Is It Possible to Measure Monobromamine Using Colorimetric Methods Based on the Berthelot Reaction, Like for Monochloramine?

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Abstract: Analytical methods based on the Berthelot reaction were recently adapted for determining monochloramine (MCA: NH₂Cl) in freshwater. The specificity of the Berthelot reaction with regard to MCA is related to the need for two exchangeable hydrogen atoms to form indophenol blue. MCA can thus be distinguished from organic N-chloramines, which have only one exchangeable hydrogen atom. Monobromamine (MBA: NH₂Br) may be formed during chlorination of seawater containing ammonium ions. Quantifying MBA is quite challenging and no method has been reported for its specific determination in seawater. As MBA also has two exchangeable hydrogen atoms, its reactivity might be analogous to that of MCA, but this hypothesis has never been investigated. The aim of this study was to examine the applicability of the so-called “indophenol method” for the determination of the MBA in freshwater and seawater samples. The reaction between MBA and Berthelot reagents was studied in both ultrapure water and artificial seawater. The reaction products were characterized by using gas chromatography coupled to mass spectrometry (GC–MS), Fourier transform-ion cyclotron resonance mass spectrometry (FT–ICR MS), and UV–vis spectroscopy. Results showed that colorimetric methods based on the Berthelot reaction were not suitable for measuring MBA in freshwater or seawater, since NH₂Br reacts with alkaline phenol derivative via electrophilic substitution to form ortho- and para-brominated phenols instead of forming indophenol.

Keywords: chlorination; seawater; monobromamine; Berthelot-based reaction; GC–MS; UV–visible spectroscopy

1. Introduction

Chlorine (Cl₂/HOCl/ClO⁻) is widely used for water treatment in various fields, such as disinfection of drinking water and wastewater, the food industry, and biofouling control [1]. While chlorine chemistry has been extensively studied in freshwater, it remains poorly documented in seawater. Bromide and ammonia largely determine the fate of chlorine in seawater. Average bromide concentrations in seawater generally range from 65 mg L⁻¹ to more than 80 mg L⁻¹ in confined sea areas [2]. When chlorine is added to seawater containing ammonia, competition takes place between two reaction pathways: bromide oxidation into bromine versus haloamines formation [3]. In addition, chlorine can also react with nitrogenous organic compounds, usually amino acids, proteins and amines, to form a variety of organic N-haloamines. It has been shown that chlorine can bind to some nitrogenous organic compounds more quickly than ammonia [4–6]. Oxidizing species likely to be formed during seawater chlorination vary widely, depending on chlorine dose and water quality.
parameters such as ammonia concentration, temperature, and natural organic matter content [7]. A general overview of the chemical reactions occurring in chlorinated seawater is provided in the Supporting Information, Figure S1. A more detailed description of chlorine reactivity in seawater can be found in Sugam and Helz [8] and Heeb et al. [9]. These species are usually divided into two distinct categories: free residual oxidants (FRO) and combined residual oxidants (CRO). The combination of FRO and CRO is “total residual oxidants” (TRO). The term “residual” refers to the amount of oxidant remaining after the oxidant demand has been met.

It has been reported that the biocidal activity of chlorine-produced oxidant species correlates directly with their redox potential. Standard redox potential values for several of these oxidative species are given in Supporting Information, Table S1. It can be seen that HOBr is a stronger oxidant than ClO\(^-\) and therefore would be expected to have a greater biocidal effect. However, the concept that correlates “biocidal efficacy” and “oxidizing power” is not of general validity. Biocidal efficacy also depends on the ability of the oxidant to penetrate target organisms [10–12]. Because some chlorine-produced oxidants have no or poor biocidal activity (e.g., organic N-chloramines), their presence can lead to an overestimation of actual treatment capabilities [13,14]. On the other hand, it is well documented that the fate of TRO in the aquatic environment, its effect on aquatic life, and its potential to generate organohalogen by-products (OXBPs) strongly depend on the chemical nature of the oxidant species that compose it. Studies have ranked chlorine-produced oxidants in ascending order of stability as: NHBr\(_2\) < NH\(_2\)Br < HOBr/BrO\(^-\) < HOCl/ClO\(^-\) < NH\(_2\)Cl [4,15,16]. Isaac and Morris [17] found that some organic N-chloramines were more stable than inorganic chloramines, while Antelo et al. [18] reported that organic N-bromamines were less stable than their chlorinated analogues. Regarding OXBPs formation potential, it was reported that bromine reacts faster than chlorine with natural organic matter [9,19,20]. Similarly, it was shown that bromamines were more reactive than chloramines, although less data are available concerning the role of bromamines in reactions leading to OXBPs formation [9,21]. Thus, on-site chemical speciation of TRO is crucial, since it provides important information on the effectiveness of the applied treatment and its environmental impact.

A literature review reported the use of five types of approach to determine TRO: colorimetric, titrimetric, potentiometric or amperometric analysis, and chromatography or membrane-introduction mass spectrometry (MIMS) [22,23]. The colorimetric approach has shown great potential, due to its simplicity, possible miniaturization, and application for real-time and on-site analysis. To date, various colorimetric reactions have been screened according to reactivity toward chlorine and the resulting oxidizing species in seawater. However, none of these methods distinguish unequivocally between TRO constituents, and a methodology combining several colorimetric analytical methods is necessary for this purpose. For this, Sollo et al. [24] examined five very promising reagents: methyl orange, N,N-diethyl-p-phenylenediamine, phenol red, bromocresol purple, and phenosafranin. They found that, although no process associated to any one of these reagents was completely free of interference, each served a particular purpose, and a combination of them may be used to determine both the quantity and nature of TRO. Of the numerous colorimetric methods currently reported, those based on the Berthelot reaction, also referred to as the “indophenol method”, are of particular interest. They were originally used for quantitative determination of NH\(_3\)-N in environmental samples before being adapted by Searle [25] to monochloramine analysis. The reaction takes place in three steps. First, active chlorine is added to the sample, in order to convert available ammonia into monochloramine. Subsequently, monochloramine reacts with one equivalent of phenol to form benzoquinone chlorimine, which further reacts with a second equivalent of phenol to produce indophenol. This reaction takes place under alkaline conditions (pH > 10) in the presence of catalytic quantities of sodium nitroferricyanide. Due to the toxic and noxious nature of phenol, several phenol-based reagents, such as sodium salicylate, thymol, o-phenylphenol, and 1-naphthol, are now used as alternatives [22,26]. Indophenol derivatives are highly conjugated and strongly absorb between 630 and 720 nm, enabling colorimetric detection. Liquid chromatography coupled with mass spectrometry has been proposed by
various researchers for determination of indophenol, firstly in order to overcome interference during spectrophotometric detection, and secondly to enhance sensitivity [27,28].

The Berthelot reaction is specific to monochloramine because it has two exchangeable hydrogen atoms, which is not the case for dichloramine, trichloramine, organic N-chloramines, and other oxidizing species. As monobromamine (MBA: NH₂Br) also has two exchangeable hydrogen atoms, its reactivity could be analogous to that of NH₂Cl. The aim of the present study was to validate or refute this hypothesis, since no studies of the indophenol blue method for NH₂Br determination in seawater have been reported.

2. Materials and Methods

2.1. Reagents and Solvents

All reagents and solvents were of analytical quality. Ammonium chloride (purity > 99.5%), sodium hypochlorite (13% as Cl₂), sulfuric acid (purity > 95.0%), and 2,6-dibromophenol (purity > 99.0%) were purchased from Sigma-Aldrich (Steinheim, Germany). Sodium nitroferricyanide dihydrate (purity > 99.0%), phenol (purity > 99.5%), sodium hydroxide (purity > 99.0%), sodium chloride (purity > 99.9%), potassium bromide (purity > 99.5%), sodium hydroxide carbonate (purity > 99.7%), bromine (purity > 99.0%), cyclohexane (GC grade, purity > 99.5%), and methyl-tert-butyl-ether (MTBE, GC grade, purity > 99.8%) were acquired from Merck (Darmstadt, Germany). 2-bromophenol (purity > 98.0%), 4-bromophenol (purity > 99.0%), and 2,4-dibromophenol (purity > 98.0%) were obtained from Alfa Aesar (Haverhill, MA, USA). DPD (N,N-diethyl-p-phenylenediamine) kits were supplied by Hach (Lognes, France). Aqueous solutions were prepared with ultrapure water (specific resistance > 18 MΩ cm⁻¹ at 25 °C) produced by a PURELAB Chorus 1 water purification system supplied by Veolia Water Technologies (Wissous, France).

2.2. Artificial Seawater Preparation

Artificial seawater (ASW) was prepared daily as follows: 33 g NaCl and 120 mg KBr (to reach chloride and bromide concentrations of 20 g L⁻¹ and 80 mg L⁻¹, respectively) were added to 1 L of ultrapure water. 200 mg NaHCO₃ were then introduced to buffer the solution at pH 8.2. The mixture was stirred with a magnetic stirrer until all salts were dissolved. The ASW solution was stored at 4 °C in darkness until use.

2.3. Analytical Devices

The Berthelot reaction was examined by gas chromatography–mass spectrometry (GC–MS), ultrahigh-resolution mass spectrometry, and UV–visible spectroscopy. GC–MS measurements used a 450-GC gas chromatograph coupled to a 240-MS mass spectrometer and fitted with a CP-8400 autosampler (Agilent Technologies, Santa Clara, CA, USA). Chromatographic separation was carried out on a 60 m “Factor Four VF-Xms” (10% phenyl, 90% methylpolysiloxane) capillary column (internal diameter: 0.25 mm, film thickness: 0.25 μm) from Agilent Technologies. High purity helium (99.9995%) was used as carrier gas, at constant flow of 1.4 mL min⁻¹. Injection was performed at 270 °C in splitless mode. Oven temperature was maintained at 40 °C for 0.5 min and then ramped up at 15 °C min⁻¹ to 300 °C, where it was held for 0.5 min, for a total time of 18 min. The transfer line, trap, and manifold temperatures were kept at 280, 200, and 120 °C, respectively. Spectra were acquired in electron ionization at 70 eV, scanning ions from 40 to 400 Th at 6000 Th s⁻¹. Ultrahigh-resolution mass spectrometric analysis was performed using a 9.4 Tesla “solarIX XR” Fourier-transform ion cyclotron mass spectrometer (Bruker Daltonics, Bremen, Germany) fitted with electrospray ionization operated in positive ionization mode. The instrumental conditions were adapted from Chayata et al. [29]. Infusion with 100 accumulated scans was preferred to liquid chromatography injection with no accumulated scan, in order to increase signal-to-noise ratio. Drying gas temperature and ion accumulation time were fixed respectively at 220 °C and 0.02 s, compared to 200 °C and 0.5 s previously.
All the others parameters were conserved. A double-beam Jenway 6800 UV–visible spectrophotometer with 5 cm quartz cells was used to measure absorbance (Essex, UK). For all samples, spectra were recorded on the 190–800 nm range against blank, using sampling intervals of 0.2 nm with a scan speed of 500 nm min\(^{-1}\). Free and total chlorine were measured using DPD method-based test kits (Hach #1406428, Loveland, CO, USA). pH was measured with a “SevenEasy” pH-meter from Mettler Toledo (Columbus, OH, USA).

3. Results and Discussion

3.1. MCA and MBA Preparation and Standardization

MCA and MBA are unstable in aqueous solution and therefore had to be synthesized and standardized prior to each set of experiments. An MCA stock solution of approximately \(1 \text{ g L}^{-1}\) (as \(\text{Cl}_2\)) was prepared in ultrapure water by mixing working solutions of sodium hypochlorite and ammonium chloride, following the procedure described by Kinani et al. [27] and Sacher et al. [30]. MBA was synthesized in ultrapure water according to the procedure described by Heasley et al. [31]. The UV–vis absorption spectra of MCA and MBA solutions are displayed in Figure 1. The maximum absorption values of 245 and 278 nm, respectively, were in good agreement with previously determined values. Traces of dibromamine, tribromamine, and bromine (HOBr) are minimized with this protocol; \(\text{NHBr}_2\), \(\text{NBr}_3\) and bromine were identified by their UV spectral maxima at 232, 258, and 260 nm, respectively. The resulting MBA solution was standardized spectrophotometrically, following the procedure described by Lei et al. [32]. TRO levels in chlorinated seawater are usually less than \(1.0 \text{ mg L}^{-1}\) (as \(\text{Cl}_2\)) and sometimes less than \(0.1 \text{ mg L}^{-1}\) (as \(\text{Cl}_2\)). In the present study, a working solution at \(0.5 \text{ mg L}^{-1}\) as \(\text{Cl}_2\) (7.00 µM) was prepared by successive dilutions of the MBA stock solution.

![Figure 1](image-url). UV–visible (UV–vis) absorption spectra of monobromamine (in red) and monochloramine (in blue) in ultrapure water at 40 mg L\(^{-1}\) (as Cl\(_2\)).

3.2. Spectrophotometric Investigation of the Berthelot Reaction to Determine MBA Level

The reaction between MBA (0.5 mg L\(^{-1}\) as \(\text{Cl}_2\)) and Berthelot reagents was carried out according to the procedure described by Kinani et al. [27]. A sample volume of 20 mL was placed in a 25 mL beaker. 0.1 mL sodium nitroferricyanide (5 g L\(^{-1}\)) and 1.2 mL phenol (100 g L\(^{-1}\)), both freshly prepared daily, were added. The pH of the solution was adjusted between 12.0 and 12.2 using a 5 M sodium hydroxide solution. The mixture was transferred to a 25 mL volumetric flask, which was then filled
up to the mark with the aqueous matrix used in the experiment. Monochloramine was shown to be fully derived into indophenol after 20 min incubation in darkness at room temperature (around 20 °C). Indophenol formation is characterized by blue color with peak absorption between 635 and 650 nm. Unlike with monochloramine, no indophenol formation was detected even after 33 h reaction with MBA. Total residual oxidants were determined using DPD method-based test kits from Hach (Reference: 1406428, Loveland, CO, USA). No residual oxidant was found, even just 1 min after onset of the Berthelot reaction with MBA. This result suggests that MBA reacted with the Berthelot reagents to form derivatives that do not absorb light at the characteristic wavelength of indophenol.

It is noteworthy that DPD colorimetry had two particularities. Firstly, seawater sample pH during DPD measurement was 10.8, due to the alkaline conditions of the Berthelot reaction, whereas a pH value between 6.2 and 6.5 is required for TRO analysis, according to the procedure described in the standard method [33]. Secondly, a reaction between DPD and the Berthelot reagents occurs after a few minutes (in both presence and absence of oxidants), producing a colored compound with peak light absorption at 680 nm (see Figure S2 in Supporting Information). This compound was identified as 4-[[4-(diethylamino)phenyl]imino]-2,5-cyclohexadien-1-one (DPICO, see Figure 2). Formation of DPICO from DPD and phenol in oxidant media was previously reported by Adachi et al. [34], who oxidized DPD with ammonium persulfate, and by Beiginejad et al. [35], who used cyclic voltammetry. DPD was first oxidized before reacting with phenolate, according to the mechanism depicted in Figure 2. The second oxidation process led to DPICO; this was thermodynamically easier than the first oxidation ($\Delta G_{\text{first oxidation}} = 945.6 \text{ kJ mol}^{-1}$ vs. $\Delta G_{\text{second oxidation}} = 857.7 \text{ kJ mol}^{-1}$).

Figure 2. Schematic representation of the reaction between DPD and the Berthelot reactant species to form DPICO.

To confirm that the colored product was DPICO, the concentrated aqueous solution was extracted with cyclohexane and the purple organic phase was analyzed by spectrophotometry in the 190–800 nm range. Peak absorption was detected at 561 nm, similar to that reported by Adachi et al. [32]. In the present study, characterization of the colored product was also confirmed by ultra-high-resolution Fourier transform-ion cyclotron resonance mass spectrometry (FT–ICR MS). For this, a DPD kit was added to the Berthelot reagents in 25 mL ultrapure water. After 1 h reaction, an intense blue color was observed. The solution was diluted 2000-fold in a solution of 50% methanol, 50% ultrapure water,
and 0.1% formic acid, and analyzed by FT–ICR MS by direct infusion in the ion source operated in
electrospray positive mode. Two ions were detected at m/z 165.13872 and m/z 255.14935, with a mass
error of 0.6 ppm. The corresponding exact formulae are C_{10}H_{17}N_{2}H^{+} and C_{16}H_{21}N_{2}O^{+}, respectively;
these correspond to protonated molecules of DPD in excess and DPICO.

In the present study, colored DPICO formed even in the absence of oxidants, unlike in the other
studies. The oxygen dissolved in the water could be responsible for both oxidation steps in the
formation of DPICO. This was confirmed by removing dissolved oxygen from the ultrapure water
by bubbling nitrogen into it for 1 h. Berthelot and DPD reagents were put in two volumetric flasks.
Degassed ultrapure water was rapidly added to completely fill the first flask, leaving no headspace.
Non-degassed ultrapure water was added to the second flask in the same way. After 30 min reaction,
the color was dark blue in the non-degassed water solution and light blue in the degassed solution,
as seen in Figure S2 (in Supporting Information). Although N_{2} bubbling did not totally remove the
oxygen from degassed water, this experiment established that dissolved oxygen was responsible for
DPD oxidation.

3.3. GC–MS Characterization of the Products of the Reaction between Monobromamine and Berthelot Reagents
in Ultrapure Water

To identify the reaction products of the reaction between monobromamine and the Berthelot
reagents, 1 mL of sample was adjusted to pH 7.0 by successive additions of 5 N and 0.05 N sulfuric
acid and extracted with 1 mL of MTBE. The resulting crude organic phase was separated, dried over
anhydrous Na_{2}SO_{4}, filtered, and then transferred to a 1 mL vial for immediate analysis by GC–MS,
using the acquisition parameters described in the Materials and Methods section.

Table S2 (in Supporting Information) summarizes GC–MS results and lists some relevant
physicochemical properties of the detected compounds. Two chemicals, 2-bromophenol and
4-bromophenol, were identified, based on comparison of their retention times and mass spectra
with those of standards. The same products were also identified in trace amounts in organic extracts
obtained without prior acidification of the aqueous samples. Bromophenols have pKa values between
6.7 and 9.2 [36]; they mainly exist as anions under Berthelot reaction conditions (pH > 10.5), which
explains the low recovery obtained without acidification. An MBA working solution 15-fold more
concentrated than the initial one was analyzed with the same protocol in order to check for other
reaction products likely to be formed at very low yields. In this experiment, the phenol-to-MBA molar
ratio was 500. Dibrominated phenols, 2,4-dibromophenol and 2,6-dibromophenol, were detected in
addition to the previous compounds. Their structures were confirmed by comparing their retention
times and mass spectra to those of their analytical standards (see Figure 3). The Berthelot reaction
with bromine led to similar results as with MBA. It can be concluded that MBA reacts with phenol by
bromination rather than by derivatization into indophenol, as is the case for MCA. This is consistent
with the kinetics results recently provided by Heeb et al. [4], who studied the reactivity of inorganic
and organic N-chloramines and N-bromamines with phenolic compounds (in aqueous solutions at
pH 7), as surrogates for dissolved organic matter (DOM); the reaction rate of MBA (2.1 × 10^{2} M^{-1}s^{-1})
with phenol was about two orders of magnitude lower than with HOBBr (6.5 × 10^{4} M^{-1}s^{-1}), but about
four orders of magnitude higher than that of MCA (1.6 × 10^{-2} M^{-1}s^{-1}).
3.4. Investigation of the Berthelot Reaction in Chlorinated Seawater

To investigate the Berthelot reaction in chlorinated seawater, artificial seawater (ASW) was used as a reaction medium. Seven experiments were designed, varying both ASW composition and reagent introduction order; these experiments are referred as A to G in Table 1. Chlorine was dosed at the concentration usually applied for biofouling control in seawater: 7.00 µM. NH₄Cl and HOCl solutions were employed with a molar ratio of 0.95 in order to limit both hydrolysis of MCA and its conversion into dichloramine and trichloramine. Each of the seven experiments was repeated three times. The following protocol was used for all experiments. After adding the last reagent, each mixture was thoroughly homogenized by vortexing for 2 min. Berthelot reagents were then added and the mixtures were incubated for 20 min in darkness at room temperature (20 °C). pH in all samples was > 12.0, so that adjusting the amount of NaOH in the ASW was not necessary. After completion of the reaction, products were characterized by both UV–vis spectroscopy and GC–MS.

Table 1. Order of reagents addition in experiments A to G.

| Experiment | Br⁻ (812 µM) | NH₄Cl (7.37 µM) | Chlorine Dose (7.00 µM; Cl/N = 0.95) | Main Oxidizing Agent(s) Formed<sup>(a)</sup> |
|------------|--------------|-----------------|-------------------------------------|---------------------------------------------|
| A          | 1            | n.a.            | n.a.                                | No product                                  |
| B<sup>(c)</sup> | n.a.        | 1               | 2                                   | NH₄Cl                                       |
| C          | 1            | n.a.            | 2                                   | HOBr/BrO⁻                                   |
| D          | 1            | 3               | 2                                   | NH₂Br                                       |
| E          | 3            | 1               | 2                                   | NH₂Cl                                       |
| F          | n.a.         | 1               | 3                                   | NH₂Cl, NH₃Br                                 |
| G          | 1            | 2               | 3                                   |                                              |

<sup>(a)</sup> Oxidant(s) expected according to known chlorine chemistry in seawater; <sup>(b)</sup> n.a.: not added; <sup>(c)</sup> Reaction conducted in ultrapure water.

Figure 4 displays the UV–vis absorption spectra following experiments A to G. Experiment A was performed in the absence of NH₄Cl and chlorine, to serve as a reference to differentiate the specific...
absorption of reagents from that of products. Experiment B was conducted in freshwater, to be used as a control for the Berthelot reaction. All UV–vis spectra showed a broad absorption band range extending from 200 to 330 nm, characteristic of phenolate, and a well-defined peak from 330 to 500 nm, characteristic of sodium nitroferricyanide. Analysis of the UV–visible spectra in experiment C revealed no presence of indophenol, as expected. 2-bromophenol and 4-bromophenol were detected, but none of their chlorinated analogues. This result is consistent with known chlorine chemistry in seawater. It is well established that chlorine rapidly oxidizes bromide ions present in water into bromine (reaction time < 10 s), which subsequently reacts with basic phenol to form brominated phenol [8]. The same results were observed when ammonium ions were added 2 min after chlorine introduction (experiment D). The absorption band between 550 and 750 nm with a peak around 630 nm, characteristic of indophenol formation, was not observed, suggesting that MCA was not formed. This may be explained by the fact that, once formed, HOBr reacts with ammonium to form MBA. This result also confirmed our earlier observations that, contrary to MCA, MBA does not react with Berthelot reagents. The addition of MCA to ASW with and without potassium bromide in experiments E and F, respectively, led to similar results: the same light intensity of indophenol was measured by spectrophotometry and no brominated phenols were detected on GC–MS. It can be concluded that the Berthelot reaction with MCA is much faster than MCA’s reaction with bromide ions under the examined conditions. The degree of similarity between the UV–vis spectra in experiments E, F, and B was about 95%, indicating that seawater does not interfere with MCA determination by the indophenol blue colorimetric method. Finally, experiment G was designed to simulate seawater containing ammonium (at a level close to the chlorination level of real seawater). Analysis of UV–vis spectra and GC–MS peak intensities showed that the formation of brominated phenols predominated over indophenol derivatization after 2 min chlorination. These results seem to be in close agreement with current knowledge of chlorine chemistry in seawater, according to which two competitive reactions occur in presence of ammonia: (a) bromide oxidation and (b) monochloramination. The reported rate constants are (1.55 × 10^6) M^−1 s^−1 and (1.9–5.7) × 10^6 M^−1 s^−1, respectively [3–5,37–39].
From a strictly kinetic point of view, ammonia content governs MCA formation, since bromide concentration remains stable in seawater. An ammonia concentration of 7.00 µM was used in experiment G. At this concentration, bromine formation predominates at the expense of monochloramine, accounting for the lower abundance of indophenol compared to experiments B, E, and F.

4. Conclusions

The culmination of this research was to examine the applicability of the colorimetric methods based on the Berthelot reaction to quantitate MBA in natural water samples. Results showed that, instead of indophenol formation as with MCA, MBA reacts with alkaline phenol by aromatic electrophilic substitution, forming brominated phenols. Consequently, the Berthelot reaction was deemed unsuitable for MBA colorimetric determination under the present analytical conditions. Optimization of the derivatization protocol has not been considered regarding the rapid formation of brominated phenol derivatives. Due to the instability of monobromamine, it is necessary to develop analytical strategies allowing for (near) real-time monitoring of this substance. Membrane-introduction mass spectrometry (MIMS) is presented as one of the promising approaches for online and real-time analysis of monobromamine and other chlorine-produced oxidant species. It is currently the subject of several works carried out by different research groups, including ours.

Supplementary Materials: The following are available online at http://www.mdpi.com/2673-4532/1/1/1/s1. Figure S1: Halogenated oxidants formed during chlorination of seawater, adapted from Haag and Lietzke (1981); Figure S2: Picture of the flasks after 30 min reaction between DPD and Berthelot reagents in degassed water (light blue, left) and non-degassed water (dark blue, right); Table S1: Comparison of standard electrode potentials in aqueous solution at 25 °C of chlorine-produced oxidants formed in seawater; Table S2: Physicochemical properties, retention times, and molecular ions of the studied compounds.

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