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# Analysis of haloacetic acids, bromate, and dalapon in natural waters by ion chromatography–tandem mass spectrometry

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ABSTRACT

The addition of oxidants for disinfecting water can lead to the formation of potentially carcinogenic compounds referred to as disinfection byproducts (DBPs). Haloacetic acids (HAAs) are one of the most widely detected DBPs in US water utilities and some of them are regulated by the US Environmental Protection Agency (USEPA). The present study developed a method to analyze all the compounds in the USEPA method 557 (nine HAAs, bromate and dalapon) plus four potentially more toxic iodinated HAAs in water by coupling ion chromatography with tandem mass spectrometry (IC–MS/MS). This aqueous direct injection method has significant advantages over traditional GC methods, which require a derivatization and sample extraction that are laborious, time-consuming, and can negatively impact reproducibility. The method developed in this study requires half the time of the current USEPA method 557 on IC–MS/MS while including more compounds and achieving sub-μg/L level method detection limits (MDLs) for all 15 target analytes. The single laboratory lowest concentration minimum reporting level (LCMRL) has also been determined in reagent water, which ranged from 0.011 to 0.62 μg/L for the analytes. The mean recoveries of the analytes during matrix spike recovery tests were 77–125% in finished drinking water and 81–112% in surface water. This method was then applied to untreated, chlorinated, and chloraminated groundwater and surface water samples. Bromate and 9 HAAs were detected at different levels in some of these samples.

## 1. Introduction

Disinfection processes were introduced in drinking water treatment for the inactivation of microbial pathogens in the early 20th century and dramatically reduced waterborne diseases [1]. However, the applied disinfectants can react with the natural organic matter and anthropogenic contaminants in the water to form disinfection by-products (DBPs). Haloacetic acids (HAAs) are one of the most commonly detected classes of DBPs in US water utilities [2]. They have captured considerable attention due to their adverse biological effects on human and aquatic organisms [3]. Dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) have been classified by The Integrated Risk Information System (IRIS) as probable (Group B2) and possible human carcinogens (Group C), respectively [4,5]. Consequently, the United States Environmental Protection Agency (EPA) has promulgated the Disinfectants/Disinfection By-Products (D/DBP) Rule and established a maximum contamination level (MCL) of 60 μg/L for the total concentrations of five HAAs ($HAA_5$), including DCAA, TCAA, monochloroacetic acid (MCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA) [6]. The $HAA_5$ along with four unregulated bromo and chloro- homologues of the acetic acids including tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA) and chlorodibromoacetic acid (CDBAA) are known as $HAA_9$, which have commonly been monitored in water for the last decade. Among the $HAA_9$, TBAA has been reported to be even more cytotoxic and genotoxic than DCAA and TCAA [7].

Recently, iodinated HAAs, such as monoiodoacetic acids (MIAA), chloroiodoacetic acid (CIAA), bromoiodoacetic acid (BIAA), and diiodoacetic acid (DIAA), have been discovered in chlorinated and chloraminated drinking waters at low ng/L to low μg/L levels [2,8,9], which were reported to be significantly more cytotoxic and genotoxic than their corresponding chlorinated and brominated analogs [8,9]. Among all HAAs and THMs, MIAA shows the highest cytotoxicity and genotoxicity [8]. Although iodinated HAAs have not been regulated, their occurrence and high toxicity have caused

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substantial public health concern. However, there have been only a few quantitative methods reported for the simultaneous analysis of these four iodinated HAAs [10–12].

Bromate ($BrO_3^-$) is a DBP primarily formed by oxidation of the bromide ion ($Br^-$) in water during ozonation [13]. Bromate is a probable human carcinogen (Group B2) [14], and currently regulated by the USEPA with an MCL of 10 μg/L in drinking water under the D/DBP Rule [6]. Dalapon (2,2-dichloropropionate, DAL) has been reported to be a DBP or potential DBP, and it is also regarded as a general use herbicide regulated by USEPA with an MCL of 200 μg/L in drinking water [15].

Gas chromatography (GC) equipped with electron capture detection (ECD) [16,17] or mass spectrometry (MS) was commonly used to analyze HAAs [18,19]. However, sample preparation steps such as sample acidification, extraction and derivatization are usually needed. In USEPA Method 552.2, derivitization and liquid–liquid microextraction steps are required before GC-ECD analysis for the $HAA_9$ and dalapon, which may induce unexpected errors and reduce reproducibility while being labor- and time-intensive [17]. Recently, ion chromatography (IC) coupled to electrospray mass spectrometry (ESI–MS or ESI–MS/MS) have been applied for analyzing HAAs and oxyhalides in water [20–22]. USEPA Method 557 was established to analyze $HAA_9$, bromate and dalapon using IC-ESI–MS/MS without a sample preparation or concentration step. The method achieves requisite detection limits in low μg/L level without extraction and derivatization for all analytes.

In this study, we developed a rapid and sensitive method for simultaneously analyzing all the target compounds in USEPA Method 557 (including $HAA_9$, bromate and dalapon) with the addition of four iodinated HAAs (monoiodoacetic acids, chloroiodoacetic acid, bromoiodoacetic acid, and diiodoacetic acid) using direct injection ion chromatography coupled with tandem mass spectrometry (IC-MS/MS), which takes less than half the time of USEPA Method 557. Method validation included matrix spike recovery tests, method reporting limit determinations, reproducibility and linearity tests. The method was then applied to environmental water samples which were treated with different disinfectants to prove its applicability for real-world samples. To the best of our knowledge, this is the first IC-MS/MS method reported for analyzing full range of HAAs, along with bromate and dalapon.

## 2. Experimental

### 2.1. Chemical standards and reagents

MCAA (≥99%), DCAA (≥99%), TCAA (≥99%), MBAA (≥99%), DBAA (98.7%), BCAA (99.9%), TBAA (≥99%), BDCAA (99.9%), CDBAA (99.9%), MIAA (≥98%), dalapon (DAL, 95.0%) and sodium bromate (NaBrO, ≥99%) were purchased from Sigma-Aldrich Ltd (St. Louis, MO). CIAA (≥90%), BIAA (≥85%), and DIAA (≥90%) were purchased from CanSyn Chem. Corp. (Toronto, ON, Canada). The isotopically enriched internal standards (IS), monochloroacetic acid-2-$^{13}C$ (MCAA-$^{13}C$), dichloroacetic acid-2-$^{13}C$ (DCAA-$^{13}C$), trichloroacetic acid-2-$^{13}C$ (TCAA-$^{13}C$) and monobromoacetic acid-1-$^{13}C$ (MBAA-$^{13}C$), were purchased from Thermo Scientific Dionex Corp. (Sunnyvale, CA). Sodium carbonate ($Na_2CO_3$, BioXtra, ≥99.0%), ammonium chloride ($NH_4Cl$, ACS reagent, ≥99.5%), and sodium hydroxide (NaOH, ACS reagent, ≥97.0%) were purchased from Sigma-Aldrich Ltd (St. Louis, MO). Potassium hydroxide (KOH, 0.5 M solution, Certified/Pre-standardized Titrant) was purchased from Metrohm USA, Inc. (Riverview, FL). LC/MS grade ultrapure acetonitrile (ACN), methanol and ethyl *tert*-butyl ether (MTBE), as well as sodium hypochlorite solution (NaClO, 6% available $Cl_2$), were obtained from Fisher Scientific Co. (Fair Lawn, NJ). Ultrapure water with a resistivity of 18.2 MΩ·cm was prepared using a Milli-Q system (Millipore, Billerica, MA).

All the analytes and internal standard stock solutions were prepared at 500 μg/mL in MTBE. A mixed substock solution of all the analytes at 10 μg/mL and of the four internal standards at 1.0 μg/mL were prepared in methanol/water (1:1, v/v), respectively. All standard solutions were stored at 4 °C and fresh working solutions were prepared daily by diluting the mixed substock solution of analytes with ultrapure water.

### 2.2. Sample preparation

The environmental samples were prepared using a surface water and groundwater sample, which were collected from Arizona, treated with free chlorine and monochloramine ($NH_2Cl$) at doses of 5 mg/L and 10 mg/L. The characteristics of water samples were detailed in Table S1. A commercial NaClO solution was used for chlorination and $NH_2Cl$ solution was freshly prepared for chloramination by dissolving $NH_4Cl$ in deionized water adjusted to pH = 8 with NaOH, followed by slowly adding NaClO solution to obtain a 1:1.2 Cl:N molar ratio [23]. The NaClO and $NH_2Cl$ solution were both standardized spectrophotometrically [24,25]. The untreated water samples were used as controls. $NH_4Cl$ was added to the samples at a final concentration of 100 mg/L after 12-h contact time to quench residual disinfectants. The samples were maintained at 4 °C and analyzed within 7 days. Prior to analysis, 5 mL of sample was taken into the autosampler vial and spiked with 25 μL internal standard solution of 1.0 μg/mL.

### 2.3. Instrument operating conditions

The ion chromatography (IC) separation was conducted using a Metrohm 850 Professional IC system with a binary high pressure gradient system, which enables up to quaternary gradients, composed of an 858 Professional Sample Processor equipped with Metrohm Inline Ultrafiltration (Metrohm USA, Inc., Houston, TX, USA) module. The ultrafiltration cell is equipped with a membrane filter of 0.2 μm pore size, which can reliably remove particles from the sample and protect the analytical column from particulate contamination. A Metrosep A Supp 7 (250 × 4.0 mm) column (Metrohm USA, Inc., Houston, TX, USA) was applied for IC separation and the column temperature was kept at 45 °C throughout the analysis. Water/ACN (85/15, v/v) containing 50 mM KOH and 7 mM $Na_2CO_3$ (eluent A) and ultrapure water (eluent B) were used as mobile phases. The elution flow rate was 0.7 mL/min, and the injection volume was 100 μL. 12-mL polypropylene conical tubes (Metrohm USA, Inc., Houston, TX, USA) were used for all samples. The binary gradient elution for the separation was programmed as: 20% A for 2.0 min; linearly increased to 65% A over 2.0 min; then increased to 95% A over 3.0 min; maintained at 100% A for 18.0 min; decreased to 20% A over 1.0 min; and equilibrated at 20% B for 1.0 min, prior to the next injection. The total run time was 27.0 min. The flow divert valve was turned to waste for the first 2.9 min for a solvent delay and to eliminate unretained salts from entering the mass spectrometer. Suppression steps were carried out by High Capacity Metrohm Suppressor Module (MSM-HC) and Metrohm $CO_2$ suppressor (MCS) at 10.0 min, 15.0 min, and 20.0 min.

An Agilent 6490 triple quadrupole mass spectrometer (Agilent Technologies, Palo Alto, CA) equipped with the Jet Stream dual electrospray source and iFunnel technology was employed for detection. The instrument was tuned and optimized to obtain sufficient sensitivity and resolution using the Agilent tune solution (p/n: G1969-85000) in all peak windows. The key optimized MS/MS conditions are listed as following: drying gas temperature, 120 °C; drying gas flow, 13 L/min; sheath gas temperature, 390 °C; sheath gas flow, 12 L/min; nebulizer gas, 45 psi; capillary voltage, 3000 V;