Kinetics, mechanisms, and influencing factors on the treatment of haloacetonitriles (HANs) in water by two household heating devices

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HIGHLIGHTS

- Haloacetonitriles (HANs) controls by two household heating devices were examined.
- HAN removal was due to a combined effect of volatilization and decomposition.
- HANs lability under heating relied highly upon the halogenation type(s) and degree(s).
- HAN treatment efficiency may be greatly enhanced by favorable handling methods.

GRAPHICAL ABSTRACT

Boiler Heating   Microwave Oven Irradiation

ARTICLE INFO

ABSTRACT

Haloacetonitriles (HANs) are a group of nitrogenous disinfection by-products (DBPs) commonly found in treated water with potential carcinogenic, cytotoxic, and genotoxic risks. In order to control HANs and understand their real intake levels by people via drinking water, this study evaluated a list of structural, operational, and environmental factors affecting the treatment of HANs by two domestic heating devices, i.e., an electric boiler and a microwave oven. Results show that the concentrations of HANs decreased exponentially over time with increasing temperature, water turbulence, and bubbles, and the phenomena were most likely due to a combined effect of volatilization and hydrolysis. Among HANs, the lability increased with increasing halogenation degrees (i.e., tri- > di- > mono- HANs) yet decreasing halogen molecular weights (i.e., Cl- > Br- > I- HANs); such trends were well captured by quantitative structure activity relationship models ($R^2 = 0.99$). Operational factors played critical roles in controlling HANs too, including the rate of heating, water volume, water temperature at time of pouring, cooling method, and capping condition, suggesting that people could benefit from proper handling methods and procedures. In addition, HANs added to tap water exhibited higher removals than those added to ultrapure water, probably because of the presence of free chlorine in tap water.

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1. Introduction

Haloacetonitriles (HANs) are a group of nitrogenous disinfection by-products (DBPs) commonly found in disinfected water (Bond et al., 2011b; Shah et al., 2011) with relatively higher toxicity than certain currently-regulated carbonaceous DBPs (Krasner, 2009; Yang and Zhang, 2013). The occurrence of HANs has been reported in the United States of America (USA), China, and many other countries (Williams et al., 1997; Krasner et al., 2006; Bond et al., 2011b; Ding et al., 2013), with concentrations ranging from

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below method detection limit (MDL) to 39.2 μg/L. Among HANs, the most frequently detected HAN species in drinking water are trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN) (Krasner et al., 1989; Singer et al., 1995; Williams et al., 1997). Although HANs account for only around 10% (by weight) of regulated DBPs, such as trihalomethanes (THMs) (Oliver, 1983; Richardson, 2003; Bond et al., 2011b), some studies have illustrated that HANs are orders of magnitude more cytotoxic and genotoxic than regulated DBPs (Plewa et al., 2004, 2008; Muellner et al., 2007; Bull et al., 2011). Therefore, HANs are currently prioritized as emerging contaminants by the US Environmental Protection Agency (USEPA), and DCAN and DBAN in drinking water are promulgated by the World Health Organization (WHO) to not exceed the maximum contaminant levels (MCLs) of 20 and 70 μg/L, respectively. Recently, when iodinated HANs were identified (Ding et al., 2013) and shown to be more harmful than chlorinated and brominated analogues (Muellner et al., 2007), considerable concerns toward the iodinated HANs have arisen as well.

Currently, removing DBP precursors (Singer, 1994; Bond et al., 2010; Kristiana et al., 2011) and applying alternative disinfectants (e.g., chloramine, chlorine dioxide, and ozone) (Richardson et al., 1999; Seidel et al., 2005) are the two major approaches used to mitigate DBP risks from drinking water. However, conventional water treatment technologies are unable to eliminate all DBP precursors, leaving remaining natural organic matter (NOM) with considerable DBP formation potential (Bond et al., 2011a); and the use of alternative disinfectants may induce formation of emerging DBPs (Richardson et al., 1999; Krasner, 2009) that are likely more of a health concern than regulated species (Muellner et al., 2007). Therefore, some amounts of DBPs may inevitably form in the presence of DBP precursors and disinfectants and, once formed, persist in water distribution systems and eventually reach consumers.

Point-of-use (POU) or household water treatment (HWT) facilities serves as the last barrier to reduce DBPs and optimize water quality. For tea drinkers in Asia and coffee consumers in Western countries, boiling water before ingestion is simply a traditional habit. Consequently, several studies have endeavored to understand the effectiveness of boiling on water quality, which sometimes showed great benefits in controlling DBPs (Wu et al., 2001; Pan et al., 2014). However, those studies often applied more than one minute of boiling time for evaluation (Wu et al., 2001; Pan et al., 2014), which is much longer than the time taken by a contemporary boiler equipped with an automatic shut-off function that usually boils for only seconds. Therefore, the real benefit of boiling may be overestimated. In addition, the mechanisms responsible for HAN losses and influencing factors are currently unknown. For example, there are no data showing if and how much volatilization and hydrolysis contributes to the DBP losses during boiling, or to what extent structural, operational, and environmental factors affect the HAN treatment efficiency. Consequently, there is a need for more research to further understand and explore the potentials of these heating processes for HAN control.

In order to fill the knowledge gaps, this study evaluated a series of influencing factors affecting the thermal treatment of six types of HANs by two heating devices. The selected heating devices, boiler and microwave oven, represent two heat delivery modes: one via electricity from the bottom and the other via microwave irradiation from the sides. Six HANs were chosen to represent compounds with various halogenation degrees and types, including monochloroacetonitrile (MCAN), monobromoacetonitrile (MBAN), monoiodoacetonitrile (MIAN), DCAN, DBAN, and TCAN. A list of environmental factors (including initial concentration, presence of free chlorine, salt, and water type) and operational factors (including water volume, cooling, pouring activity, and capping method) were assessed to represent typical conditions and handling habits of common people in daily life. Ultimately, the aim of this study was to provide fundamental and practical insights on how to control HANs.

2. Materials and methods

2.1. Chemicals and reagents

Except for DBAN, which was supplied by J&K Scientific Ltd., the other five HANs used in this study were purchased in liquid form at analytical reagent grade (>97% in purity) from Aladdin. Inc. Prior to testing, a mixture of six HANs was dissolved in ultrapure water at 1.5 g/L for each compound and stored in a freezer at 4 °C as stock solution.

To understand the influence of water matrix on HANs treatment, HANs were spiked into two types of water, a tap water and an ultrapure water, for comparison studies. The tap water was collected from the laboratory facuet and filtered by a 0.45 μm glass fiber filter (Xingya, Co., Ltd) before use, and its characteristics were typical of this city, with total organic carbon (TOC) as 2.0 mg/L, total dissolved solid (TDS) as 54.4 mg/L, pH as 7.9, and residual free chlorine as 0.4 mg/L. Ultrapure water was produced by a Millipore water generator (Direct-Q_3).

2.2. Analytical methods

HANs were analyzed using a liquid/liquid extraction-gas chromatography/electron capture detector (LLE-GC/ECD, Fuli 7920, China) based on the USEPA method 551.1. Haloacetamides (HAcAms) were proven to be the major products of HAN hydrolysis before (Glezer et al., 1999; Chen, 2011; Yu and Reckhow, 2015) and relatively lower in volatility than HANs (Table S1), thus serving as good indicators of HAN hydrolysis effect. However, since not all HAcAms are commercially available in market, they were indirectly analyzed by converting them to their corresponding haloacetic acids (HAAs) first under strong acidic conditions (5 ml H_2SO_4 in 20 mL water) according to a literature (Gao et al., 2011), and then HAAs were determined by the EPA method 552.3. Because it facilitates conversion of HAcAms to HAAs but do not favor HANs hydrolysis (Yu and Reckhow, 2015; Liu et al., 2017), the indirect method was appropriate to quantify the formation of HAcAms and HAAs together, both are known hydrolysis products of HANs. Before use, a calibration curve with R^2 of 0.999 (Fig. S1a) was built for an exemplary compound, trichloroacetamide (TCAcAm), using the indirect method; and during experiment, the differences in detecting TCAcAm between the indirect method and direct measurement method, which applied EPA 551.1, were also documented (Fig. S1b). All these compounds have MDLs below 1 μg/L. Free chlorine was analyzed by a DPD method using a spectrophotometer (Hach 3900, USA) according to the EPA 330.5 method. Inorganic halides including chloride, bromide, and iodide were analyzed by an ion chromatography (IC2010, Tosoh Inc., Japan) with MDLs $\leq$ 10 μg/L, and the appearance of halides was used to indicate the decomposition of HANs.

2.3. Apparatus and procedures

The boiler (BQ-150GA, Shenyi Electronics Inc., China) is made of stainless steel and equipped with an automatic switch-off function, which has a water capacity of 2 L and a power input of 1500 W. It takes 4.3 min and 7.5 min to heat 1 L (half-volume) and 2 L (full-volume), respectively, of water to the boiling point (BP); and once BP is reached, the boiling phenomenon lasts for 20 s with bubbles