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Halogen-specific total organic halogen analysis: Assessment by recovery of total bromine

Markus Langsa[1,3], *Sebastien Allard*[1], *Ina Kristiana*[1], *Anna Heitz*[2], *Cynthia A. Joll*[1,*]

1. *Curtin Water Quality Research Centre, Department of Chemistry, Curtin University, Perth, Western Australia 6102, Australia*
2. *Department of Civil Engineering, Curtin University, Perth, Western Australia 6102, Australia*
3. *Jurusan Kimia, Fakultas Matematika dan Ilmu Pengetahuan Alam, Universitas Papua, Manokwari, Papua Barat 98314, Indonesia*

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ABSTRACT

Determination of halogen-specific total organic halogen (TOX) is vital for studies of disinfection of waters containing bromide, since total organic bromine (TOBr) is likely to be more problematic than total organic chlorine. Here, we present further halogen-specific TOX method optimisation and validation, focusing on measurement of TOBr. The optimised halogen-specific TOX method was validated based on the recovery of model compounds covering different classes of disinfection by-products (haloacetic acids, haloacetonitriles, halophenols and halogenated benzenes) and the recovery of total bromine (mass balance of TOBr and bromide concentrations) during disinfection of waters containing dissolved organic matter and bromide. The validation of a halogen-specific TOX method based on the mass balance of total bromine has not previously been reported. Very good recoveries of organic halogen from all model compounds were obtained, indicating high or complete conversion of all organic halogen in the model compound solution through to halide in the absorber solution for ion chromatography analysis. The method was also successfully applied to monitor conversion of bromide to TOBr in a groundwater treatment plant. An excellent recovery (101%) of total bromine was observed from the raw water to the post-chlorination stage. Excellent recoveries of total bromine (92%–95%) were also obtained from chlorination of a synthetic water containing dissolved organic matter and bromide, demonstrating the validity of the halogen-specific TOX method for TOBr measurement. The halogen-specific TOX method is an important tool to monitor and better understand the formation of halogenated organic compounds, in particular brominated organic compounds, in drinking water systems.

Introduction

Natural processes, such as salt water intrusion, high evaporation conditions in arid watersheds and natural salt deposits from ancient seas, as well as pollution from industrial activities, can result in elevated bromide and iodide concentrations in natural waters (Agus et al., 2009; von Gunten, 2003). Bromide is usually detected in natural waters in the range of ~10 to >1000 μg/L (Heeb et al., 2014), while iodide is found at much lower concentrations (~50 μg/L) (Agus et al., 2009). We have found that many source waters in Western Australia (WA) contain moderate to extremely high concentrations of bromide (up to 8.5 mg/L) (Gruchlik et al., 2014), likely demonstrating all three natural processes of salt water intrusion, arid climate and

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* *Corresponding author*. E-mail: c.joll@curtin.edu.au (Cynthia A. Joll).

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ancient sea deposits, and leading to our focus on studies of the impact of bromide in drinking water treatment (*e.g.*, Allard et al., 2013a, 2013b, 2015; Criquet et al., 2012, 2015; Tan et al., 2016; Langsa et al., 2017). Conventional coagulation/flocculation drinking water treatment processes do not effectively remove bromide (Kristiana et al., 2015; Tan et al., 2016), leading to bromide being present during the disinfection process. Bromide is rapidly oxidised by oxidants such as chlorine to produce hypobromous acid (HOBr), which can then react with natural organic matter (NOM) in the water to form brominated disinfection by-products (DBPs), in a similar way to chlorine (hypochlorous acid, HOCl) forming chlorinated DBPs. These DBPs may lead to potential adverse health effects (Hua and Reckhow, 2006). In fact, brominated DBPs have been reported to be hundreds of times more toxic than their chlorinated analogues in cell bioassays (Richardson and Kimura, 2016; Richardson et al., 2007; Yang et al., 2014).

Total organic halogen (TOX) represents all the chlorinated, brominated and iodinated organic compounds in a water sample. In drinking water treatment, TOX is generally used as a measure of the total halogenated DBP formation in disinfected water. In chlorinated waters, the measured individual DBPs have been reported to account for only 16%–70% of TOX (Pressman et al., 2010; Richardson and Ternes, 2011; Tan et al., 2016), while in chloraminated waters, less than 20% of TOX can reportedly be assigned to individually measured species of DBPs (Hua and Reckhow, 2007; Li et al., 2002). Therefore, the measurement of TOX includes both known DBPs and the significant fraction of TOX which remains unidentified and uncharacterised. Analysis of TOX offers the water industry and regulators a method to quantify all halogen incorporation into DBPs to better protect the public against the potential adverse health risks (*e.g.*, bladder cancer (Richardson et al., 2007)) from chlorinated or chloraminated drinking water. This is in contrast to the existing focus on two sets of individual DBPs (the trihalomethanes (THMs) and haloacetic acids (HAAs)) which are not believed to be causative for the health risks (Bull et al., 2011). Moreover, recent studies have found that TOX not only represents the total concentration of all halogenated DBPs but is also an indicator of the overall toxicity of these halogenated DBPs (*e.g.*, Yang et al., 2014).

Analytical methods used to identify and measure TOX in water systems involve: adsorption of dissolved organic matter (DOM), including halogenated organic compounds, onto activated carbon; combustion of the activated carbon; collection of resultant hydrogen halide gases in an absorber solution; determination of the concentration of halide ions in the absorber solution; and calculation of the concentrations of halogen originally incorporated into DOM in the water sample. While a method for the analysis of bulk TOX has long been standardised (APHA et al., 1995), more recently, it has become apparent that determination of the three specific TOX species, total organic chlorine (TOCl), total organic bromine (TOBr) and total organic iodine (TOI), is vital for studies of disinfection of waters containing bromide and iodide. This is because TOI is likely to be of greater health concern than TOBr, which itself is likely to be more problematic than TOCl (Plewa et al., 2004). Ion chromatography (IC) is the preferred detection method due to instrumentation costs and availability (Brandt and Kettrup, 1987; Hua and Reckhow, 2006; Li et al., 2011; Oleksy-Frenzel et al., 2000), and it enables the quantification of TOCl, TOBr and TOI in the original water sample by separation of chloride, bromide and iodide ions present in the absorber solution.

Brandt and Kettrup (1987) first reported the use of IC to separate between TOCl, TOBr and sulphur compounds in water samples. In their method, the combustion was conducted at 1050°C in the presence of oxygen at a flow rate of 300 mL/min. Hydrogen peroxide solution was chosen to collect the resultant gases in the absorber, followed by off-line IC detection of halides in the absorber solution. Recoveries of model compounds containing chlorine and bromine varied from 3% to 109%. Chloramin-T, a biocide chemical, exhibited the lowest recovery, while the highest recovery was obtained for trichloroacetic acid (Brandt and Kettrup, 1987). The poor recovery of Chloramin-T is likely due to its decomposition in water to form hypochlorite, which would not be absorbed onto the activated carbon but rather oxidise the carbon surface (Potwora, 2009), forming chloride which would remain in the water phase and not be recovered in the TOX method. Oleksy-Frenzel et al. (2000) then developed a method of differential TOX analysis with IC detection which optimised the combustion conditions and the gas absorption system. The combustion temperature chosen was also 1050°C but the oxygen flow rate was 150 mL/min. A sulphuric acid solution was used prior to the absorber for drying of the combustion gases, followed by collection of the gases in a sodium sulphide absorber solution. Recoveries of model compounds containing chlorine, bromine and iodine were reported to range from 14% to 103% (Oleksy-Frenzel et al., 2000). While the selection of model compounds by Brandt and Kettrup (1987) focussed on halogenated non-phenolic based compounds, Oleksy-Frenzel et al. (2000) covered a wider range of halogenated compounds including iodinated X-ray contrast media. The lowest recoveries were found for chloro- and iodo-acetamide (14% and 37%, respectively), while the highest recovery corresponded to iodoacetic acid (103%) (Oleksy-Frenzel et al., 2000). Echigo et al. (2000) used a similar combustion system to the system described by Brandt and Kettrup (1987), except that ultrapure water was used as the absorber solution. Recoveries of chlorinated and brominated model compounds ranged from 76% to 84%.

Hua and Reckhow (2006) developed a method for the analysis of halogen-specific TOX using a conventional Euroglass TOX analyser (similar to the combustion system reported by Oleksy-Frenzel et al. (2000)) and an off-line IC, and reported high recoveries (92%–104%) of model compounds containing chlorine, bromine and iodine. Finally, in a more recent study, we established a halogen-specific TOX method using a state-of-the-art on-line TOX-IC system (Kristiana et al., 2015). In this study, a broad assessment of key analytical parameters for accurate measurement of halogen-specific TOX in waters was performed, including the use of different types of granular activated carbon, two different absorber solutions, and selected model compounds covering different classes of DBPs. The recoveries of the model compounds were all reported to be greater than 85% (Kristiana et al., 2015).

The accuracy of the halogen-specific TOX measurement depends on the performance of each step of the process, which includes several analytical challenges, such as the activated carbon adsorption process. Previous studies applied