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Optimization of disinfection by-product analysis methods for IMO G9 approval

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ABSTRACT

This study assessed the methods for analyzing disinfection by-products (DBPs) to determine which were most suitable for ballast water in an approval test according to the Procedure for Approval of Ballast Water Management Systems that make use of Active Substances (G9). The existing analysis methods are optimized for drinking water. Therefore, it is necessary to assess the characteristics of ballast water, which has high levels of total residual oxidants (TROs) and salinity, prior to applying the existing methods. Sample preservation, pre-treatment and instrumental analysis methods were summarized based on certified test methods and the G9 final approval reports. Following the assessment, applicable methods were selected in consideration of the matrix effect arising from the high levels of TROs and salinity. The applicability was assessed using seawater and brackish water. The results are expected to be applied to the G9 test as well as in investigations of DBPs in ballast water.

1. Introduction

Ballast water is used to maintain the stability of ships during sailing, and is known to cause serious problems to the marine ecosystem due to the introduction of alien species through the traffic between countries (Burkholder et al., 2007; Gregg and Hallegraeff, 2007; Tsolaki and Diamadopoulos, 2010). For this reason, the International Maritime Organization (IMO) adopted the International Convention for the Control and Management of Ships Ballast Water and Sediments in 2004, and has mandated the installation of ballast water management systems (BWMSs) (Tsolaki and Diamadopoulos, 2010). The main purpose of a BWMS is to disinfect ballast water to remove organisms. The main disinfection processes used in a BWMS are chlorination, ultraviolet irradiation and ozonation (Delacroix et al., 2013; Duan et al., 2016).

Active substances are known to generate disinfection by-products (DBPs) harmful to the human body through reactions with the diverse range of substances present in seawater (Boorman, 1999; Richardson et al., 2007). For this reason, the active substances used in a BWMS should be approved by the Marine Environment Protection Committee (MEPC) prior to use in accordance with the "Procedure for Approval of Ballast Water Management Systems that Make Use of Active Substances" (G9) (IMO, 2008b). Within the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) of the IMO, the Ballast Water Working Group (BWWG) has recognized the importance of active substances and related substances, and extended the list of active substances from 18 chemicals (MEPC 65/INF.14) to 41 (MEPC 67/INF.17) (IMO, 2014a). This includes DBPs, including trihalomethanes (THMs), volatile organic compounds (VOCs), haloacetic acids (HAAs), haloacetonitriles (HANs), bromate and aldehydes (IMO, 2014a). A precise analysis of these substances in ballast water is very important because DBPs are directly associated with both the environmental and the health risk assessments required for G9 approval.

The disinfection process is considered to be essential in water treatment facilities to ensure the safety of drinking water. Therefore, studies of DBPs have largely focused on drinking water (Boorman, 1999; Richardson et al., 2007). The analysis methods used for detecting DBPs have also been developed in accordance with the requirements for drinking water. The United States Environmental Protection Agency (USEPA), for example, published the EPA Methods 500 series, which describes suitable methods for analyzing DBPs in drinking water (USEPA, 2003a). Target substances include THMs/VOCs, HAAs, HANs, bromate and aldehydes. The International Organization for Standardization (ISO) also recommends standardized methods for analyzing DBPs, which include VOCs, HAAs and bromate (ISO, 2016). The methods for analyzing DBPs recommended by these organizations are optimized for drinking water, in which matrix effects are relatively trivial. Therefore, it is necessary to assess their applicability in the analysis of ballast water, which has distinctive properties that differ from those of drinking water.

The salinity conditions of ballast water may vary depending on the

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differences in the water that ships pass through; thus, the analysis of DBPs should be applicable to fresh seawater, brackish water and fresh water (IMO, 2008a). Only fresh water has a salinity level similar to that of drinking water, while seawater and brackish water have higher salinity. The matrix effect in ballast water samples can interfere with the process of pre-treatment and instrumental analysis (Cavalcante et al., 2010; Wu et al., 2010). Additionally, ballast water has a higher level of total residual oxidants (TROs) than typical samples from water treatment facilities. Because DBPs continue to be generated when TROs are present, TROs should be immediately eliminated for the precise analysis of DBPs (Pepich et al., 2004). However, some of the TROs may remain due to their high level in ballast water, even though a preservation reagent, as suggested in the analysis method, is used. DBPs can also be generated during the transfer and storage of samples. For these reasons, DBPs should be analyzed in consideration of the properties of ballast water, but this has not previously been investigated.

In this study, suitable analysis methods for the measurement of DBPs in ballast water were determined in order to ensure that reliable chemical analysis results can be obtained. First, this study reviewed the existing certified test methods for DBPs suggested by the GESAMP-BWWG and related literature. The analysis methods for DBPs discussed in the MEPC active substance approval reports were investigated to identify the methods that are most frequently used around the world. In particular, when a ballast water sample with high levels of TROs and salinity was analyzed by the conventional test methods (i.e., those suitable for drinking water), the effect of interfering elements on the analysis was investigated in detail. Finally, to draw reliable conclusions regarding the methods investigated, measures to improve the most suitable analysis methods were suggested based on a test of effectiveness. This study is expected to make a large contribution to future investigations of the GESAMP-BWWG regarding the generation of DBPs and their activity.

2. Material and methods

2.1. Reagents and standards

This study analyzed the DBPs suggested by the GESAMP-BWWG, which are listed in Table 1. Except for 1,1-dibromoethane, standards for the analysis of DBPs were all purchased from AccuStandard (New Haven, CT, USA). A 1,1-dibromoethane standard was obtained from TCI (Tokyo, Japan). Methyl tert-butyl ether (MTBE), methanol, acetone and n-hexane (all HPLC grade) were purchased from Burdick & Jackson (Muskegan, MI, USA). Ultra-pure water was produced through the Milli-Q system (Millipore, Billerica, MA, USA). Daigo's artificial seawater was purchased from Nihon Pharmaceutical (Tokyo, Japan). The other chemicals used in the study were all guaranteed reagents.

2.2. Optimization procedure and literature review

The factors influencing the analytical procedures were assessed to obtain accurate measurements of DBPs in ballast water. Because high levels of TROs and salinity are the main characteristics of treated ballast water, this study was conducted with an emphasis on these factors (see Fig. 1). The level of TROs is related to the sample preservation procedure, and salinity affects both the pre-treatment and the instrumental analysis. First, the existing methods used to analyze DBP groups were surveyed in a literature review. Selected analysis methods were assessed by investigating the stages of sample preservation, pre-treatment and instrumental analysis. As a result, their limitations were determined. Sample preservation was assessed with an emphasis on TRO removal and pH. In the case of new preservation agents, changes in the concentration of target compounds were determined over time. In the pre-treatment and instrumental analysis stages, the matrix effect due to salinity was the main factor assessed. To offset the matrix effect due to salinity, artificial seawater and blank samples were used to produce a calibration curve. Finally, optimized analysis methods for DBPs in ballast water were determined.

Table 1
List of disinfection by-products proposed by the GESAMP-BWWG (37 types).

Group	Compound	CAS No.	Formula	M.W.
THMs/VOCs (16)	1,2-Dibromo-3-chloropropane	96-12-8	$C_3H_5Br_2Cl$	236.33
	Dibromochloromethane	124-48-1	$CHBr_2Cl$	208.28
	1,1-Dichloroethane	75-34-3	$C_2H_4Cl_2$	98.96
	1,1-Dibromoethane	557-91-5	$C_2H_4Br_2$	187.86
	Dibromomethane	74-95-3	CH_2Br_2	173.83
	Dichlorobromomethane	75-27-4	$CHBrCl_2$	163.83
	1,2-Dichloroethane	107-06-2	$C_2H_4Cl_2$	98.96
	Dichloromethane	75-09-2	CH_2Cl_2	84.93
	1,2-Dichloropropane	78-87-5	$C_3H_6Cl_2$	112.99
	Tetrachloromethane	56-23-5	CCl_4	153.82
	Tribromomethane	75-25-2	$CHBr_3$	252.73
	1,1,1-Trichloroethane	71-55-6	$C_2H_3Cl_3$	133.40
	1,1,2-Trichloroethane	79-00-5	$C_2H_3Cl_3$	133.40
	Trichloroethene	79-01-6	C_2HCl_3	131.39
	Trichloromethane	67-66-3	$CHCl_3$	119.38
	1,2,3-Trichloropropane	96-18-4	$C_3H_5Cl_3$	147.43
HAAs (10)	Bromochloroacetic acid	5589-96-8	$C_2H_2BrClO_2$	173.39
	Dalapon	75-99-0	$C_3H_4Cl_2O_2$	142.97
	Dibromoacetic acid	631-64-1	$C_2H_2Br_2O_2$	217.84
	Dibromochloroacetic acid	5278-95-5	$C_2HBr_2ClO_2$	252.29
	Dichloroacetic acid	79-43-6	$C_2H_2Cl_2O_2$	128.94
	Dichlorobromoacetic acid	71133-14-7	$C_2HBrCl_2O_2$	207.84
	Monobromoacetic acid	79-08-3	$C_2H_3BrO_2$	138.95
	Monochloroacetic acid	79-11-8	$C_2H_3ClO_2$	94.50
	Tribromoacetic acid	75-96-7	$C_2HBr_3O_2$	296.74
	Trichloroacetic acid	76-03-9	$C_2HCl_3O_2$	163.39
HANs (6)	Bromochloroacetonitrile	83463-62-1	$C_2HBrClN$	154.39
	Dibromoacetonitrile	3252-43-5	C_2HBr_2N	198.84
	Dichloroacetonitrile	3018-12-0	C_2HCl_2N	109.94
	Monobromoacetonitrile	590-17-0	C_2H_2BrN	119.95
	Monochloroacetonitrile	107-14-2	C_2H_2CN	75.50
	Trichloroacetonitrile	545-06-2	C_2Cl_3N	144.39
Aldehydes (2)	Acetaldehyde	75-07-0	CH_4O	44.05
	Formaldehyde	50-00-0	CH_2O	30.03
Others (3)	Chloral hydrate	302-17-0	$C_2H_3Cl_3O_2$	165.39
	Chloropicrin	76-06-2	CCl_3NO_2	164.38
	Bromate ion	15541-45-4	BrO_3^-	127.90

M.W.: molecular weight.

The first stage was to review the literature regarding existing methods used to analyze DBPs. The methods recommended for DBP analysis in MEPC final approval reports were also investigated (Table S1 of the Supplementary Material). Based on the MEPC results, only internationally recognized analysis methods such as the USEPA and ISO methods were reviewed, as shown in Table S2 of the Supplementary Material. The analysis methods could be divided into sample preservation, pre-treatment and instrumental analysis stages, and their applicability was assessed. Where studies were available that documented new analytical methods, their applicability was also assessed.

2.3. Sample preservation – assessment of the TRO elimination method

If TROs are not removed from the ballast water, the concentration of DBPs may continually increase during the sample storage period. For this reason, TROs must be removed after sampling at the test site. The target TRO level set by the BWMS in land-based tests is 10 mg/L as Cl_2, while the removable TRO level reported in existing analysis methods is a maximum of 8 mg/L as Cl_2. Because of this difference, the removal of TROs from treated ballast water should be assessed following the use of the sample preservation procedures in existing analysis methods. Thus, in this study, the TRO elimination method described in the investigated analysis methods was assessed to determine whether it can also be applied to ballast water with high levels of TROs (10 mg/L as Cl_2 or higher). For this determination, calcium hypochlorite [$Ca(OCl)_2$] was