Trends in Analytical Chemistry ■■ (2016) ■■–■■

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Formation and determination of organohalogen by-products in water – Part I. Discussing the parameters influencing the formation of organohalogen by-products and the relevance of estimating their concentration using the AOX (adsorbable organic halide) method

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ARTICLE INFO

Keywords:
Organohalogen
Halogen-based oxidants
By-products
Water
AOX parameter
Material balance

ABSTRACT

Halogen-based oxidants are widely used in water treatment processes in order to inactivate pathogenic microorganisms. They react with naturally occurring organic matter as well as with other contaminants, leading to the formation of a wide range of unwanted by-products including organohalogen by-products (OXBPs), which have shown toxic properties. The quantity of OXBPs in a water sample can be estimated by a parameter called AOX (halogenated organic compounds adsorbable on activated carbon). Despite the growing number of quantified OXBPs, the material balance (percentage of known OXBPs measured individually divided by the AOX value) indicates that a significant portion of OXBPs remains unknown. This lack of knowledge is a barrier in the assessment of the effects of water treatments on ecosystems and human health. This manuscript is the first part of a review trio on OXBPs; the 2d and 3rd articles are devoted to OXBPs extraction processes and analytical techniques, respectively.

Contents

Abbreviations: AOX, Adsorbable organic halides; CX, Cyanogen halides; DBPs, Disinfection by-products; DCAcAm, Dichloroacetamide; DCAN, Dichloroacetonitrile; DOM, Dissolved organic matter; DOC, Dissolved organic carbon; EOX, Extractible organic halides; HAAs, Haloacetic Acids; HAcAms, Haloacetamides; HALs, Haloaldehydes; HANs, Haloacetonitriles; HKs, Haloketones; HNMs, Halonitromethanes; HX, Hydrogen halides; IAA, Iodoacetic acid; IC, Ion chromatography; I-THMs, Iodinated trihalomethanes; NOM, Natural organic matter; OXBPs, Organohalogen by-products; POM, Particulate organic matter; POX, Purgeable organic halides; 1,1,1-TCP, 1,1,1-trichloropropanone; THMs, Trihalomethanes; UOXBPs, Unknown organohalogen by-products.

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http://dx.doi.org/10.1016/j.trac.2016.06.008
0165-9936/

Please cite this article in press as: Aziz Kinani, Said Kinani, Bertille Richard, Mélanie Lorthioy, Stéphane Bouchonnet, Formation and determination of organohalogen by-products in water – Part I. Discussing the parameters influencing the formation of organohalogen by-products and the relevance of estimating their concentration using the AOX (adsorbable organic halide) method, Trends in Analytical Chemistry (2016), doi: 10.1016/j.trac.2016.06.008

1. Introduction

Halogen-based oxidants, such as chlorine (gaseous form: Cl_2, liquid bleach: NaOCl or calcium hypochlorite ($Ca(OCl)_2$), chlorine dioxide (ClO_2), and monochloramine (NH_2Cl)), are widely used in water treatment processes in order to inactivate pathogenic microorganisms, control biofouling and reduce the risk of introducing invasive species into local aquatic ecosystems. The first applications were for disinfection of wastewater and drinking water in order to eradicate waterborne bacterial diseases, such as typhoid, cholera and dysentery [1]. Chlorine is the most widely used biocide in industry today due to its low cost, ease of use, its high efficiency and wide range of applications. A "side-effect" of water treatment by halogen-based oxidants is that they react with naturally occurring organic matter as well as with bromide and iodide ions, microorganisms, biofilms, anthropogenic contaminants, etc., leading to the formation of a wide range of unwanted chemical by-products, commonly called disinfection by-products (DBPs) [2]. Among the chemical compounds formed, organohalogen by-products (OXBPs) have received particular attention from the scientific community and public authorities, since the discovery in the mid-1970s of the carcinogenic effect of trihalomethanes (THMs), following the discovery of these chlorination by-products in drinking water [3]. OXBPs can be quantitatively estimated using the AOX group parameter (Adsorbable Organic Halides), which represents the sum of the organically bound chlorine, bromine and iodine. However, these indicator parameters may not provide a final answer because the toxicological significance of the obtained values cannot be established without knowledge of the chemical structures of the measured compounds [4]. To date, more than 600 DBPs have been identified. The main OXBPs identified with regular frequency in water are THMs, haloacetic acids (HAAs), haloacetonitriles (HANs), cyanogen halides (CX), haloketones (HKs), haloaldehydes (HALs), halonitromethanes (HNMs), haloacetamides (HAcAms), halophenols (HPs), haloaldehydes, halofuranones, halopyrroles, and haloquinones [5]. Some of these substances have shown toxic effect [6]. Nitrogenous and iodinated organohalogen by-products have recently received increased attention, since toxicological studies suggest that they have higher toxicity than the currently regulated carbonaceous by-products [7]. THMs and HAAs are still considered to be the dominant OXBPs groups on a weight basis in drinking water. Their formation mechanism is now well understood and their concentration levels are regulated in various countries [8]. Despite the growing number of quantified OXBPs and the increasing sensitivity of analytical methods, the material balance (MB), defined as the percentage of known OXBPs, indicate that a significant portion of OXBPs remains unknown: only 50% of the AOX can be attributed to individual known OXBPs under typical chlorination conditions. In the case of monochloramine and chlorine dioxide, the MB is even lower (<20%) [9]. More than 40 years after the discovery of THMs, the determination of UOXBPs identity and toxicity remains a major objective and a continuously evolving challenge. This highlights the need for development of new analytical methodologies and alternative approaches to identify UOXBPs or to monitor OXBPs previously identified.

This manuscript is the first part (part 1) of a literature review on OXBPs generated through water treatment by halogen-based oxidants, which is divided into three sections. The first section summarizes the state of knowledge concerning OXBPs formation, including an overview of the different factors influencing their concentration and speciation. The second section presents the main OXBP groups commonly produced in water and a selection of regulatory and guidelines values. In this section, we also discuss the percentage of unknown organohalogen by-products. The last section presents a detailed description and critical analysis of the methods used to estimate the total quantity of OXBPs presents in a water sample (group parameters).

2. Origin of organohalogen by-products in water

There is considerable evidence that organic matter constituents act as precursors in the formation of organohalogen by-products during water treatment. Incorporation of halogen into organic compounds takes place through three possible reaction pathways namely oxidation, substitution and addition. Oxidation may be the dominant reaction occurring between oxidant and organic matter in water [10]. However, addition and substitution are the reactions that lead to the formation of more organohalogen by-products [11]. The formation of low molecular weight organohalogen by-products involves successive isomerization, rearrangement, hydrolysis, and elimination reactions. It is important to note that only a very small amount of the oxidant introduced for water treatment turns into organohalogen by-products [12]. The OXBP concentration and speciation is influenced by the water quality and treatment modalities. These two parameters encompass many influencing factors, including the nature and form of the organic matter, the presence of amino-nitrogen, bromide and iodide, the nature and amount of the halogen-based oxidant, the removal of organic matter prior to introducing the oxidant, the contact time, temperature and pH [13,14]. The effect of each parameter on the potential generation and speciation of OXBPs is summarized in the following sections.

2.1. Influence of the nature of organic matter

Organic matter in aquatic environments is a heterogeneous complex mixture of organic compounds with different molecular weight, elemental composition, hydrophobicity and functional groups. Moreover, its composition varies considerably, depending on the water source, season, local geology, water flow, weather and pollution events, etc. According to its origin, organic matter can be divided into four categories: (1) natural organic matter (NOM), (2) organic matter from algal blooms, (3) organic matter from biological sources such as microorganisms and biofilms, and (4) anthropogenic organic chemicals. Substantial studies have been conducted to evaluate the effect of NOM on the formation of OXBPs and to understand the chemical mechanisms involved in their formation [15].

NOM is a major contributor to dissolved organic carbon (DOC) in natural waters (river and lake waters). It consists predominantly of humic substances (50 to 80%), mainly composed of humic and fulvic acids. They are natural biopolymers with heterogeneous functional groups and a wide molecular weight distribution. The contribution of natural organic matter is dominant in the formation of several families of OXBPs, particularly THMs, HAAs, HANs and HKs [16]. The NOM characteristics (e.g. relative proportions of fractions of hydrophilic/hydrophobic, aromatic/aliphatic, low/high molecular weight and dissolved organic carbon/dissolved organic nitrogen compounds) have strong influences on the OXBPs concentrations and speciation.

OXBPs are not only formed from reactions between halogen-based oxidants and dissolved NOM in the treated water. The treated water also contains particulate organic matter (POM) including bacteria, algae, protozoa, etc. [17]. The reactivity of these biological sources of organic matter with halogen-based oxidants has not been thoroughly studied. Recently, Huang et al. showed that chlorination of POM significantly contributes to the formation of OXBPs [18]. The chlorination tests performed on the effluents from secondary domestic wastewater showed that POM accounts for 26 to 46% of the total amount of dichloroacetonitrile (DCAN) and dichloroacetamide (DCAcAm). Chlorination tests carried out on two model bacteria, *Escherichia coli* and *Escherichia faecalis*, also revealed the formation of DCAN and DCAcAm, confirming the precursor role of microorganisms in the formation of OXBPs. A study by Wang et al. reported that chlorination and monochloramination of *Escherichia coli* leads to the

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