Analysis of Haloacetic Acids, Bromate, and Dalapon in Natural Waters by Ion Chromatography Tandem Mass Spectrometry

Application Note

Authors

Shimin Wu and Shane A. Snyder
Department of Chemical & Environmental Engineering
BIO5 Institute
University of Arizona
Tucson, AZ
USA

Jay Gandhi
Metrohm USA
Riverview, FL
USA

Tarun Anumol
Agilent Technologies, Inc.
Wilmington, DE
USA

Abstract

A direct injection ion chromatography tandem mass spectrometry method for analysis of haloacetic acids, bromate, and dalapon in water has been developed using a Metrohm 850 ion chromatograph (IC) system coupled to an Agilent 6490 Triple Quadrupole LC/MS system. It requires half the time of the current USEPA Method 557, while including more compounds and achieving low µg/L reporting limits. Mean recoveries in matrix spike studies were between 77.5% and 124.6%, and linear calibration curves provided correlation coefficients R^2>0.995 for all analytes.

Agilent Technologies

Introduction

Beginning in the early twentieth century, the use of disinfectants in water treatment dramatically reduced waterborne diseases [1]. However, these disinfectants can also react with the natural organic matter and anthropogenic contaminants in the water to form other chemicals commonly referred to as disinfection by-products (DBPs). Haloacetic acids (HAAs) comprise one of the most abundantly detected classes of DBPs in US water utilities [2]. Some of these HAAs are classified as probable human carcinogens by the International Agency for Research on Cancer (IARC) [3].

Consequently, the United States Environmental Protection Agency (USEPA) has regulated five of the most commonly detected HAAs (HAA_5) in US drinking waters at 60 µg/L [4]. The nine analogues of the chloro and bromo acetic acids (HAA_9) have commonly been monitored for the last decade. Recently, studies have indicated that the toxicity of iodinated HAAs is several orders of magnitude greater than its chlorinated and brominated counterparts, hence, interest in monitoring these HAAs has increased [5]. Bromate is a human carcinogen with a maximum contaminant limit (MCL) of 10 µg/L set by the USEPA. It is generally formed by oxidation of bromide in water by ozonation, and is difficult to attenuate once formed. Dalapon is a herbicide, and is regulated by the USEPA with a higher MCL of 200 µg/L in drinking water.

HAA analysis has traditionally been performed by gas chromatography (GC). The USEPA method 552.3 uses GC with an electron capture detector (ECD) for the analysis of the HAA_9 and dalapon. The method prescribes a derivatization step and liquid-liquid microextraction involving several sample handling steps that are labor and time-intensive, and a source of potential error and reduced reproducibility. Later, USEPA Method 557 was created to analyze the same compounds using an ion chromatography (IC) system coupled to tandem mass spectrometry (IC-MS/MS) [6]. The main advantages of the method were the ability to skip any sample extraction or concentration steps and still achieve requisite detection limits in the low µg/L range for all target analytes while adding specificity to detection with the use of a mass spectrometer.

This application note describes an IC-MS/MS method using a Metrohm IC and an Agilent 6490 Triple Quadrupole LC/MS system that analyzes all the compounds from USEPA Method 557, with the addition of four of the more toxic iodinated HAAs. It uses direct injection with a carbonate/hydroxide buffer eluent and multiple reaction monitoring. This method requires less than half the run time of the USEPA method, using a linear gradient instead of the step gradient prescribed in Method 557. This prevents salt shock to the column, and enhances column life. The direct injection of water 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 was validated by matrix spike studies on five replicates in drinking water and in a surface water sample. Some real world samples analyzed were found to contain low levels of a number of HAAs.

Experimental

Standards and reagents

All 13 HAAs and sodium carbonate (BioXtra, ≥99.0%) were purchased from Sigma-Aldrich Ltd. The four internal standards used were supplied by the USEPA Region 6 laboratory (Houston, TX). Potassium hydroxide (0.5 M solution, Certified/Pre-standardized Titrant) was purchased from Metrohm USA, Inc. Ultrapure water and acetonitrile (both LC/MS grade) were purchased from Burdick & Jackson.

Sample preparation

All HAA, bromate, and dalopon standards were prepared at 500 µg/mL, then diluted in a mix to the required concentrations in ultrapure water. All samples were quenched for any residual oxidant with 100 mg/L of ammonium chloride after sample collection, in accordance with USEPA Method 557.

Instruments

A Metrohm 850 Professional IC AnCat–MSM-HC–MCS ion chromatography system was coupled to an Agilent 6490 Triple Quadrupole LC/MS system for this analysis. The IC system was set up to hold 12.5-mL conical vials, and to do a 100-µL injection with a Dosino® (partial loop injection setup). Separation on the IC was performed using a Metrohm A Supp 7 (250 × 4.0 mm) column with gradient elution using a binary pump. Table 1 shows the IC method conditions and column parameters.

A 6490 Triple Quadrupole LC/MS system equipped with a Jet Stream dual electrospray source and iFunnel Technology was operated in the negative mode for this analysis. The mass spectrometer was tuned using the Agilent tune solution (p/n G1969-85000) in all peak windows. Table 1 shows the MS optimized conditions.

The Metrohm IC and Agilent MassHunter Software (V. B.06.01) were synchronized using a Metrohm remote box and custom cable, permitting both instruments to run in tandem and provide data collection unattended.

Table 1. Ion Chromatography and Triple Quadrupole MS Optimized Run Parameters

Ion chromatography	
Column	Metrohm Metrosep A Supp 7 - 250/4.0
IC software	MagIC Net Professional Ver 3.1
Mobile phase	A) Water/ACN (85/15, v/v) + 50 mM KOH + 7 mM Na_2CO_3 B) Water
Chemical suppressor	Regen: 200 mM nitric acid/Rinse: ultrapure water
Injection volume	100 µL
Flow rate	0.7 mL/min
Gradient	Time (min) B (%) 0.0 80 2.0 80 4.0 35 7.0 5 25.0 5 26.0 80
Run time	27.0 minutes
Column temperature	45 °C
Divert flow to waste	0.0–2.0 minutes
Triple quadrupole MS	
Ionization mode	Negative electrospray ionization with Jet Stream technology
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
Fragmentor	380 V
Capillary	3,000 V
Nozzle voltage	1,500 V
High pressure RF	160 V
Low pressure RF	40 V

Optimized compound acquisition parameters

The acquisition parameters were optimized using the Agilent SourceOptimizer software tool, and infusing individual 500 ng/mL standards prepared in water into the mass spectrometer. Table 2 shows the optimized multiple reaction monitoring (MRM) parameters for the 6490 Triple Quadrupole LC/MS system.

Table 2. Optimized MRM Compound Acquisition Parameters

Compound	Abbreviation	Precursor *m/z*	Product *m/z*	Collision energy (eV)	Retention time (min)
Bromate	BrO_3^-	126.9	110.8(95)	24(36)	8.36
Bromochloroacetic acid	BCAA	173	128.9(80.9)	8(24)	11.27*
Bromodichloroacetic acid	BDCAA	163	80.9	8	18.73
Bromoiodoacetic acid	BIAA	262.8	218.7	8	12.93
Chlorodibromoacetic acid	CDBAA	206.9	81(78.9)	8(8)	21.06
Chloroiodoacetic acid	CIAA	218.9	126.9	20	11.82*
Dalapon	DAL	141	97	6	11.10
Dibromoacetic acid	DBAA	216.8	173	8	11.83
Dichloroacetic acid	DCAA	127	83	6	10.52
Diiodoacetic acid	DIAA	310.8	266.6	4	14.63
Monobromoacetic acid	MBAA	137	78.9	6	8.71
Monochloroacetic acid	MCAA	93	34.9	6	8.42
Monoiodoacetic acid	MIAA	184.9	126.7	20	9.07
Tribromoacetic acid	TBAA	250.9	78.9	20	24.12
Trichloroacetic acid	TCAA	163(117)	119(34.9)	8(8)	16.68
Trichloroacetic acid-$^{13}C_2$	TCAA-$^{13}C_2$	118	34.9	8	16.68
Dichloroacetic acid-$^{13}C_2$	DCAA-$^{13}C_2$	128	84	6	10.52
Monobromoacetic acid-$^{13}C_1$	MBAA-$^{13}C_1$	138	79	6	8.71
Monochloroacetic acid-$^{13}C_2$	MCAA-$^{13}C_2$	94	35	6	8.42

* Two fully resolved peaks
() secondary ions

Results and Discussion

Method performance

The final method for analysis of the 15 target analytes was optimized to 27 minutes. While good separation was achieved for most analytes, the goal was to develop a faster high throughput method than the current EPA method, and rely on the specificity of the tandem mass spectrometer. The method used a linear gradient instead of the step gradient used in Method 557 to prevent shocking the column with salt from the eluent, and to extend the column life. Quantification of the target analytes was performed with the use of four isotopically labeled surrogate standards. However, some analytes for which identical isotopically labeled standards were not available showed better performance when external calibration was used. Figure 1 shows a typical extracted ion chromatogram (EIC) of all 15 target analytes at 10 µg/L in water. The run time (27 minutes) was less than half that of Method 557 (55 minutes)

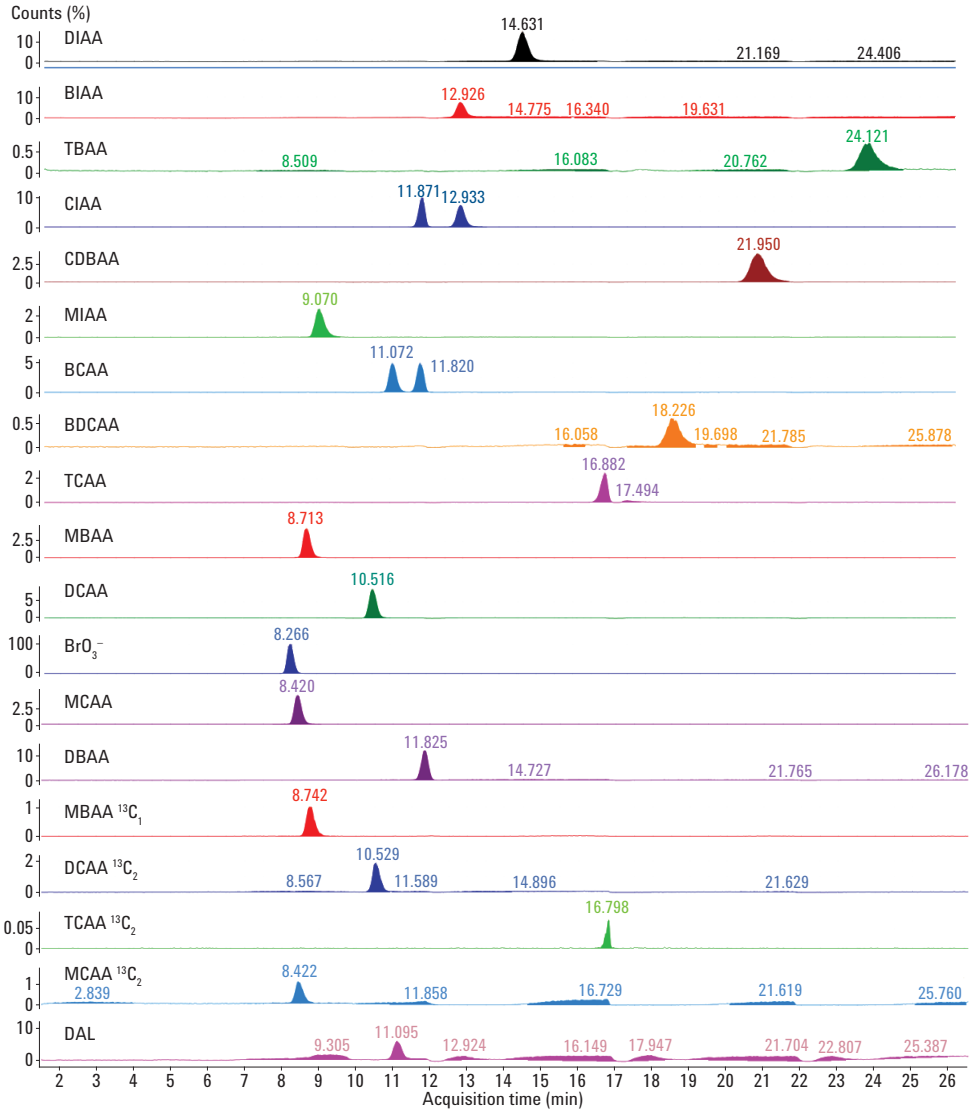

Figure 1. Extracted ion chromatogram of HAAs, bromate, dalapon, and isotopically labeled standards at 10 µg/L.

Method validation

The method reporting limits (MRLs) were statistically calculated based on the USEPA method from Glaser, *et al.* [7]. Initially, seven replicates of all 15 target analytes were prepared at 0.5 µg/L, and analyzed on the instrument. The concentration of each analyte was then calculated using a calibration curve, and the standard deviation for the seven replicates was multiplied by the student's t-test value with six degrees of freedom. The resulting values are a measure of the statistical MRL. MRLs were in the range of 0.03–1.3 µg/L, and < 0.5 µg/L for most HAAs and bromate (Table 3). The MRLs reported here are not statistically equivalent to the lowest calculated method reporting limits (LCMRLs) defined in Method 557, but they serve as a realistic representation of reporting limits achievable using this method.

Calibration standards were prepared fresh daily, but the authors did not notice any degradation of HAAs from the stock solutions. Therefore, no online temperature control in the autosampler was required.

The linearity of quantification was measured by determining the correlation coefficient of linearity (R^2). A seven point calibration curve from 0.5–50 µg/L in ultrapure water was prepared for each analyte except DAL, BDCAA, TBAA, and TCAA. These four compounds had a six-point calibration curve from 1.0–50 µg/L prepared. A linear fitting with no weighting was used for all analytes. An $R^2 > 0.995$ was achieved for all compounds (Table 4).

Matrix spike recoveries

Recoveries of the 15 target analytes were determined using five replicates in a drinking water sample and a surface water sample from Arizona. The five replicates were prepared by spiking 10 µg/L of each of the analytes. The recoveries were determined by subtracting the concentration determined in the unspiked sample (blank) from that of the spiked sample for each analyte, and dividing that by the known spiked concentration. Mean recoveries for all target analytes were between 77.5% and 124.6% in both matrices, while most were between 90% and 110%. Recovery in the finished drinking water, which had a total organic carbon (TOC) of 0.5 mg/L, ranged from 77.5% to 124.6%, while the surface water (TOC 3.2 mg/L) had recoveries of 80.7–112.0% for the analytes. The precision of recovery was measured by calculating the relative standard deviation (RSD) in both matrices. The RSD for the finished drinking water ranged between 1.7% and 12.5%, while the surface water RSD range was 1.3–12.0%. The average RSDs in the drinking water and surface water were 7.6% and 6.1%, respectively. Figure 2 shows the recoveries with error bars for each analyte in both water matrices.

Table 3. Statistical MRL Values for all HAAs, Bromate, and Dalapon (µg/L)

Compound	Statistical MRL
BrO_3^-	0.03
BCAA	0.38
BDCAA	1.3
BIAA	0.49
CDBAA	1.0
CIAA	0.04
DAL	0.9
TCAA	0.45
DBAA	0.33
DCAA	0.16
DIAA	0.18
MBAA	0.06
MCAA	0.06
MIAA	0.24
TBAA	1.2

Table 4. Linearity of Calibration Curves for 15 Target Analytes

Compound	R^2
BrO_3^-	0.9996
BCAA	0.9993
BDCAA	0.9961
BIAA	0.9962
CDBAA	0.9958
CIAA	0.9979
DAL	0.9960
TCAA	0.9985
DBAA	0.9987
DCAA	0.9994
DIAA	0.9961
MBAA	0.9991
MCAA	0.9997
MIAA	0.9995
TBAA	0.9975

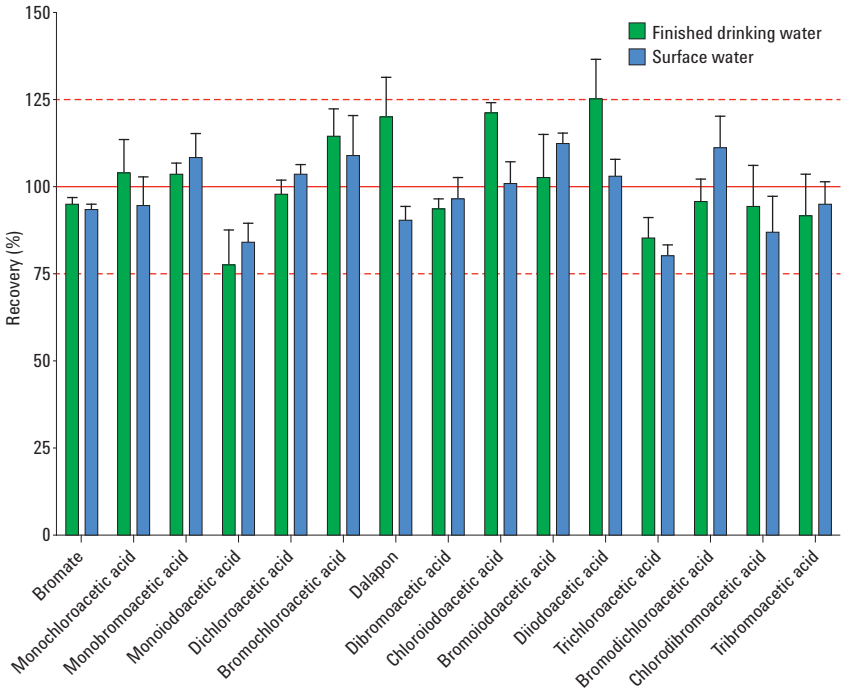

Figure 2. Spike recoveries at 10 µg/L of the 15 target analytes in finished drinking water and surface water (n = 5).

Analysis of real samples

A sample of each of three matrices (finished drinking water, surface water, and chloraminated surface water) was analyzed for all HAAs, bromate, and dalapon (Table 5). The drinking water (which had a chlorine residual) was found to possess the highest number of HAAs (seven), while the chloraminated surface water had the highest total concentration of HAAs despite having only four HAA species detected. None of the samples were above the 60 µg/L maximum contaminant level (MCL) required by the USEPA for the HAAs. Neither bromate nor dalapon was detected in any of the three samples.

Table 5. Concentration and Species of HAAs Detected in Actual Samples

Finished drinking water		Surface water		Chloraminated surface water	
HAA detected	**Concentration (µg/L)**	**HAA detected**	**Concentration (µg/L)**	**HAA detected**	**Concentration (µg/L)**
MCAA	0.2	MCAA	0.8	TBAA	2.2
MBAA	0.6	TBAA	2.0	DCAA	3.3
BIAA	1.1	N/D	N/D	MCAA	5.6
TBAA	2.0	N/D	N/D	MBAA	19.4
DBAA	2.5	N/D	N/D	N/D	N/D
TCAA	2.7	N/D	N/D	N/D	N/D
CIAA	3.0	N/D	N/D	N/D	N/D
Total	12.1	Total	2.8	Total	30.5

N/D = Not detected

Conclusions

The method described, using a Metrohm ion chromatography (IC) system coupled with an Agilent 6490 Triple Quadrupole LC/ MS system, was shown to provide analysis of 13 HAAs, bromate, and dalapon in water. The method requires no sample extraction and is able to achieve low µg/L detection limits while being more than two times faster than the current USEPA method for analysis of these compounds. Matrix spike recoveries ranged from 77.5% to 124.6% for all analytes in finished drinking water and surface water, while linearity of calibration curves (R^2) was >0.995 for all analytes. Real samples were analyzed using the method, and many HAAs were detected at low levels, indicating the sensitivity and robustness of the method.

Acknowledgments

The authors would like to thank Austin Ziska and Scott Jauch at the University of Arizona for assistance in the preparation of standards and reagents. We also acknowledge Johnson Mathew at the USEPA region 6 (Houston, TX) for providing isotopically labeled analytical standards for this study.

References

1. USEPA, 25 Years of the Safe Drinking Water Act: History and Trends. 2000, United States Environmental Protection Agency, Office of Water.
2. S. W. Krasner, *et al*. "Occurrence of a New Generation of Disinfection Byproducts." *Environ. Sci. Technol*. **40(23)**, 7175-7185 (2006).
3. IARC, Monographs on the Evaluation of Carcinogenic Risks to Humans. 2006, International Agency for Research on Cancer.
4. S. D. Richardson, *et al*. "Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research." *Mutation Research-Reviews in Mutation Research* **636(1-3)**, 178-242 (2007).
5. X. Wei, *et al*. "Occurrence and Mammalian Cell Toxicity of Iodinated Disinfection Byproducts in Drinking Water" *Environ. Sci. and Technol.* **42(22)**, 8330-8338 (2008).
6. USEPA Method 557: Determination of Haloacetic acids, Bromate, and Dalapon in Drinking Water by Ion Chromatography electrospray Ionization Tandem Mass Spectrometry (IC-ESI-MS/MS). 2009.
7. J. A. Glaser, *et al*. "Trace analyses for wastewaters." *Environ. Sci. and Technol.* **15(12)**, 1426-1435 (1981).

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
November 17, 2015
5991-6417EN

Agilent Technologies