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

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Overview

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

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

Results: Quantitative 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 by-products (DBPs) that include HAAs. Of the nine species of HAAs, five are currently regulated by the 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 nine HAAs, plus bromate and the pesticide dalapon in the same IC-MS/MS run without sample preparation.

According to the U.S. Environmental Protection Agency (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 the level of all nine HAAs in drinking water.[2,3,4] These methods require derivatization and multiple extraction steps followed by gas chromatography (GC) with electron capture detection (ECD).

By comparison to the conventional EPA methods using GC with ECD, the combination of ion chromatography and mass spectrometry (IC-MS and IC-MS/MS) offers sensitive and rapid detection without the need for sample pre-treatment. In order to develop a simple, easy-to-use direct-injection method, the U.S. EPA promulgated Method 557[5] for the analysis of haloacetic acids, bromate, and dalapon in drinking water by IC-MS/MS.

Methods

Sample Preparation

Drinking water samples were collected from municipal tap water sources. NH_4Cl was added as a preservative at 100 mg/L to all water samples. No further sample preparation was performed prior to injection.

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.

Hydroxide eluent is generated using an electrolytic eluent generation which provides smoother gradients than conventional pump proportioning valves, and a continuously regenerated trap column continuously removes contaminants to provide pure eluent throughout the run. A Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor™ is placed in line after the column and electrolytically converts hydroxide eluent into water and simultaneously removes cations present in the drinking water and eluent. The gradient profile used is shown in Table 2. An overall schematic diagram of the system is shown in Figure 1.

A matrix diversion valve was placed in line prior to the mass spectrometer to divert the high sample matrix anions from the MS source that normally cause signal suppression in the MS. Thus the use of hydroxide eluent and suppression in the Reagent-Free IC system is more powerful for the separation and detection of organic acids than reversed phase separations that require acidic addition (to protonate the compounds to acetic acids) or addition of stabilizing salts, both of which undermine analysis. Isopropyl alcohol was added into the eluent stream via a mixing T immediately after the matrix diversion valve. The isopropyl alcohol was added at a flow rate of 0.2 mL/min. The isopropyl alcohol had two main purposes: to assist in the desolvation of the mobile phase and to act as a makeup flow when the IC eluent was diverted to waste. Acetonitrile can also be used instead of isopropyl alcohol, however the lower cost of isopropyl alcohol is an advantage to the chemist.

Mass Spectrometry

MS analysis was carried out on a Thermo Scientific™ TSQ Endrua™ triple stage 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	ASRS 300 2mm
Column Temperature	15° C
Injection Volume	100 uL
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	60
46	60
47	7
58	7

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

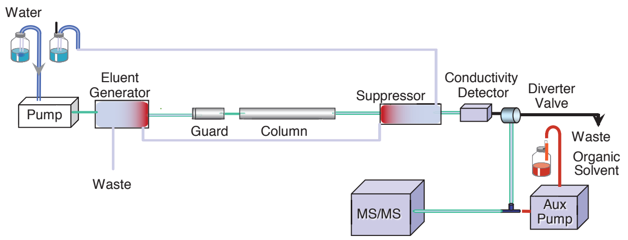

TABLE 3. Mass Spectrometer Source Conditions.

Parameter	Value
Ion Source Polarity	Negative Ion Mode
Spray Voltage	3200 V
Vaporizer Gas Pressure	45 units N_2
Auxiliary Gas Pressure	10 units N_2
Capillary Temperature	200 C
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 250 mg/L 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 eleven 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. Figure 3 shows the conductivity detector response chromatogram. The response from the Cl–, SO4–, and NO3– can be seen in the trace. 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 minutes, 16–22.75 minutes, 30–37 minutes, and from 48 minutes 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. Additionally, to improve the TCAA detection, the effect of temperature of the MS source on TCAA's response was tested. Temperatures of 200° C for both the ion transfer tube and vaporizer were found to be optimal for TCCA 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 were calculated by seven replicate injections of 0.5 ppb of each analyte and the equation $MDL = t99\% \times S\ (n - 7)$, where: t is Student's t at 99% confidence intervals ($t99\%$, $n = 7 = 3.143$) and S is the standard deviation. These MDLs are listed in Table 5.

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 the EPA Method 557 procedure, with NH_4Cl added as a preservative as it reacts with residual chlorine preventing further formation of haloacetic acids. 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 0.060 mg/L. This sample was below that limit, at 0.03021 mg/L.

TABLE 4. Optimized MS transitions for each compound analyzed in this experiment. 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)
MCAA	92.9	35.0	67	10
MBAA	136.9	79.0	60	13
DCAA	126.9	82.9	70	10
DBAA	216.8	172.8	72	12
BCAA	172.9	128.9	70	11
TCAA	160.9	116.9	45	8
BDCAA	162.9	81.0	60	10
DBCAA	206.9	81.0	90	16
TBAA	252.8	81.0	70	17
Dalapon	140.9	96.8	56	7
Bromate	126.9	110.9	90	22
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.

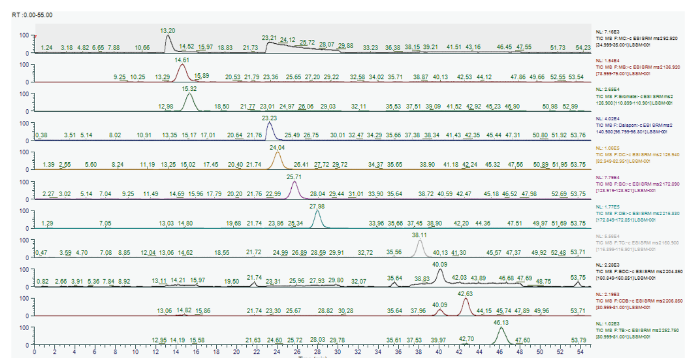

FIGURE 3. Conductivity detector response showing signals from LSSM salts.

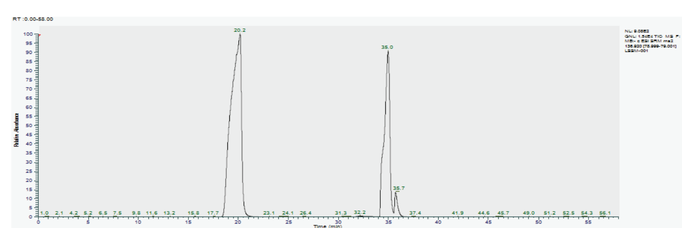

TABLE 5. Method Detection Limits for each compound.

Analyte	MDL (ppb)
MCAA	0.105
MBAA	0.104
DCAA	0.044
DBAA	0.021
BCAA	0.059
TCAA	0.033
BDCAA	0.141
DBCAA	0.214
TBAA	0.159
Dalapon	0.050
Bromate	0.059

Conclusion

- Reagent-Free IC systems coupled with an MS/MS detector is a powerful tool used in the quantitation of haloacetic acid samples.
- When compared to the conventional EPA methods using GC with electron capture, using the combination of the Dionex ICS-5000 ion chromatography 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. *Microbial Health Effects Tables: Potential Adverse Health Effects from High/Long-term Exposure to Hazardous Chemicals in Drinking Water;* U.S. Environmental Protection Agency, 2002.
2. *Method 552.1, Determination of Haloacetic Acids and Dalapon in Drinking Water by Ion Exchange Liquid-Solid Extraction and Gas Chromatography with Electron Capture Detection* (Rev. 1.0); U.S. Environmental Protection Agency, 1992.
3. *Method 552.2, Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Extraction, Derivatization, and Gas Chromatography with Electron Capture Detection* (Rev. 1.0); U.S. Environmental Protection Agency, 1995.
4. *Method 552.3, Determination of Haloacetic Acids and Dalapon in Drinking Water Liquid-Liquid Microextraction, Derivatization, and Gas Chromatography with Electron Capture Detection* (Rev. 1.0); U.S. Environmental Protection Agency, 2003.
5. *Method 557, Determination of Haloacetic Acids, Bromate, and Dalapon in Drinking Water by Ion Chromatography Electrospray Ionization Tandem Mass Spectrometry (IC-ESI-MS/MS)* (Rev. 1.0); U.S. Environmental Protection Agency, 2009
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.

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