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An improved method for total organic iodine in drinking water

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A B S T R A C T

A concise, rapid, and sensitive method is developed to measure organically-bound iodine in water. Total organic iodine (TOI) is used as an integrative surrogate that reflects the amount of iodinated organics in a water sample and is quantified using a refined method that builds on previous adsorption and detection approaches. The proposed method combines adsorption, combustion, and trapping of combustion products, with an offline inductively coupled plasma/mass spectrometer (ICP-MS) for iodide detection. During method development, three analytical variables (factors) were varied across two levels each in order to optimize the method for iodine recovery: 1) the sample pH prior to adsorption on the granular activated carbon (GAC); 2) the amount of base addition to the trap solution; and 3) composition of the ICP-MS wash solution. These factors were tested with solutions of eight iodinated model organic compounds, two iodinated inorganic compounds, and field water samples using a full factorial experimental design. An analysis of variance (ANOVA) and related statistical methods were deployed to identify the best combination of conditions (i.e., *treatment*) that results in the most complete recovery of iodine from the model compounds and the highest rejection of inorganic iodine. The chosen *treatment* for TOI measurement incorporates a sample pH of less than 1 prior to adsorption onto the GAC, a solution of 2% (v/v) tetramethyl ammonium hydroxide (TMAH) for trapping of combustion products, and a TMAH wash solution of 0.1% (v/v) for the ICP-MS.

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1. Introduction

The use of chlorine as a chemical disinfectant to purify drinking water is one of the most important public health achievements of the twentieth century, having led to a significant decrease in water-borne diseases in the U.S. (Centers for Disease Control and Prevention, 1999). However, the non-selective properties of powerful oxidants such as chlorine, ozone, and chlorine dioxide means that they not only act on pathogens, but they also oxidize natural organic matter (NOM), bromide, and iodide naturally present in source waters to form halogenated disinfection by-products (DBPs). Moreover, organic-bound sources of iodine in raw waters may participate as well. For example, iodinated X-ray contrast media (ICM) commonly used in medical imaging are poorly removed in wastewater treatment and as a result, they have been detected in rivers and streams (Carballa et al., 2004; Oleksy-Frenzel et al., 2000; Putschew et al., 2001; Putschew and Jekel, 2006), as well as in groundwater and drinking water (Drewes et al., 2001;

Hirsch et al., 2000; Putschew et al., 2001; Sacher et al., 2001; Ternes et al., 2003; Schittko et al., 2004). These compounds have the ability to react with the added disinfectants during treatment, releasing iodine and forming iodinated-DBPs (I-DBPs).

The complex nature of organic matter in chlorinated and chloraminated water leads to the formation of a large number of halogenated-DBPs that cannot all be individually identified and quantified. Measures of total organic chlorine (TOCl), total organic bromine (TOBr), and total organic iodine (TOI) have been commonly adopted as surrogates for total chlorinated, brominated, and iodinated organics in water sources, respectively (Oleksy-Frenzel et al., 2000; Hua and Reckhow, 2006; Hua and Reckhow, 2007; Hua et al., 2006Kristiana et al., 2009), in a similar manner to the use of total organic halide, or TOX, as a surrogate for the sum of all halogenated organics (Li et al., 2002; Reckhow et al., 1990; Richardson, 2003). Since I-DBPs are of particular concern due to their elevated cyto- and geno-toxicity compared to their brominated and chlorinated analogs (Hunter et al., 1996; Plewa et al., 2008, 2010; Richardson et al., 2008), there is increasing interest in the measurement and tracking of TOI as a surrogate for the total amount of iodinated organics in disinfected water.

The most widely used methods for TOI measurement entail the

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adsorption of the organic iodine in an acidified water sample (pH ~ 2) onto activated carbon, pyrolysis of the organic iodine to form hydrogen iodide (HI) off-gas, and collection of the HI into an aliquot of water (trap solution). For iodide detection and separation from the aliquot of water, the use of either offline ion chromatography (IC; Hua and Reckhow, 2006; Kristiana et al., 2009; Oleksy-Frenzel et al., 2000) or offline ultra-performance liquid chromatography/electrospray ionization-mass spectrometry (UPLC/ESI-MS; Ding and Zhang, 2009; Gong and Zhang, 2015; Pan and Zhang, 2013) have been used. Both detection methods have drawbacks. The standard IC method has poor sensitivity for iodide (method detection limit of about 100 µg/L as I). Although iodide sensitivity can be improved by using a proper ratio of sample volume to trap solution volume (Kristiana et al., 2009), an IC run takes about 25 min per sample, precluding its routine analysis. The UPLC/ESI-MS detection method showed improvements over standard IC with faster analysis, better sensitivity (method detection limit of 3.7 µg/L as I), and higher chromatographic resolution. However, it failed to detect iodide peaks for iopromide, designated by the authors as a representative of ICM compounds (Pan and Zhang, 2013). This raises questions regarding the use of UPLC/ESI-MS for the detection of some of the major ICM compounds. Considering that the presence of ICM compounds in raw water may lead to the formation of I-DBPs upon disinfection, the chosen method has to be able to detect these compounds.

The inductively coupled plasma − mass spectrophotometer (ICP-MS) has superior sensitivity for iodine (I) in comparison to other detection techniques (Takaku et al., 1995). For that reason, many studies have utilized ICP-MS in various natural waters after separation of organic and inorganic halogens with high performance size exclusion (Gilfedder et al., 2010, 2011; Heumann et al., 1998; Radlinger and Heumann, 1997, 2000). The objective of this study was to develop and optimize a method that takes advantage of the superior sensitivity of ICP-MS and therefore overcomes the limitations of previous methods. The proposed method entails adsorption, combustion, and trapping, with offline ICP-MS for iodide detection. Key to any TOI method is the ability to achieve near complete recovery of iodinated compound that represent those expected to form as DBPs, while exhibiting high rejection of inorganic forms of iodine (e.g., iodide, triiodide, iodate).

2. Materials and methods

2.1. Instrumentation

The instrumentation for TOI analysis includes adsorption and combustion units and an off-line ICP-MS. The adsorption systems used were either an EFU 1700 Filtration Unit (Euroglas BV, Delft, The Netherlands) or an XPREP-A6 (Trace Elemental Instruments, Delft, The Netherlands), both equipped with pressurized sample reservoirs and granular activated carbon (GAC) adsorption columns (CPI International, Santa Rosa, CA). The ECS 1200 combustion system (Euroglas BV, Delft, The Netherlands) includes a combustion glass tube, a boat sampler, a motor-driven boat sampler, a furnace, sulfuric acid scrubbers, a gas bubbler/diffuser and trap, and an oxygen gas supply (99.99% high-purity grade). The ICP-MS (Perkin Elmer Elan 9000) was used for measuring iodide concentration in the trap solution. Argon (99.9 9% high-purity grade) was used as the carrier and reaction gas.

2.2. Chemicals and reagents

Ultra-pure water was obtained by filtering de-ionized water with a resistivity greater than 18.3 MΩ cm (Billerica, MA) and used in preparing procedural calibration standard solutions, laboratory reagent blanks, model compound solutions, and the ICP-MS wash solutions. Potassium iodide (KI), sodium iodide (NaI), sodium iodate (NaIO$_3$), and nitric acid (HNO$_3$; 70%, Trace Metal grade, Certified ACS) were purchased from Fisher Scientific. Tetramethylammonium hydroxide (TMAH; 25% W/W aqueous solution, Electronic Grade 99.999%) was obtained from Alfa Aeser. The model compounds iodoacetic Acid (IAA, 98%), 2-hydroxy-3-iodo-5-nitropyridine (97%), and 3-iodo-4-methylbenzoic acid (97%) were obtained from Aldrich Chemical Company, while bromoiodoacetic acid (BIAA, 90+%) and triiodoacetic Acid (TIAA, 90%) were purchased from CanSyn Chem Corp and Toronto Research Chemical, respectively. The three ICM model compounds iopromide, diatrizoic acid, and iopamidol were obtained from European Pharmacopeia, Sigma Chemical Company, and USP, respectively.

2.3. Experimental design

The new proposed method builds on some of the previous methods presented in Table 1. During method development, three experimental factors were varied across two levels each to find the optimal combination of levels, hereafter referred to as "*treatment*", for TOI recovery. The factors include: (Factor 1) the pH of the solution prior to GAC adsorption; (Factor 2) the amount of TMAH added to the iodide trap solution; and (Factor 3) the choice of ICP-MS wash. A detailed description of the entire process along with the reasons behind choosing the three factors is presented below.

2.3.1. Factor 1 (F1) − sample pH during adsorption

Both adsorption efficiency and compound stability are affected by pH. In these experiments, the water sample to be analyzed was acidified using HNO$_3$ to either pH = 2 ± 0.2 (Level 1) or pH < 1 (Level 2). During our experimental runs, the range of pH < 1 corresponded to a pH range between 0.76 and 0.99. Decreasing the pH shifts speciation of acidic compounds to protonated forms which are more readily adsorbed by activated carbon. Fifty mL of the acidified sample is then applied at a flow rate of 3 mL/min onto two consecutive GAC columns (*Col#1 and Col#2*). The two GAC columns are then sequentially placed in a ceramic boat that is introduced into a 1000 °C oven to be combusted in the presence of oxygen gas for 10 min. Upon combustion, the organic iodine is released as HI in the gas phase that gets carried through sulfuric acid scrubbers and into a custom-made absorber cell that contains about 15 mL of ultra-pure water (the trap solution). At the end of the trapping cycle, the trap solution is adjusted to 20 mL by rinsing out the walls of the absorber cell.

2.3.2. Factor 2 (F2) − composition of the trap solution

The trap solution should be selected to retain all gaseous HI and keep the iodine in a form that is effective for subsequent analysis by ICP-MS. An important consideration is that iodine is known for its volatile nature and its tendency to persist on interior surfaces in analytical instruments, and undergo slow release during analysis of subsequent samples. These "memory effects" can introduce substantial error, particularly in acidic solutions (Takaku et al., 1995). Often, memory effects can be partly mitigated by long wash periods between samples, but this is far from an ideal solution. To prevent this problem, previous studies have suggested preparing the samples in an alkaline solution to improve iodine retention and signal stability, and to reduce the memory effect (Baumann, 1990; Gélinas et al., 1998; Muramatsu and Wedepohl, 1998; Takaku et al., 1995; Vanhoe and Van Allemeersch, 1993). The choice of TMAH in particular as the alkaline solution in this study was motivated by its small matrix effect and good stability with the ICP (Takaku et al., 1995). In addition, its use results in high pH values without increasing the salt concentration; a problem that can occur with the