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Determination of iodide, iodate and organo-iodine in waters with a new total organic iodine measurement approach

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ABSTRACT

The dissolved iodine species that dominate aquatic systems are iodide, iodate and organo-iodine. These species may undergo transformation to one another and thus affect the formation of iodinated disinfection byproducts during disinfection of drinking waters or wastewater effluents. In this study, a fast, sensitive and accurate method for determining these iodine species in waters was developed by derivatizing iodide and iodate to organic iodine and measuring organic iodine with a total organic iodine (TOI) measurement approach. Within this method, organo-iodine was determined directly by TOI measurement; iodide was oxidized by monochloramine to hypoiodous acid and then hypoiodous acid reacted with phenol to form organic iodine, which was determined by TOI measurement; iodate was reduced by ascorbic acid to iodide and then determined as iodide. The quantitation limit of organo-iodine or sum of organo-iodine and iodide or sum of organo-iodine, iodide and iodate was 5 μg/L as I for a 40 mL water sample (or 2.5 μg/L as I for an 80 mL water sample, or 1.25 μg/L as I for a 160 mL water sample). This method was successfully applied to the determination of iodide, iodate and organo-iodine in a variety of water samples, including tap water, seawater, urine and wastewater. The recoveries of iodide, iodate and organo-iodine were 91–109%, 90–108% and 91–108%, respectively. The concentrations and distributions of iodine species in different water samples were obtained and compared.

1. Introduction

Iodine is a trace element that exists in natural waters such as seawater, freshwater and rain (Schwehr and Santschi, 2003; Gilfedder et al., 2008, 2009). Iodine is also a biologically essential nutrient for all mammals including humans (Gilfedder et al., 2009), and thus various physiological fluids, such as milk, serum, and urine, contain iodine (Hou et al., 2000; Verma et al., 1992). Iodine deficiency in the human body causes goitre as well as some other malfunctions and the normative daily iodine intake for an adult has been reported to be 1 μg/kg body weight (Merian et al., 2004). Humans ingest iodine mainly through drinking water and foods. Therefore, to ensure the proper daily iodine intake for humans, iodine has been added to table salts and some other foodstuffs. Owing to the occurrence in natural waters, iodine has also been

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detected in tap water (Blount et al., 2010; Pan and Zhang, 2013). Besides, large amounts of iodine-containing organic compounds are used as X-ray contrast media for medical purposes, which add iodine to hospital wastewater (Duirk et al., 2011). Iodine is widely used in the manufacture of chemicals, iodophors, biocides, herbicides, pharmaceuticals and nylon (Piñeiro et al., 2011), which ends up in industrial wastewater. The typical iodine concentrations in seawater, freshwater, rain and urine are 45–90, 0.5–20, 0.5–5.0 and 0–300 μg/L, respectively (Whitehead, 1984; Schwehr and Santschi, 2003; Hou et al., 2000; Ünak et al., 1999). With all these natural and artificial iodine sources, wastewater tends to contain a certain level of iodine.

The dominant iodine species in waters are iodide, iodate and organo-iodine (Hansen et al., 2011; Gilfedder et al., 2009). Different iodine species may exhibit dramatically different mobility, bioavailability and chemical behaviors in the environment. For example, iodide is rather mobile, while iodate is efficiently sorbed by soils (Gilfedder et al., 2009); iodide, rather than iodate, is the bioavailable iodine form (Eskandari et al., 1997; Küpper et al., 1998); inorganic and organic iodine species have different hydrophilic and biophilic properties (Hu et al., 2005). Furthermore, the "three" dominant iodine species, i.e., iodide, iodate and organo-iodine, may undergo transformation to one another in the environment and during water/wastewater treatment. Nitrate-reducing, iron-reducing and sulfate-reducing bacteria have the potential to reduce iodate to iodide (Farrenkopf et al., 1997; Councell et al., 1997); certain bacteria can oxidize iodide to molecular iodine (Amachi et al., 2005a); iodide undergoes transformation in natural and wastewater systems by fixation on humic substances to form organo-iodine (Rädlinger and Heumann, 2000). Therefore, the study of iodine speciation in waters is of great significance.

Drinking water needs to be disinfected during treatment. Wastewater effluents are also subjected to disinfection before discharge to inactivate the microorganisms. During disinfection, iodide can be oxidized by disinfectants to HOI/OI^-, which further reacts with natural/effluent organic matter to form iodinated disinfection byproducts (DBPs) (Bichsel and von Gunten, 1999, 2000; Krasner et al., 2006; Hua and Reckhow, 2006, 2007; Richardson et al., 2008; Ding and Zhang, 2009; Duirk et al., 2011; Jones et al., 2012; Chu et al., 2012). Iodinated DBPs have drawn more and more concerns due to their significantly higher toxicity than their brominated and chlorinated analogues (Plewa et al., 2004; Cemeli et al., 2006; Richardson et al., 2007, 2008). Since the three iodine species can undergo transformation to one another, all the three iodine species in source water and wastewater need to be determined to predict the iodine levels that are possible to participate in the formation of iodinated DBPs.

To date, a number of methods for the determination of iodine species have been reported. However, most of them can determine only one or two iodine species (iodide and/or iodate) (Mishra et al., 2000; Hou et al., 2000). Recently, a couple of methods involving the determination of all the three iodine species (iodide, iodate and organo-iodine) have been reported. In one method, the three iodine species were derivatized to iodide and then iodide was determined by high performance liquid chromatography; however, the derivatization time for organo-iodine to iodide was more than 20 h, which was time-consuming (Schwehr and Santschi, 2003). A gas chromatography–mass spectrometry (GC–MS) method has also been developed by derivatizing all the three iodine species to a specific organic iodine derivative followed by GC–MS detection; however, it involved a complex derivatization process for organo-iodine, which was a three-step derivatization; moreover, it required the formation of only one isomer of the iodine derivative, so iodine must react only with the selected iodine scavenger and form only one iodine derivative. Thus the organic compounds which might react with iodine must be removed from the original water samples and the selection of the iodine scavenger was limited to the organic compounds with only one available substitution position for iodine (Zhang et al., 2010a). Ion chromatography with conductivity detection is also not amenable for the detection of inorganic iodine species since conductivity detection responds to all ionic species, resulting in a high quantitation limit (up to 100 μg/L as I). Therefore, the purpose of this study was to develop a method which involves a simple and short derivatization process for each iodine species and provides lower detection limits for those iodine species.

In this study, a fast, sensitive and accurate method was developed for the quantitation of iodide, iodate and organo-iodine in waters. The developed method was applied to the determination of iodine species in a variety of water samples, including tap water, seawater, urine and wastewater. The concentrations and distributions of iodine species in different water samples were illustrated.

2. Materials and methods

2.1. *Chemicals and reagents*

Potassium iodide (100%) was purchased from BDH. Ascorbic acid (≥99.7%), potassium iodate (≥99.7%), ammonium chloride (≥99.5%) and potassium nitrate (≥99.0%) were purchased from Riedel-deHaën. A sodium hypochlorite stock solution was purchased from Sigma Aldrich and diluted to around 2000 mg/L as Cl_2 and periodically standardized by the N,N-diethyl-p-phenylene diamine (DPD) ferrous titrimetric method (APHA et al., 1995). All other chemicals used in this study were purchased at the highest purities available from Sigma Aldrich. Ultrapure water (18.2 MΩ cm) was supplied by a NANOpure Diamond purifier system (Barnstead).

2.2. *Preparation of solutions*

The iodide and iodate stock solutions (100 mg/L as I) were prepared by dissolving potassium iodide and potassium iodate in ultrapure water, respectively. They were stored in amber glass bottles at 4 °C and newly prepared every month. The working solutions of iodide and iodate with lower concentrations were freshly prepared daily by diluting the stock solutions with ultrapure water.

An ammonium chloride solution (1.0 g/L as N), a phenol solution (10.0 g/L as C), an ascorbic acid solution (1.0 g/L) and a sodium arsenite solution (13.0 g/L) were prepared. They were stored in amber glass bottles at 4 °C. The phenol, ascorbic acid