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A fully-automated analyzer for determining haloacetic acid concentrations in drinking water

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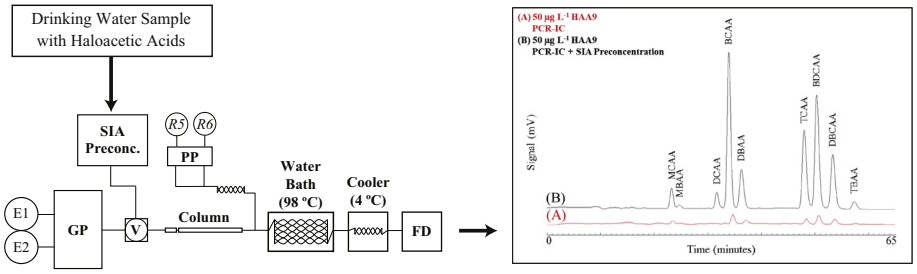
HIGHLIGHTS

- Sequential injection analysis optimized and used for automated preconcentration.
- Nicotinamide post-column reaction for selective analysis of haloacetic acids.
- On-line, real-time preconcentration and analysis of haloacetic acids.
- Comparable results to USEPA Method 552.3.

GRAPHICAL ABSTRACT



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ABSTRACT

A fully-automated, on-line, real-time analyzer has been developed for preconcentration and analysis of haloacetic acids (HAAs). Preconcentration of HAAs is achieved by sample acidification and solid phase extraction onto a hydrophobic polymeric resin using sequential injection analysis (SIA). The HAAs preconcentrate is then analyzed using post-column reaction-ion chromatography (PCR-IC), which is selective for HAAs. Systematic optimization of SIA preconcentration parameters are described followed by detailed method detection limit (MDL), accuracy, precision, and linearity studies. MDL values for the individual HAA9 species range from 0.4 to 0.9 μg L^{-1}. Side-by-side comparison studies of HAAs analysis in 14 real-world drinking water samples from Alabama, Arkansas, Kentucky, Minnesota, Missouri, Mississippi, New York, Pennsylvania and Tennessee are presented that compare the optimized SIA-PCR-IC to USEPA Method 552.3. Trace levels of HAAs detected in select samples are reported, and the bias values calculated between the two methods are typically less than 5 μg L^{-1} for eight of the nine individual HAAs.

1. Introduction

Chlorination of drinking water is a major public health success (Baird and Cann, 2008), but results in the formation of halogenated disinfection by-products (DBPs) through the reaction of free available chlorine species with natural organic matter (Richardson and Postigo, 2012). The two most common classes of halogenated DBPs are the trihalomethanes (THMs) and the haloacetic acids (HAAs). THMs and HAAs are carcinogens and considered surrogates for more than 900 organic DBPs detected in drinking water (Krasner et al., 2006). Nine HAAs can be found in drinking water, five of which (HAA5) are regulated (USEPA, 2006) by the U.S. Environmental Protection Agency (USEPA), through the Safe Drinking Water Act (Trussell, 2006), at a maximum contaminant level (MCL) of 0.060 mg L^{-1}. HAA5 includes: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA). HAA9 includes HAA5 plus bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA).

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USEPA Method 552.2 (USEPA, 1995) and 552.3 (USEPA, 2003) are the two methods most used by contract laboratories and utilities for analyzing HAA9 concentrations. Both methods are designed well for grab sample analysis of HAA9 in diverse drinking water matrices with excellent method detection limit (MDL; <0.5 μg L^{-1}), accuracy, and precision values. However, both methods require highly skilled analysts and are cumbersome for real-time monitoring and treatment optimization.

Researchers have embraced MS for HAAs analysis (Duan et al., 2011; Zhang et al., 2011; Li et al., 2012, 2013; Prieto-Blanco et al., 2012; Casas Ferreira et al., 2013; Hung and Her, 2013; Luo et al., 2013). Derivatization methods (Li et al., 2013) convert the HAAs to volatile species amenable for GC–MS analysis, similar to USEPA methods (USEPA, 1995, 2003) and others (Hammami and Driss, 2013; Liu et al., 2013), but have high labor costs. An effort to automate the grab sample derivatization (Casas Ferreira et al., 2013) proved successful, thus minimizing the labor. Tandem MS techniques typically use some form of pretreatment or preconcentration coupled with GC (Li et al., 2013), high pressure liquid chromatography (HPLC) (Li et al., 2012; Prieto-Blanco et al., 2012), ultra pressure LC (UPLC) (Duan et al., 2011; Luo et al., 2013), or capillary electrophoresis (CE) (Zhang et al., 2011; Hung and Her, 2013) to detect and quantify HAAs. Two reports (Duan et al., 2011; Li et al., 2012) and USEPA 557 (USEPA, 2009) use direct aqueous injection and avoid complex pretreatment and preconcentration techniques with excellent results. However, on-site analysis is problematic due to the environmental and power requirements of MS instruments.

Regulations for THMs and HAAs have become more strict over the past two decades (USEPA, 2006; Trussell, 2006). Drinking water utilities without expert personnel and high-end technology face the challenge of minimizing HAAs formation in drinking water treatment systems with few choices for real-time analysis. Alternatives to MS-based analysis have been reported using solid phase extraction (SPE) with CE to analyze HAAs at high levels (greater than 50 μg L^{-1}) in swimming pools (Ding and Rogers, 2010), mid-levels (6–12 μg L^{-1}) (Kubáň et al., 2012), and low levels (less than 5 μg L^{-1}) (Bernad et al., 2011). SPE has also been used with 2-D ion chromatography with membrane suppressed conductivity detection (IC-MSCD) (Verrey et al., 2013) and UPLC with UV absorbance (Nsubuga and Basheer, 2013) for HAAs analysis in drinking water and swimming pools, respectively.

The first report of post-column reaction ion chromatography (PCR-IC) for HAA5 (Simone et al., 2006) used two different forms of selectivity: (1) separation by anion exchange chromatography and (2) reaction with nicotinamide and fluorescence detection. Subsequent improvements include analysis of all HAA9 species (Simone et al., 2009) and internal standardization (IS) with 2-bromobutanoic acid (Ranaivo et al., 2011). These reports show that the fully automated PCR-IC compared well to USEPA 552.3 at concentrations from 5–900 μg L^{-1} for individual HAA9 species and is efficient for on-line, real-time analysis. However, individual HAA9 concentrations at a drinking water treatment plant can be less than 5 μg L^{-1}, thus utilities need analyzers capable of routine analysis of HAA9 at these concentrations.

Traditionally, HAAs preconcentration has used techniques such as liquid–liquid extraction (USEPA, 1995, 2003; Hammami and Driss, 2013; Liu et al., 2013) or solid phase extraction (Barron and Paull, 2004; Paull and Barron, 2004; Ding and Rogers, 2010; Prieto-Blanco et al., 2012; Kubáň et al., 2012; Nsubuga and Basheer, 2013) via manual or semi-automated analysis. For continuous, on-line, real-time analysis, an automated preconcentration module must do all of the sample handling and preparation steps for SPE preconcentration from sample intake and acidification to elution onto the analyzer for injection. Flow injection analysis (FIA) and sequential injection analysis (SIA) have been regularly used for drinking water sample analysis (Karlberg and Pacey, 1989; Simone et al., 2006, 2009; Emmert et al., 2007, 2009; Mesquita and Rangel, 2009; Ranaivo et al., 2011). SIA includes many of FIA's advantages such as highly reproducible flow rates and timing, and is a more appropriate choice here because it uses discontinuous, reversible flow, versus FIA's continuous, unidirectional flow (Skoog et al., 2006).

The focus of this research was to develop an on-line, real-time analyzer capable of fully-automated SIA preconcentration and PCR-IC analysis of HAAs for use at drinking water treatment plants. The analyzer reported here improves upon previous reports of the PCR-IC analyzer in both the MDL values and minimizing matrix effects with a modest increase in analysis time (Ranaivo et al., 2011). Systematic optimization of the analytical parameters, based on % Recovery of the HAA9 species, for each step in the preconcentration method is described. Detailed MDL, accuracy, precision, and linearity studies were conducted. Side-by-side, real-world sample analyses comparing the SIA-PCR-IC to USEPA 552.3 are also presented.

2. Materials and methods

2.1. Chemicals and reagents

The purity of all chemicals used was 97% or higher, except for 85% reagent grade potassium hydroxide (KOH). All standards, reagents, and eluents were prepared in reagent grade water produced by a Barnstead E-pure (ThermoFisher Scientific; Waltham, MA, USA) with a resistivity of 18.2 MΩ cm. Glassware was cleaned with concentrated detergent and rinsed thoroughly with reagent water. MCAA, MBAA, DCAA, BCAA, DBAA, TCAA, BDCAA, DBCAA, TBAA, and nicotinamide were obtained from Sigma–Aldrich (St. Louis, MO, USA). KOH, NaOH, sulfuric acid (H_2SO_4), methanol, methyl tert-butyl ether (MTBE), and 2-bromobutanoic acid (2-BBA) were obtained from ThermoFisher Scientific.

A 1000 mg L^{-1} HAA9 stock standard solution was prepared by adding 25.0 mg of each HAA9 to a 25.00 mL volumetric flask and diluting with MTBE. A 10.0 mg mL^{-1} IS stock standard solution was prepared by adding 0.100 g of 2-BBA to 10.00 mL of MTBE. These stock solutions were diluted accordingly with reagent water daily for optimization and calibration studies. The nicotinamide and KOH post-column reagents were prepared by dissolving 75.0 g nicotinamide in 140 mL reagent water for a total volume of 200 mL (3.07 M), and 25.5 g KOH dissolved in 200 mL reagent water (2.0 M). The reagent water used for eluent preparation was degassed using nitrogen. The 200 mM KOH eluent was prepared by dissolving 12.75 g KOH in 1.0 L of degassed reagent water. The sulfuric acid preconcentration reagent was prepared by appropriately diluting concentrated H_2SO_4 into reagent water. A 1.0 M NaOH solution was prepared by weighing 40.0 g of NaOH into 1.0 L of reagent water and diluted appropriately for the optimization studies.

2.2. Instrumentation

The SIA-PCR-IC instrument is a bench-top scale instrument (~72″ length × 12″ height × 24″ deep) comprised of two major components: the SIA module and PCR-IC analyzer. The SIA module conducts all sample preparation, preconcentration, and elution of the HAAs from the LiChrolut EN resin onto the sample loop on the PCR-IC injection valve. The SIA module outputs a remote start signal initiating the PCR-IC analysis of the HAA9 preconcentrate. The PCR-IC separates the HAAs, reacts with nicotinamide, and detects via fluorescence (excitation 365 nm, emission 455 nm) (Ranaivo et al., 2011). The SIA-PCR-IC reagents are safe when used