24 (2 × 250mm)
Suppressor	Dionex ASRS 300, 2 mm
Column Temp.:	15 °C
Injection Volume	100 µL
Flow Rate	0.3 mL/min KOH gradient, electrolytically generated

Table 2. Electrolytically formed hydroxide gradient.

Retention Time (min)	[KOH] mM
0.0	7.0
15.1	7.0
30.8	18.0
31.0	60.0
46.0	60.0
47.0	7.0
58.0	7.0

Table 3. Mass Spectrometer Source Conditions

Parameter	Value
Spray Voltage	3200 V, negative
Vaporizer Gas Pressure	45 units N_2
Auxiliary Gas Pressure	10 units N_2
Capillary and Vaporizer Temperature	200 C
Collision Gas Pressure	1.5 mTorr Argon
Ion Cycle Time	0.5 seconds

RESULTS

Calibrators and Simulated Sample Matrix

The separation of the nine HAAs and two other analytes is shown in Figure 2. This chromatogram is from the laboratory synthetic sample matrix (LSSM) fortified at 20 ppb. The LSSM is a prepared matrix of of 250 mg/L of each of chloride and sulfate, 150 mg/L of bicarbonate, 20 mg/L of nitrate, and 100 mg/L ammonium chloride preservative, for a total chloride concentration of 316 mg/L. All 11 compounds are shown in Figure 2. The selectivity of the IC-MS/MS system allows separation of the HAAs from common inorganic matrix ions. This allows matrix peaks of chloride, sulfate, nitrate, and bicarbonate to be diverted to waste during the analytical run and avoids premature fouling of the ESI-MS/MS instrument source. These ions do not coelute with the HAAs and are diverted to waste using the method controlled 6-port valve on the mass spectrometer. The IC stream is diverted to waste from 0–12, 16–22.75, and 30–37 min, and from 48 min until the end of the run.

An internal standard mixture of ^{13}C labeled MCAA, MBAA, DCAA, and TCAA was spiked into each sample at 4 ppb. All calibration standards were prepared in deionized water containing 100 mg/L NH_4Cl as a preservative. The calibration curves were generated using internal standard calibrations for all of the HAA compounds in water. Excellent linearity results were observed for all compounds. Analytes were run at levels of 250 ppt to 20 ppb in a seven-point calibration curve. All of the HAAs were detected at all concentration levels. It should be noted that TCAA sensitivity is very strongly correlated with the source temperature of the mass spectrometer as well as the column temperature of the IC column. For this reason, the column temperature was maintained at 15 °C as specified in the EPA method. Temperatures of 200 °C for both the ion transfer tube and vaporizer were found to be optimal for TCAA detection without impacting the detection of the other eight analytes. This phenomenon of TCAA temperature sensitivity has been reported in studies with other MS instrumentation configurations.[6]

Method detection limits (Table 4) were calculated by seven replicate injections of 0.5 ppb of each analyte and the equation *MDL=t99%xS(n-7)*, where: t is Student's t at 99% confidence intervals (t99%, n=7 = 3.143) and S is the standard deviation.

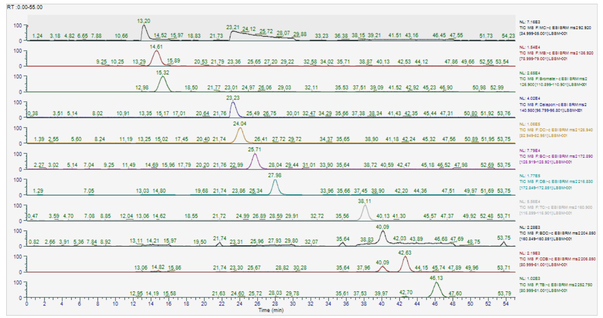
Tap Water Sample Analysis

Additionally, tap water from San Jose, CA was analyzed for the presence of any of the analytes contained in the method. Tap water samples were collected in accordance with EPA method 557, with NH_4Cl added as a preservative. Internal standards were added and the samples were quantified. The levels of each compound detected in the samples are shown in Table 7. The total amount of haloacetic acids for all nine HAAs was 35.62 ppb. For the regulated HAA5, the total was 30.21 ppb. The MCL set by the U.S. EPA for the HAA5 is 60 ppb.

Table 4. Optimized MS transitions for each compound and MDL results. As per the EPA method, only one product ion was monitored for each precursor ion.

Analyte	Q1 (m/z)	Q3 (m/z)	RF lens (V)	CE (V)	MDL (ppb)
MCAA	92.9	35.0	67	10	0.105
MBAA	136.9	79.0	60	13	0.104
DCAA	126.9	82.9	70	10	0.044
DBAA	216.8	172.8	72	12	0.021
BCAA	172.9	128.9	70	11	0.059
TCAA	160.9	116.9	45	8	0.033
BDCAA	162.9	81.0	60	10	0.141
DBCAA	206.9	81.0	90	16	0.214
TBAA	252.8	81.0	70	17	0.159
Dalapon	140.9	96.8	56	7	0.050
Bromate	126.9	110.9	90	22	0.059
MCAA-ISTD	94.0	35.0	67	10	
MBAA-ISTD	138.0	79.0	60	13	
DCAA-ISTD	128.0	84.0	70	10	
TCAA-ISTD	162.0	118	45	8	

Figure 2. Laboratory Synthetic Sample Matrix (LSSM) spiked with 20 ppb haloacetic acids, bromate, and dalapon. The internal standard peaks are not shown. From top to bottom, MCAA, MBAA, bromate, dalapon, DCAA, BCAA, DBAA, TCAA, BDCAA, DBCAA, and TBAA.



CONCLUSIONS

- A reagent-free IC system coupled with an MS/MS detector is a powerful tool used in the quantitation of haloacetic acid samples.
- When compared to the conventional U.S. EPA methods using GC with electron capture, using the combination of the Dionex ICS-5000⁺ HPIC system and the TSQ Endura triple quadrupole mass spectrometer to analyze for haloacetic acids saves analysts several hours of sample preparation.
- The resolution between the matrix peaks and haloacetic acids is excellent, which allows for minimum interference in detection, as well as ensuring a cleaner ion source of the mass spectrometer.
- Excellent reproducibility and quantitation of HAAs was achieved when samples were spiked into a simulated matrix

REFERENCES

1. U.S. EPA, *Microbial Health Effects Tables: Potential Adverse Health Effects from High/Long-term Exposure to Hazardous Chemicals in Drinking Water,* 2002.
2. U.S. Environmental Protection Agency, Method 552.1
3. U.S. Environmental Protection Agency, Method 552.2
4. U.S. Environmental Protection Agency, Method 552.3
5. U.S. Environmental Protection Agency, Method 557
6. Slingsby, R.; Saini, C.; Pohl, C.; Jack, R. *The Measurement of Haloacetic Acids in Drinking Water Using IC-MS/MS–Method Performance,* Presented at the Pittsburgh Conference, New Orleans, LA, March 2008.

TRADEMARKS/LICENSING

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