



Analysis of halogen-specific TOX revisited: Method improvement and application



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ABSTRACT

A method was optimised and evaluated for the analysis of total organic halogen (TOX) in drinking water samples. It involved adsorption of organic halogen onto activated carbon, followed by combustion of the activated carbon and adsorbed material, absorption of the resulting hydrogen halide gases in an absorbing solution, and analysis of halide ions in the solution using an on-line ion chromatograph. Careful optimisation and validation of the method resulted in significant improvements compared to previously reported methods. Method detection limits were $5 \mu\text{g L}^{-1}$ for TOCl (as Cl^-), $2 \mu\text{g L}^{-1}$ for TOBr (as Br^-), and $2 \mu\text{g L}^{-1}$ for TOI (as I^-). Interferences with TOI measurement occurred when iodide or iodate was present in the sample at concentrations at or above $100 \mu\text{g L}^{-1}$ and $500 \mu\text{g L}^{-1}$, respectively. In general, excellent method recoveries were determined for a wide range of model compounds. The method was used to investigate the formation of halogen-specific TOX through a water treatment plant and in laboratory-scale disinfection experiments. Up to 70% of bromide in the water was converted to TOBr following disinfection at the plant. In the disinfection experiments, TOI was preferentially formed in chloraminated samples, and trihalomethanes only constituted a small fraction ($\leq 20\%$) of TOX, highlighting the significant proportion of halogenated organic DBPs that are not measured regularly. This is the first report of a comprehensive assessment of the key parameters influencing the efficiency and reliability of the analysis of halogen-specific TOX in drinking water with demonstration of its applications.

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1. Introduction

Disinfection of drinking water is critical for the prevention of waterborne diseases. However, one unintended result of disinfection is the reaction of the disinfectant with organic and inorganic materials in the water producing disinfection by-products (DBPs). The formation of DBPs is a public health concern, prompting regulation of the concentrations of some DBPs in drinking waters. Over 600 DBPs have been identified [17]. However, toxicological, epidemiological and occurrence studies have only been conducted on a small number of these DBPs, with some DBPs being shown to be genotoxic and carcinogenic, and associated with adverse health effects such as bladder cancer [18].

The majority of identified DBPs in drinking waters are halogenated compounds, consistent with the fact that chlorine and chloramine are the most commonly used disinfectants. In the presence of naturally occurring bromide and iodide in water, brominated and

iodinated DBPs are formed along with chlorinated DBPs. Halogenated DBPs can be measured as individual species, e.g. trihalomethanes (THMs) and haloacetic acids (HAAs), or as a bulk parameter such as total organic halogen (TOX). TOX provides a measure of all the halogenated species present in a sample. The measurement of TOX is an attractive alternative to the measurement of individual DBPs since analytical methods do not exist for many of the individual compounds of which the TOX present in drinking water is comprised. In chlorinated waters, the measured individual DBPs have been reported to account for only 40–70% of TOX, while in chloraminated waters, less than 20% of TOX can reportedly be assigned to individual species of DBPs [17].

Conventionally, TOX in waters has been measured as chloride equivalents by microcoulometric titration [4]. In this analysis, the contribution of the different halides cannot be differentiated and quantified, and the concentration of organic halides is reported as an equivalent concentration of organically-bound chlorine. As such, the method underestimates the contribution of bromide and iodide on a mass basis since bromide and iodide are heavier than chloride. Brominated and iodinated DBPs have been reported to be more genotoxic, cytotoxic and carcinogenic than their chlorinated analogues [14,18]. Depending on the disinfection process and the concentrations

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of bromide and iodide in waters, the combined formation of brominated and iodinated DBPs (measured as halogen-specific TOX) could be up to 50% of the chlorinated DBPs [11,6,9]. Therefore, there is a need to differentiate brominated (TOBr) and iodinated (TOI) compounds from chlorinated (TOCl) compounds, to provide a better understanding of the formation characteristics of these DBPs.

Developments in ion chromatography (IC) have provided an alternative method of sensitive halide detection, enabling the measurement of halogen-specific TOX in waters, to give separate measurements of chlorinated (TOCl), brominated (TOBr), and iodinated (TOI) organic compounds. There are only a few reported studies on the use of IC for the analysis of halogen-specific TOX in waters [13,2,5,7]. In addition, there are only a few reports on the development, optimisation, and validation of methods for the analysis of halogen-specific TOX [10,13,2,5,7]. These studies reported varying degrees of recoveries of halogenated organic compounds reflecting the complex analytical challenges involved in the analysis of halogen-specific TOX and highlighting the need to conduct further investigation to address these challenges and improve the overall performance of the method.

The objective of our study was to optimise and validate the method for the analysis of halogen-specific TOX, giving particular attention to key parameters affecting the recoveries of halogen-specific TOX and to the common interferences that may affect the accuracy and the overall performance of the analysis. The impacts of matrix effects from real waters were also investigated. In this study, we used state-of-the-art instrumentation comprised of an AQF-100 (Mitsubishi) combustion system with a solid autosampler attached to an absorption unit and coupled to a reagent-free ion chromatography system (Dionex), allowing for the automated on-line analysis of halogen-specific TOX. This is the first report of a comprehensive assessment of the key parameters influencing the efficiency and reliability of the analysis of halogen-specific TOX in waters.

2. Experimental section

2.1. Chemicals and standard solutions

All chemicals, including organic solvents, used in this study were of analytical grade purity or better and were used without further purification. Specific details on these chemicals are provided in the Supporting information S11.

2.2. Analysis of halogen-specific TOX using the AQF-IC system

Standard solutions and water samples (50 mL) were acidified to pH 2 with nitric acid, and adsorbed onto two activated carbon microcolumns using a Mitsubishi TOX Sample Preparator (Model TX-3AA; Mitsubishi, Japan). The activated carbon onto which the organic halogens were adsorbed was washed with dilute nitric acid and then placed in a sample boat, transferred to the automatic quick furnace (AQF-100; Mitsubishi, Japan) by the automatic solid sampler and combusted in the furnace. The hydrogen halide and other halogen gases formed from combustion were transferred from the furnace via a quartz gas line and collected in a gas absorption unit containing ultrapure water automatically dispensed from a reservoir (GA-100; Mitsubishi, Japan) (Supporting information S12, Fig. S1). The Ar/O₂ and O₂ gas flow rates through the furnace were 200 and 400 mL min⁻¹, respectively. A small amount of water was passed through the quartz gas lines leading into the gas absorption tube to ensure that all halogen gases were collected before an aliquot (500 µL) of the absorption solution was automatically injected from the absorption tube into an IC system (ICS-3000, Dionex, Sunnyvale, CA, USA) via a sampling line. The concentrations of halogen-specific TOX (i.e. TOCl, TOBr, and TOI) were measured by the conductivity detector as

chloride (Cl⁻), bromide (Br⁻), and iodide (I⁻), respectively. Separation of halide ions was conducted using an IonPac[®] AS19 ion chromatography column (4 × 250 mm) with an IonPac[®] AG19 (4 × 50 mm) guard column (Dionex). The mobile phase was generated using a potassium hydroxide eluent generator at a flow rate of 1.0 mL min⁻¹. A diagram of the components of the AQF-IC system (Fig. S1) and the optimised conditions for the separation of the halide ions (Table S5) are given in the Supporting information.

2.3. Collection and analysis of water samples

Water samples from several source waters and a water treatment plant (WTP1) were collected. The source water samples (raw, untreated water samples: SW1, SW2, SW3, and SW4) were diluted to identical dissolved organic carbon (DOC) concentrations (2 mg L⁻¹), and were chlorinated (8 mg L⁻¹ Cl₂, pH 7) or chloraminated (4 mg L⁻¹ as Cl₂, Cl:N weight ratio of 4:1, pH 8) in the presence of bromide and iodide (added to achieve concentrations of 0.5 mg L⁻¹ and 0.06 mg L⁻¹, respectively). At the end of the experimental period (72 h), the disinfectant residual in each sample was quenched with an excess of sodium sulphite and each sample was analysed for THMs and halogen-specific TOX. Analysis of THMs was conducted by solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS).

Samples collected from the water treatment plant were analysed for halogen-specific TOX. Free chlorine equivalent concentrations were also measured (on-site) using a pocket colorimeter (HACH, Loveland, CO, USA). The water treatment process at WTP1 included aeration, water softening and pH adjustment, filtration, chlorination (initial concentration: 2.2 mg L⁻¹), and fluoridation. Any disinfectant residual contained in the samples to be analysed for TOX was quenched with sodium sulphite immediately after sampling.

Dissolved organic carbon concentrations were measured using a Shimadzu TOC-V_{ws} Total Organic Carbon Analyser according to the Standard Method 5310C [4]. Bromide, bromate, iodide, and iodate concentrations were analysed according to the method of Salhi and von Gunten [19] using a Dionex ICS-3000 IC system (UV detector).

3. Results and discussion

3.1. Method evaluation and optimisation

The first objective of our study was to evaluate and optimise the conditions for the analysis of halogen-specific TOX using an AQF-IC instrument. Halophenol standard solutions (2,4,6-trichlorophenol, 2,4,6-tribromophenol, and 2-iodophenol; each halophenol at 100 µg L⁻¹, unless otherwise stated) were used to optimise conditions for the analysis of halogen-specific TOX. Although they may not be the ideal representatives of the overall pool of halogenated compounds in waters, they have been prescribed as calibration standards by Standard Methods and used in all previous studies (e.g. [4,13,9]). The analysis of halogen-specific TOX using an AQF-IC instrument involved several steps, each associated with parameters that may affect the performance of the method: sample adsorption, sample combustion, gas absorption, and ion chromatography. For each parameter, the range of conditions and values tested, as well as the selected, optimised, conditions are given in Supporting information (Table S2).

3.1.1. Evaluation and optimisation of sample adsorption procedure

Conventionally, in the analysis of TOX, the pH of samples has been lowered to 2 prior to sample adsorption onto activated carbon (e.g. [4]), since halogenated organic acids are protonated at low pH leading to greater adsorption and reported higher recoveries of TOX

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