Talanta 79 (2009) 523–527

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Rapid IC–ICP/MS method for simultaneous analysis of iodoacetic acids, bromoacetic acids, bromate, and other related halogenated compounds in water

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ARTICLE INFO

Article history:
Received 20 December 2008
Received in revised form 8 April 2009
Accepted 9 April 2009
Available online 3 May 2009

Keywords:
Haloacetic acid
Iodoacetic acid
Bromoacetic acid
Bromate
Disinfection by-product
Ion chromatography–inductively coupled plasma-mass spectrometry

ABSTRACT

Haloacetic acids (HAAs) and bromate are toxic water disinfection by-products (DBPs) that the U.S. Environmental Protection Agency has regulated in drinking water. Iodoacetic acids (IAAs) are the emerging DBPs that have been recently found in disinfected drinking waters with higher toxicity than their corresponding chloro- and bromo-acetic acids. This study has developed a new rapid and sensitive method for simultaneous analysis of six brominated and four iodinated acetic acids, bromate, iodate, bromide, and iodide using ion chromatography–inductively coupled plasma-mass spectrometry (IC–ICP-MS). Mono-, di- and tri-chloroacetic acids are not detected by this method because the sensitivity of ICP-MS analysis for chlorine is poor. Following IC separation, an Elan DRC-e ICP-MS was used for detection, with quantitation utilizing m/z of 79, 127, and 74 amu for Br, I, and Ge (optional internal standard) species, respectively. Although the primary method used was an external standard procedure, an internal standard method approach is discussed herein as well. Calibration and validation were done in a variety of natural and disinfection-treated water samples. The method detection limits (MDLs) in natural water ranged from 0.33 to 0.72 $\mu g\,L^{-1}$ for iodine species, and from 1.36 to 3.28 $\mu g\,L^{-1}$ for bromine species. Spiked recoveries were between 67% and 123%, while relative standard deviations ranged from 0.2% to 12.8% for replicate samples. This method was applied to detect the bromine and iodine species in drinking water, groundwater, surface water, and swimming pool water.

1. Introduction

Haloacetic acids (HAAs), including chloroacetic acids (CAAs), bromoacetic acids (BAAs), and iodoacetic acids (IAAs), are toxic DBPs that are potentially formed during drinking water disinfection treatment. The potential adverse health effects from exposure to HAAs include increased cancer risk, spontaneous abortions, and birth defects [1–3]. The five haloacetic acids (HAA5) regulated by the U.S. Environmental Protection Agency (USEPA) include mono-chloroacetic acid (MCAA), di-chloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA). The HAA5 regulatory limit under the Stage 2 DBP Rule is 60 $\mu g\,L^{-1}$ maximum contaminant level (MCL) for the sum of the five HAAs [4].

A significant fraction of the unregulated BAAs was found in some water treatment systems [5,6]. Similarly, IAAs were also reported to be present in some of the drinking waters in the U.S. in treatment plants using chloramination [7,8]. In a recent occurrence and mammalian cell toxicity study of iodinated DBPs in drinking water [9], monoiodoacetic acid (MIAA) and bromoiodoacetic acid (BIAA), together with three lower levels of other iodoacids, were found in the chloraminated drinking water in most of the 23 cities studied in the USA and Canada. MIAA was found to be at the highest level (1.7 $\mu g\,L^{-1}$) in the chloraminated drinking water, as compared with levels of other iodoacids [9]. Iodoacetic acid was also the most cytotoxic and genotoxic DBP analyzed in a mammalian cell system [9,10]. Further, chloroiodoacetic acid (CIAA) was reported to be formed when municipal chlorinated tap water reacted with iodized table salt during cooking [11]. Recent interest in IAAs has greatly increased because of the fact that they are reported to be much more cytotoxic and genotoxic than the regulated CAAs and BAAs. It is possible, though not certain, that these currently unregulated BAAs and IAAs may be included in future drinking water regulations. Thus, the detection of these emerging iodoacetic acids and bromoiodoacetic acids in drinking water and other waters is

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doi:10.1016/j.talanta.2009.04.037

crucial in order to assess the potential public health risks posed, particularly by drinking water.

Bromate is a DBP formed primarily during ozonation when the bromide ion is present [12,13]. Ozonation of water containing bromide ion (Br^-) results in the oxidation of Br^- to hypobromous acid (HOBr) and further oxidation of the hypobromite ion (BrO^-) to (BrO_3^-) [13,14]. The degree of bromate formation depends on ozone concentration, pH, and contact time. Bromate is a possible human carcinogenic [12,13]. The USEPA current regulation MCL for bromate is 10 $\mu g\,L^{-1}$ in drinking water. In the near future, water treatment systems will need to have a bromate running annual average (RAA) of 2.5 $\mu g\,L^{-1}$ (or less), based on 1 year of monthly data, to qualify for reduced bromate monitoring [4]. In a background document for bromate in drinking water, the World Health Organization (WHO) has indicated that the health-based value of bromate concentration in drinking water is 2 $\mu g\,L^{-1}$ [13]. However, due to the higher attainable practical quantification level (PQL) in many laboratories, a provisional guideline value of 10 $\mu g\,L^{-1}$ is currently recommended in *Guidelines for Drinking-water Quality* (GDWQ) [15].

The standard analytical method for the CAAs and BAAs is gas chromatography with electron capture detection (GC-ECD), after time-consuming extraction and derivatization [16]. Guo et al. have analyzed BAAs and bromate using ion chromatography–inductively coupled plasma-mass spectrometry (IC–ICP-MS) and achieved very good sensitivity [17]. A direct liquid chromatography/electrospray tandem mass spectrometry method has been developed for determination of MIAA with a negative ion detection mode [18]. A new GC–MS method, using negative ionization method, was also recently developed for detecting iodoacids [9]. There are some advantages and limitations for each of these methods, both of which utilize a variety of different instruments. With increasing health concern for iodinated and bromated DBPs, a rapid and simple analytical method is desirable.

Several USEPA standard methods have been used for detecting bromate in drinking water, including EPA Method 321.8, an IC–ICP-MS method [19]; EPA Method 300.1, an ion chromatography (IC) method with conductivity detection [20]; EPA Method 317.0, revision 2.0 [21]; and EPA Method 326.0 [22], ion chromatography (IC) methods with post-column reagent addition and UV/vis absorbance detection.

EPA Method 300.1, with a practical quantification level (PQL) of approximately 5 $\mu g\,L^{-1}$, will not be sufficient for analyze drinking water for reduced bromated monitoring to a lowered RAA of 2.5 $\mu g\,L^{-1}$ in the near future [4]. Sensitive and simple detection methods will assist in the analysis of bromate at lower levels in drinking water.

In addition to the toxic HAAs and bromate, the detection of other related halogenated compounds, bromide, iodide, and iodate, are also important in raw water and finished water because they play a critical role as DBP precursors or competitive products in the water. It is a great advantage if a method can be used to detect all of these compounds simultaneously.

In this study, a new fast, sensitive and simultaneous detection method for iodo- and bromo-acetic acids, bromate, iodate, bromide, and iodide, has been developed by coupling ion chromatography with ICP-MS. Specifically, the method allows separation and detection of MIAA, diiodoacetic acid (DIAA), MBAA, DBAA, tribromoacetic acid (TBAA), chloroiodoacetic acid (CIAA), BIAA, bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), bromate, bromide, iodide, and iodate. No complex sample preparation is required except for the filtration of the water sample with a membrane filter. However, the method does not detect mono-, di- and tri-chloroacetic acid because ICP-MS does not discern well the chlorine atom.

This method was validated and applied to drinking water, groundwater, surface water, and swimming pool water. These compounds are the important regulated DBPs and their precursors in drinking water, swimming pool water, aquaria water, and marine water. The other iodoacids, such as triiodoacetic acid (TIAA) and iodo-propenoic acid, were not tested due to their unstable nature, and reportedly very low levels in drinking water [9].

2. Experimental

2.1. Reagent and preparation

Three IAAs – CIAA, BIAA, and DIAA – were purchased from Orchid Cellmark (New Westminster, BC, Canada). MIAA and all of the bromoacetic acids – MBAA, BCAA, DBAA, BDCAA, DBCAA, and TBAA – were purchased from Sigma–Aldrich (St. Louis, MO, USA). All of these chemicals were of the highest purity available. All the other ACS certified reagent grade chemicals were purchased from Fisher Scientific (Pittsburgh, PA, USA) and Sigma–Aldrich. Deionized (DI) water (18.2 MΩ cm) was prepared with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

The DI water used for standards and mobile phase preparations was pre-degassed by vacuum filtration and/or ultrasonication to prevent any possible oxidation of iodide and bromide. Continuous online degas of mobile phases was also performed during the IC–ICP-MS analysis. Stock standard solutions were prepared by dissolving the chemicals in freshly degassed DI water at a concentration of 100–1000 mg/L, except iodide, which was prepared by dissolving sodium iodide in 0.5% ammonium hydroxide at pH 10 to minimize the possible oxidation of the iodide. All standard solutions were stored in amber glass vials, capped with Teflon-lined caps, in a freezer or refrigerator. The GeO_2 stock solution (used as an optional internal standard) was prepared in DI water at 500 mg/L. All of the standards were freshly prepared monthly. The more diluted working standard solutions were freshly prepared daily by dilution with DI water.

IC mobile phase A was DI water, and mobile phase B was 200 mM ammonium nitrate in DI water. Both mobile phases were filtered through a 0.22-μm nylon membrane filter, and degassed prior to use.

2.2. Instruments and operation conditions

IC separation was conducted using a PerkinElmer 200 Series high pressure liquid chromatography (HPLC) system composed of a 200 Series pump and autosampler (PerkinElmer, Norwalk, CT, USA). An automated switching valve was used between the HPLC and ICP-MS nebulizer to direct the mobile phase to the waste or ICP-MS. The tubing and sample loop were PEEK material. The analytical column was an AS11-HC high capacity ion exchange column (4.0 mm × 250 mm), with an AG11-HC guard column (4.0 mm × 50 mm) (Dionex, Sunnyvale, CA). The elution flow rate was 1.0 mL/min, and the injection volume was 100 μL. Amber glass sampler vials were used for all samples. Both the autosampler and column were kept at room temperature (~20 °C). The binary gradient elution for the separation was programmed as: 15% B for 3 min; increased to 50% B over 5 min; increased to 100% B over 18 min; maintained at 100% B for 10 min; decreased to 15% B over 5 min; and equilibrated at 15% B for 2 min, prior to the next injection. The total run time was 43 min.

The detection system was a Model Elan DRC-e ICP-MS (PerkinElmer SCIEX, Norwalk, CT, USA). Chromaria software was used to control the IC–ICP-MS systems for analysis. Table 1 lists the important ICP-MS instrumental conditions and method parameters used for this method.

Quantitation was performed at a mass/charge (m/z) ratio of 79 and 127 amu for Br and I, respectively. (*Note*: An isomeric m/z of 81 amu was sometimes also monitored for additional confirmation for the bromo-compounds.)