Feasibility study of combined ozone and UV systems (DOPFR-UV)

Literature study and lab experiments on bromate formation

BTO 2010.003
January 2010

KWR Watercycle Research Institute

BTO

KWR Watercycle Research Institute

Feasibility study of combined ozone and UV systems (DOPFR-UV)

Literature study and lab experiments on bromate formation

BTO 2010.003
January 2010

Postbus 1072 3430 BB Nieuwegein T 030 606 95 11 F 030 606 11 65 E info@kwrwater.nl I www.kwrwater.nl

Colophon

Title
Feasibility study of combined UV and ozone systems (DOPFR-UV)

Projectnummer
B111661-001

Onderzoeksprogramma(‘s)
TTI , BTO

Projectmanager
E. Beerendonk

Opdrachtgever
TTI-W en BTO

Kwaliteitsborger
M. Nederlof

Auteur(s)
C.H.M. Hofman, D.J.H. Harmsen, R. v. Leerdam

Verzonden aan

Programmatafel TTI Advanced Clean Water Technology

This work was performed in the TTIW-cooperation framework of Wetsus, centre of excellence for sustainable water technology (www.wetsus.nl). Wetsus is funded by the Dutch Ministry of Economic Affairs. The authors like to thank the participants of the research theme “clean water technology” for the fruitful discussions and their financial support.

Preface

In the framework of the project TTI DOPFR-UV (B111661-001), it was studied whether the combination of ozone and UV in a DOPFR-UV system results in a substantial decrease in the bromate content of the treated water. The results of this study are described in this report.

Summary

The presence of several (types of) contaminants in water requires advanced purification technologies. An "Advanced Oxidation Technology" is the DOPFR-UV system, in which UV irradiation is combined with ozone, in order to obtain both disinfection and organic contaminant control. However, it is known that ozone treatment of bromide containing water results in the formation of bromate, which is suspected to be carcinogenic. On the other hand, UV irradiation may reduce the bromate formed to bromide or interfere with the bromate formation process, thus decreasing the bromate content. It was decided to study the bromate formation and decrease in our DOPFR-UV system. After this study a go/no go decision is to be made, whether or not to continue with the DOPFR-UV project. This decision depends on the final bromate concentration, which should be lower than 5 µg/l, preferably even lower than 1 µg/l.

First, a literature study was carried out to establish the reactions involved and to determine whether the combination of ozone and UV in one system can be successful. The information found appeared to be ambiguous, so it was decided to carry out an investigation into the bromate formation and reduction in our DOPFR-UV system. Five tests were carried out to determine:

1. The ozone concentration and half-life in our system
2. The bromate reduction by UV irradiation in water spiked with bromate
3. The bromate formation by means of ozone in bromide containing water
4. The combined effects of bromate formation by ozone and bromate reduction by means of UV, using Soestduinen water
5. The combined effects of bromate formation by ozone and bromate reduction by means of UV, using Leiduin water

For tests 1-4 Soestduinen water was used, as this type of water has a very low TOC and thus little scavenging of the OH· radicals. As a result, this can be considered as a "worst case scenario" for the formation of bromate.

It was found that the bromate concentration increases with increasing ozone content, independent of the contact time of the ozone. This indicates an instantaneous reaction of ozone and bromide, with ozone as the limiting factor. UV irradiation of an aqueous solution containing bromate using a MP lamp results in a decrease in bromate concentration. There seems to be a more or less linear relation between the UV-dose applied, and the bromate reduction observed.

Combination of ozonation and UV irradiation in water with a very low TOC (and thus little scavenging of the OH· radicals) seemed to result in an enhanced bromate formation. As the water used for this test had a very low NOM content, we decided to repeat this test using water from ps. Leiduin, which has a higher NOM content. In Leiduin ozonation is part of the actual purification process, so the circumstances with this type of water can be considered as more realistic for an ozonation process (N.B. we used water from ps. Leiduin which had not yet been treated with ozone). In this test too it was found that ozone combined with UV irradiation does not result in a lower bromate content than application of only ozone.

It can be concluded that UV irradiation can lower the bromate content only to a small extend. Although UV irradiation may interfere with the intermediates of bromate formation, the reaction of bromide into bromate as a result of ozonation probably is very fast, as a result of which UV irradiation does not seem to lower the bromate concentration in a DOPFR-UV system.

Contents

1 Introduction

Bromide levels in natural waters are highly variable and were found in a range of 10–1000 µg L^{-1}. Both natural processes (salt water intrusion, water from special geological formations) and anthropogenic activities (potassium mining, coal mining, chemical production, etc.) may contribute to increased bromide levels in natural waters (von Gunten, 2003).

Application of ozone in drinking water production has the drawback that bromate (BrO_3^-) is formed if bromide (Br^-) is present. Bromate itself is not expected to be present in raw water. Bromate is suspected to be carcinogenic (Kurokawa *et al.*, 1990) and therefore an unwanted by-product for drinking water production. Low levels of bromide (< 20 µg L^{-1}) are unproblematic for bromine-derived by-products. For bromide levels in the range 50–100 µg L^{-1} bromate formation may already become a problem (idem). In these waters, optimization and control options can be applied.

A Dissolved Ozone Plug Flow Reactor (DOPFR-UV) set-up is shown in Figure 1. In this set-up it is possible to vary the time between ozone dosage and UV application, thus varying the ratio between oxidation and disinfection. Other advantages of the DOPFR-UV system would be its relatively low energy consumption and that no residual radical forming compounds are present in the resulting water. In the TTI DOPFR-UV project (B111661-001) three subsequent phases were defined: the study of the bromate formation, the optimization and scale up of the DOPFR-UV system, and the building and testing of a prototype optimized system. After the first step a go/no go decision is to be made, depending on the bromate content obtained in the water. It was suggested to define 5 µg/l as the maximum acceptable content, although it also was argued that should be aimed at a maximum concentration of 1 µg/l.

In this project the bromate formation in the DOPFR-UV was studied. At the moment it is not clear whether the bromate formation rate in the DOPFR-UV concept is higher or lower compared with conventional ozone systems. Experiments by Wedeco and KWR in the past clearly indicated that bromate is formed (Kruithof, 1998.). At a UV energy input of 2.4 kWh $\cdot m^{-3}$ and an ozone dose of 4.6 g m^{-3}, a bromate concentration of almost 10 µg/l was measured, which was higher than for O_3/H_2O_2 treatment with a H_2O_2 ratio of 2.0 g/g, while for UV/H2O2 treatment bromate formation was absent
On the other hand in the DOPFR-UV system, depending on the distance between the ozone dosing point and the UV reactor, and the UV dose, the ozone is converted to hydroxyl radicals (HO•). Direct bromate formation from radicals is in general lower than from molecular ozone. Furthermore, UV light has a reducing nature and bromate can possibly be reduced to bromide again when passing the UV reactor. Optimizing this system may result in a lower bromate formation (Hofman, 2008).

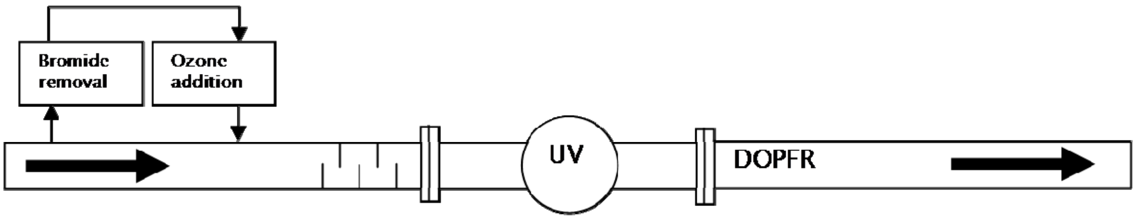


Figure 1. The DOPFR-UV concept (TTI-W project plan, 2008).

In chapter 2 the literature on bromate formation and reduction by (the combination of) ozone oxidation and UV treatment is reviewed. The reaction schemes involved are very complicated, and strongly depend on conditions like pH, temperature and NOM (natural organic material). From this literature study no conclusions could be drawn, whether or not UV irradiation can be applied to prevent or decrease bromate formation in our system. Chapters 3 and 4 describe the experimental part of the research. The goal of these experiments was to find out whether bromate formation could be reduced in an ozone system by applying UV irradiation.

2 Literature search

2.1 Aims of literature review

In this section an overview of relevant articles in literature is given. This chapter does not refer to the experimental work carried out at KWR.

This literature search tries to find answers on the following research questions:

- What is the influence of the ozone and UV dose on the bromate formation?
- What is the influence of other water quality parameters (DOC, Alkalinity, and pH) on bromate formation?
- What is the influence of the time between ozone dosing and applying UV light?
- General: can bromate concentrations be kept below the water quality norm in UV-O_3 systems?

2.2 Reaction mechanisms of bromate formation

The ozonation of bromide (Br^-) can result in the formation of the bromate ion (BrO_3^-). The bromate ion is the highest oxidation state of the bromide ion. It is formed through a complex web of pathways with several bromine-containing intermediates that undergo reactions with both molecular ozone and hydroxyl radicals. Molecular ozone (O_3) oxidizes bromide to form hypobromite ions (OBr^-). Hypobromite continues to be oxidized to form bromate via BrO_2^- as an intermediate. The reactions of bromide with molecular ozone are presented in Table 1. The reactions of molecular ozone with bromide and hypobromite ions are relatively slow compared to indirect oxidation of bromide by radicals (Table 2).

2.2.1 Reactions with molecular ozone

For the rate constants listed in Table 1, 77 % of the hypobromite formed reacts through reaction 2 back to bromide and 23 % through reactions 3a and 4 to form bromate.

Temperature and pH are determining parameters on the HOBr/BrO^- ratio (eq. 5) and thus on bromate formation by molecular ozone, because the oxidation of hypobromous acid by ozone is very slow (eq. 3b) and, therefore, does not contribute significantly to bromate formation (Gunten and Hoigné, 1994). Thus, whereas reaction 1 is independent of pH, the overall rates of reactions 2 and 3 decrease with decreasing pH due to the masking of hypobromite through protonation. In the pH range of 7-8, only 1-10% of $[HOBr]_{tot}$ (in the form of OBr^-) takes part in reactions with molecular ozone (Gunten and Hoigné, 1994).

It is important to note that ozonation under higher pH conditions produces higher bromate concentrations, such that with sufficient ozone applied to meet an ozone residual for disinfection, tens of micrograms per liter of bromate can be formed (Bonacquisti et al., 2006).

Table 1 Reactions and rate constants for molecular ozone mechanisms (Von Gunten and Hoigné, 1994).

No	Reaction	k or pKa (20°C)
1	$O_3 + Br^- \rightarrow O_2 + OBr^-$	160 $M^{-1}s^{-1}$
2	$O_3 + OBr^- \rightarrow 2O_2 + Br^-$	330 $M^{-1}s^{-1}$
3a	$O_3 + OBr^- \rightarrow BrO_2^- + O_2$	100 $M^{-1}s^{-1}$
3b	$O_3 + HOBr \rightarrow BrO_2^- + O_2 + H^+$	0.01 $M^{-1}s^{-1}$

4	$BrO_2^- + O_3 \rightarrow BrO_3^- + O_2$	$> 10^5$ $M^{-1}s^{-1}$
5	$HOBr \leftrightarrow H^+ + OBr^-$	9
6	$HOBr + NH_3 \rightarrow NH_2Br + H_2O$	8×10^7 $M^{-1}s^{-1}$

2.2.2 Radical mechanisms

In water, O_3 forms radicals, which, by various reaction mechanisms depending on the pH will lead to the formation of OH radicals (Rodriguez, 2008).. In the absence of scavengers, OH radical reactions contribute significantly to bromate formation (Von Gunten and Hoigné, 1994). At high pH values (e.g. pH 10, 11) the OH radical plays an import role in the oxidation of bromide. The decay of ozone in such solutions is initiated by OH^- and accelerated by a chain reaction, in which OH radicals act as chain carriers.

The initial reactions can be summarized by reactions 11-13 given in Table 2. The first step of the interaction of bromide with hydroxyl radicals (eq. 11) is the reversible formation of an intermediate adduct $BrOH^- \cdot$. The reversibility of this reaction leads to a limitation of the production of $Br_2^- \cdot$. $Br_2^- \cdot$ formed can either disproportionate (eq. 14) or further oxidize OBr^- (eq. 15; OBr^- formed according to eq. 5).

In 1998 Von Gunten and Oliveras showed that hydroxyl radicals too can lead to the formation of bromate, even in the absence of ozon (Von Gunten, 1998).
To proceed towards higher oxidation states of bromine, hypobromite is needed as a further reactant. In solutions containing bromide and ozone, hypobromite accumulates as a primary intermediate. The possible reactions of secondary oxidants with hypobromite are shown by reactions 15-18 in Table 2.

$CO_3^- \cdot$ radicals are formed through reactions 19-22. In contrast to $CO_3^- \cdot$ radicals no kinetic data are available for the reactions of HCO_3 radicals with $HOBr/OBr^-$. The latter reactions do not alter the rate of formation of bromate since reaction 18 is fast enough to guarantee a maximum production of $BrO \cdot$.
The common product of reactions 15-18 is $BrO \cdot$. This radical undergoes disproportionation to form bromite and hypobromite (eq. 23). According to reaction 4, bromite is then readily oxidized to bromate by molecular ozone. In waters with high OH radical concentrations (i.e. advanced oxidation), bromite can also be oxidized to bromate by the reaction sequence 24-27.

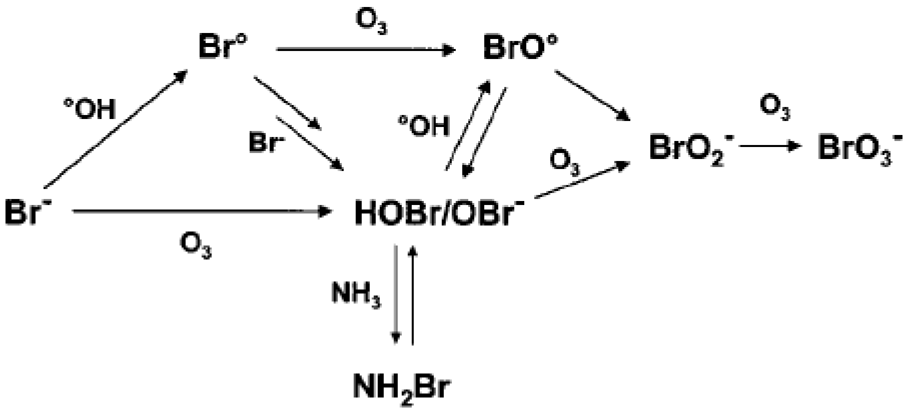
Table 2 Reactions and rate constants for hydroxyl radical mechanisms (Von Gunten and Hoigné, 1994)

No	Reaction	K or pKa (20°C)
11	$Br^- + OH\cdot \leftrightarrow BrOH^-\cdot$	10^{10} $M^{-1}s^{-1}$; 3.3 x 10^7 s^{-1}
12	$BrOH^-\cdot \rightarrow Br\cdot + OH^-$	4.2 x 10^6 s^{-1}
13	$Br\cdot + Br^- \rightarrow Br_2{}^{-}$	10^{10} $M^{-1}s^{-1}$
14	$Br_2^-\cdot + Br_2^-\cdot \rightarrow Br_3^-\cdot + Br^-\cdot$	2 x 10^9 $M^{-1}s^{-1}$
15	$Br_2^-\cdot + OBr^- \rightarrow BrO\cdot + 2\ Br^-$	8 x 10^7 $M^{-1}s^{-1}$
16	$OH\cdot + OBr^- \rightarrow BrO\cdot + OH^-$	4.5 x 10^9 M^{-1} s^{-1}
17	$OH\cdot + HOBr \rightarrow BrO\cdot + H_2O$	2 x 10^9 M^{-1} s^{-1}
18	$CO_3^-\cdot + OBr^- \rightarrow BrO\cdot + CO_3^{2-}$	4.3 x 10^7 M^{-1} s^{-1}
19	$CO_3^{2-} + OH\cdot \rightarrow OH^- + CO_3^-\cdot$	3.9 x 10^8 M^{-1} s^{-1}
20	$HCO_3^- + OH\cdot \rightarrow OH^- + HCO_3\cdot$	8.5 x 10^6 M^{-1} s^{-1}
21	$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	10.3
22	$HCO_3\cdot \leftrightarrow H^+ + CO_3^-\cdot$	9.6
23	$2\ BrO\cdot + H_2O \rightarrow BrO^- + BrO_2^- + 2\ H^+$	4.9 x 10^9 M^{-1} s^{-1}
24	$BrO_2^- + OH\cdot \rightarrow BrO_2\cdot + OH^-$	2 x 10^9 M^{-1} s^{-1}
25	$BrO_2^- + CO_3^-\cdot \rightarrow BrO_2\cdot + CO_3^{2-}$	1.1 x 10^8 M^{-1} s^{-1}
26	$2\ BrO_2\cdot \leftrightarrow Br_2O_4$	1.4 x 10^9 M^{-1} s^{-1}; 7 x 10^7 s^{-1}
27	$Br_2O_4 + OH^- \rightarrow BrO_3^- + BrO_2^- + H^+$	7 x 10^8 M^{-1} s^{-1}

In summary:
Under standard drinking water treatment conditions (pretreatment, pH ≥ 7, room temperature) , molecular ozone plays an important role for two oxidation steps within the OH radical mechanism: (i) formation of hypobromite (eq. l), which then reacts with $Br_2^-\cdot$, $OH\cdot$, and $CO_3^-\cdot$ to form $BrO\cdot$; and (ii) oxidation of bromite (eq. 4), which leads to the formation of bromate. A schematic representation of bromate formation through the interaction of the molecular ozone mechanism and the OH radical mechanism is shown in Figure 2.
Hypobromite is a decisive intermediate in bromate formation through the OH radical mechanism: as soon as hypobromite is formed, it can be rapidly transformed into bromate by OH radicals according to reactions 11-27. However, the first step is the reaction of bromide with molecular ozone to HOBr/OBr^- (Von Gunten and Hoigné, 1994).

Pinkernell and Von Gunten (2001) mention that HOBr can also be formed by conversion of $Br\cdot$ (Figure 2), which is formed through oxidation of Br^- by $\cdot OH$ (eq. 11, 12).
Another possible reaction pathway to bromate includes the oxidation of the $Br\cdot$ radical by ozone to $BrO\cdot$ (Figure 2), which disproportionates to bromite (BrO_2^-, eq. 23), which in turn is quickly oxidized to bromate by ozone (eq. 4).

Figure 2. Reaction scheme for bromate formation during ozonation of bromide-containing waters (Pinkernell and von Gunten, 2001). Hydroxyl radicals too can play a role in the oxidation of bromite into bromate.



Generally, more than 90% of the oxidation of bromide occurs with molecular ozone. Only during the initial phase of an ozonation process (higher OH·/O$_3$ ratio) the fraction of bromide oxidized by OH radicals can make up for as much as 50% of the total bromide oxidation. This means that during the initial phase a high production of bromate through the Br· pathway can be expected, while during the main ozonation phase bromate formation is initiated by the oxidation of bromide by ozone. The bromate formation mechanism cannot simply be divided into a "radical" and "molecular pathway" because both oxidants can react simultaneously or in sequence (Pinkernell and Von Gunten, 2001).

2.3 Bromate control strategy

In order to minimize the bromate formation potential during ozonation, several treatment options have been tested such as (Zhang et al., 2008):

- ammonia addition,
- pH depression,
- OH radical scavenging,
- scavenging or reduction of HOBr by organic compounds,
- minimize ozone doses

Furthermore, hydraulic optimizations (like the homogeneous addition of ozon by means of static mixers and e.g. the improvement of the plug –flow reactor by means of baffles, have been shown to result in sufficient disinfection at low CT-values, thus also resulting in a lower bromate formation (v.d. Aa, 2010, personal communication).

2.3.1 Dosings

Only ammonia addition and pH depression may be applicable to drinking water ozonation (Meunier et al. 2006; Zhang et al., 2008), which can lead to a 50% decrease in BrO$_3^-$ formation. Ammonia (NH$_3$) efficiently scavenges HOBr to NH$_2$Br (eq. 6). However, this reaction is reversible which leads to higher required NH$_3$ concentrations than expected. Furthermore, mono bromo amine will react with ozone to form bromide, resulting is a subsequent bromate formation. Once BrO$_3^-$ is formed, its elimination through adsorption or chemical reduction is difficult in water treatment (Zhang et al., 2008).

pH depression influences bromate formation by shifting the HOBr/OBr$^-$ equilibrium to HOBr and altering the oxidant exposures (ozone and OH radicals). The shift of the equilibrium towards HOBr slows down its oxidation by molecular ozone since only OBr$^-$ can be oxidized by O$_3$. However, in drinking waters the oxidation of HOBr is dominated by OH radicals, which react at a comparable rate with HOBr and OBr$^-$. Therefore, at this level no huge effects will be observed.
A more important feature of pH depression is increased ozone stability. As a consequence, for a certain ozone exposure, the OH radical exposure decreases with decreasing pH. This means that for similar disinfection targets the overall oxidant exposure will be smaller at the lower pH, which leads to a lower bromate formation. With this measure the initial bromate formation (table 1, eq. 1-4)) cannot be reduced since it is independent of the pH. The reactions summarized in table 2, however, do depend on pH. In high alkalinity waters pH depression might be an expensive treatment option because high amounts of acid have to be added to the waters (Pinkernell and Von Gunten, 2001).

Minimizing ozone doses, especially to waters at a relatively low temperature, during a brief period of time, i.e. ozonation at low Ct-values (product of average concentration of dissolved ozone in the reactor and the hydraulic residence time t), should lead to a low oxidation yield of bromide ion to bromate ion. This is only possible if an additional disinfection step is introduced in the treatment train which does not lead to formation of bromate (Meunier et al. (2006). At Waternet the bromate formation was minimized by optimizing hydraulic conditions. Brominated by-product formation in ozonated waters is influenced by bromide ion concentration, the source and concentration of natural organic matter (NOM), pH, ozone dose, and reaction time (Bonacquisti et al., 2006).

Recently, Zhang et al. (2008) investigated the effect of several metal oxides including α-FeOOH, α-Fe_2O_3, γ-FeOOH, and CeO_2 on bromate formation potential during ozonation of bromide-containing water. CeO_2 could most effectively minimize the bromate formation among these metal oxides taking ozonation alone as control. The minimization of bromate formation by O_3/CeO_2 favored a relatively low Br^- concentration (i.e., <1.0 mg L^{-1}) and $pH < 7$. Water temperature ranging from 5 to 25 °C had no significant impact on the percent reduction of BrO_3^-.

2.3.2 MIEX pretreatment

Using MIEX (magnetic ion exchange resin) technology prior to ozonation improves the water quality, because MIEX removes NOM, natural color and bromide from raw drinking water. Bromide removal depended on the alkalinity and initial bromide concentration of the water. Bromide removal decreased as alkalinity increased and relatively increased with increasing initial bromide concentration. These findings are consistent with the competitive nature of anion exchange. MIEX pre-treatment of the water prior to ozonation substantially lowered the ozone demand and formation of bromate during subsequent ozonation. Bromate formation decreases in MIEX pretreated Costa Mesa water compared to raw Costa Mesa water because of the decreased ozone demand and reduced bromide concentration following MIEX treatment (Johnson and Singer, 2004).

MIEX provides a pretreatment alternative that could maximize ozonation disinfection while decreasing bromate formation in bromide-containing waters. During a 5-week pilot study, the MIEX process removed up to 30 % of the dissolved organic carbon (DOC) and reduced ultraviolet absorbance at 254 nm (UV 254) by up to 60%. When MIEX pretreated water was ozonated, ozone decay rates were reduced, increasing the disinfection levels (CT) achieved by 40% to 65%. The increased disinfection capability reduced the transferred ozone dosages required for Cryptosporidium inactivation by 15% to 25% and bromate formation by 35%. Bromide removal itself by MIEX was negligible (Wert et al., 2005). At the moment, at Waternet a study is being carried out with fluidized ion exchange (FIX).

2.4 Experimental studies on oxidation of bromide

In this section, effects of several environmental factors on the bromate formation by ozonation will be discussed. Distinction is made between direct ozonation and radical reaction. The last part of the Result section deals with the reduction of bromate by UV irradiation.

2.4.1 Results oxidation of bromide by Molecular Ozone

Effect of bromide concentration
The first chemical parameters to take into account obviously are the bromide and ozone concentrations. An increase of the ozone concentration (expressed as Ct-value) leads to an increase in bromate formation rate (Figure 3). The Ct-value is the product of the average concentration of dissolved ozone in the reactor and the hydraulic residence time t. Legube et al. (2004) investigated the effect of Ct-value on bromate formation by ozonation of sand filtrated water in a water treatment plant. Bromate formation was a linear function of Ct-value.

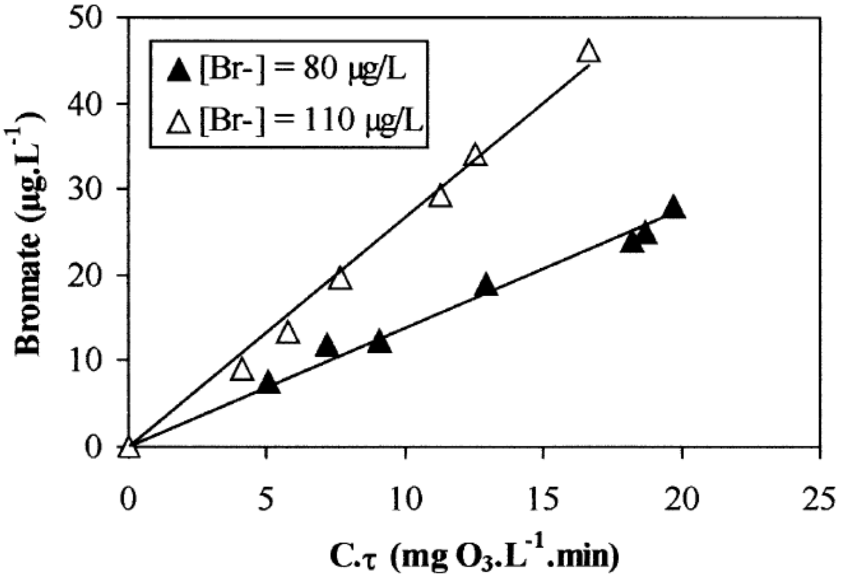


Figure 3. Effect of Ct-value on bromate formation during ozonation of sand filtrated water; bubble diffuser ozone contactor; pH = 7.6; DOC = 2.7 mg/L; N-NH_4^+ < 10 µg/L; 21°C (Legube et al., 2004).

Similar results were obtained by KWR, some years ago.
Taking into account only the direct reaction of ozone, a linear relationship between bromate and $[O_3]$*t can be explained only by a constant concentration of hypobromite (BrO^-) for each studied Ct-value, since $d[BrO_3^-]/dt = k[O_3][BrO^-]$ (with $k=100\ M^{-1}s^{-1}$). Taking into account the three reactions of hypobromite formation or disappearance (eq. 1-3), $d[BrO^-]/dt = 0$ required a constant ratio $[Br^-]/[BrO^-]$ for each Ct-value (Legube, 2004), during the observation period of the reaction (with the exception of very low and very high Ct-values where this hypothesis obviously cannot be verified). Of course, the involvement of OH radical complicates the reasoning, taking into account the number of reactions included in the mechanisms.

A bench-scale study was carried out on the impact of bromide concentrations on disinfection byproduct formation (Bonacquisti et al., 2006). Ozonation testing was performed on Occoquan reservoir settled water. The pH was kept constant at 6.0 while bromide concentrations in the settled waters tested range from 0 to 300 µg/L. These samples were ozonated with transfer doses of 3.2 - 6.4 mg/L. At pH 6.0, bromate was only detected at the highest transferred ozone dose of 6.4 mg/L and the highest bromide spike of 300 µg/L (Table 3). The bromate concentration was 11 µg/L, thus 1 µg/L higher than the current drinking water standard. Maintaining low pH during ozonation and a raw water level of bromide significantly lower than 300 µg/L is necessary to prevent bromate formation (Bonacquisti et al., 2006).

Effect of ionic strength
Gunten and Hoigné (1994) tested oxidation of bromide by only molecular ozone (reactions 1-4). Experiments were performed at pH 7 in the presence of bicarbonate and octanol (2 mg/L). Initial bromide concentrations varied between 0.2 and 1 mg/L. For such conditions, the transformation of ozone into OH radicals is slow, and OH radicals are efficiently scavenged. Increasing the ionic strength from 1 to 50 mM (Na_2SO_4), resulted in an increase of the rate of bromate formation by a factor of approximately 1.5. This observation could be fully accounted for by considering the dependence of the dissociation constant of HOBr (eq. 5) on ionic strength, which causes changes in equilibrium.

2.4.2 Oxidation of bromide by hydroxyl radicals

Effect of alkalinity
Carbonate radicals, which are formed through OH radical scavenging (reactions 19 and 20 in table 2), react as secondary oxidants for hypobromite. This was tested by Von Gunten and Hoigné (1994) through ozonation experiments on bromide-containing solutions at pH 8 with carbonate concentrations ranging from 1 to 10 mM. The calculated fraction of OH radicals scavenged by $[CO_3^{2-}]_{tot}$ fluctuated between 50% (1 mM $[CO_3^{2-}]_{tot}$ and 90% (10 mM $[CO_3^{2-}]_{tot}$). These results support the assumptions in eqs. 16-18, where $[HOBr]_{tot}$ can react either with OH or carbonate radicals. Correspondingly, kinetic simulations based on reactions 1-27 have shown that the bromate formed through the OH radical mechanism is nearly independent of total carbonate concentrations (Von Gunten and Hoigné, 1994). Carbonate radicals are transient species that act as secondary oxidants in ozonated water.

Effect of organic matter
The presence of natural organic matter (NOM), both concentration and nature, may also have an effect on the mechanism of bromate formation, as consumer of molecular ozone, or hydroxyl radical, or still bromine. The hydrophobic or hydrophilic nature of natural organic matter is an important parameter. Hydrophobic NOM (humic substances) is a poorer ''scavenger'' of hypobromite than hydrophilic NOM, probably because hydrophilic fractions of NOM includes more amino groups in their structure than hydrophobic fractions. Indeed, experiments performed in a continuous reactor with sand filtered water spiked with small concentrations of free amino acids showed that organic nitrogen contribute, as ammonia, to a decrease of bromate formation at a given Ct-value Legube et al. (2004).
Dissolved organic carbon accelerates the transformation of ozone into OH radicals but also scavenges them. In experiments of Von Gunten and Hoigné (1994) the OH radical yield per ozone exposure (c*t) appeared to be independent of organic material.

Effect of pH
The pH of water is also an essential parameter, because it controls both the presence of hypobromite ions (eq. 5) favoring the direct mechanism, and OH radical production promoting the radical pathway. Hence, it is not surprising that an increase in pH leads to an extensive formation of bromate for a given Ct-value (Figure 4) (Legube et al., 2004).

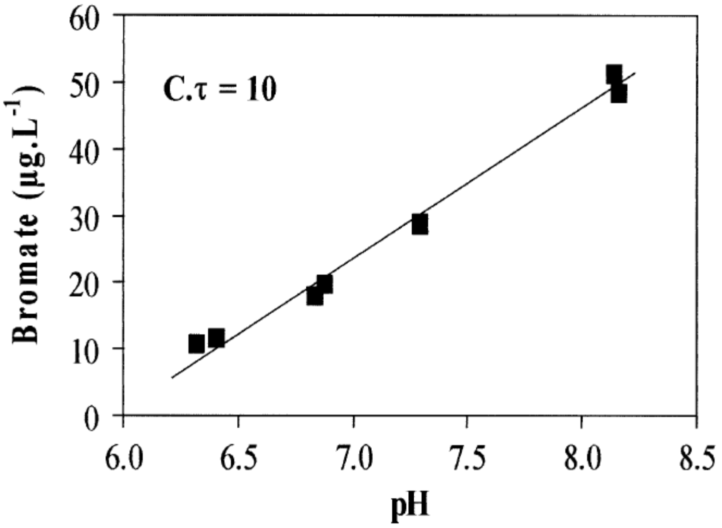


Figure 4. Effect of pH on bromate formation for Ct=10 mg L^{-1} *min. (sand filtrated water; bubble diffuser ozone contactor; [Br-] = 80 mg/L; DOC=1.9 mg/L; N-*NH_4^+ *< 10 µg/L; 25°C) (Legube et al., 2004).*

At pH 11 half life of ozone was approximately 2 s in Lake water (Von Gunten and Hoigné, 1994). The oxidation of bromide to hypobromite by molecular ozone is the rate limiting step in the formation of bromate when ozone is rather quickly reacts to form OH radicals. As soon as hypobromite is formed, it can be rapidly transformed into bromate by OH radicals. At pH 10 the half life of ozone was approximately 20 s. Bromate formation rates from bromide and from hypobromite were about equal, due to the longer half-life of ozone, allowing preliminary production of hypobromite from bromide (Von Gunten and Hoigné, 1994). At a typical pH range for drinking water treatment (pH 7-8), the ozone decomposition is much slower. This means the reaction of ozone with bromide species (eq. 1-4) plays a more important role at pH 7-8 than at pH 10 or 11.
The effects described above will not always be observed in processes where ozone and hydrogen peroxide are combined. In that case, an increase in pH will result in a lower bromate formation.

Effect of temperature
The temperature of water can intervene both in the reaction kinetics and the HOBr/BrO^- ratio. The Arrhenius law predicts a decrease of reaction rate at decreased temperatures. Applying the Van't Hoff law shows a decrease of acidity constant when temperature decreases (i.e. Ka_{HOBr} (25°C) = 2.06 10^{-9}, Ka_{HOBr} (5°C) = 1.19 10^{-9}). These cumulated effects lead to a decrease of bromate formation with decreasing temperature (Figure 5, Legube et al., 2004).

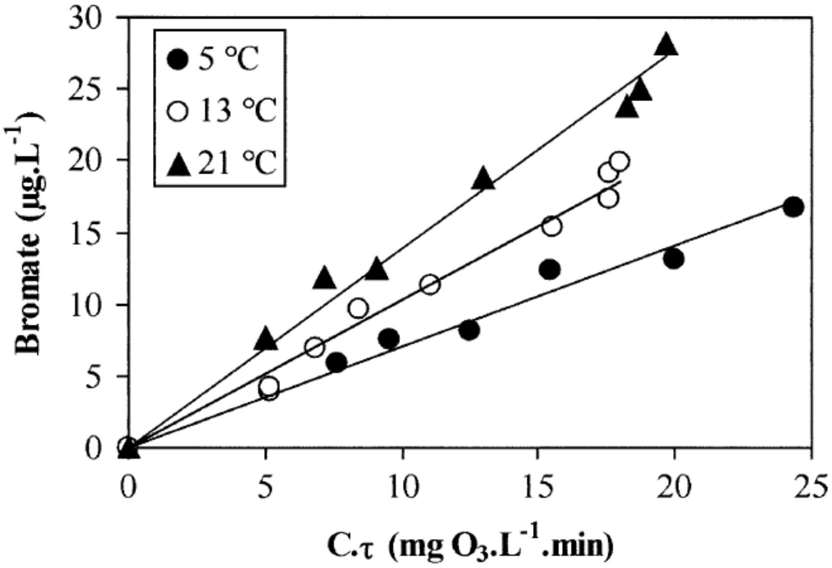


Figure 5. Effect of temperature on bromate formation versus Ct (sand filtrated water; bubble diffuser ozone contactor; [Br-] = 80 µg/L; pH=7.6; DOC=2.6mg/L; N-NH_4^+ <10 µg/L) (Legube et al., 2004).

Ammonia concentration

The presence of ammonia may have an important effect because ammonia can react quickly with bromine to give bromamine (eq. 6) that can react further with ozone to give bromide and nitrate. Consequently, such a phenomenon leads to a slower bromate formation for a given Ct-value (Legube et al., 2004, Figure 6).

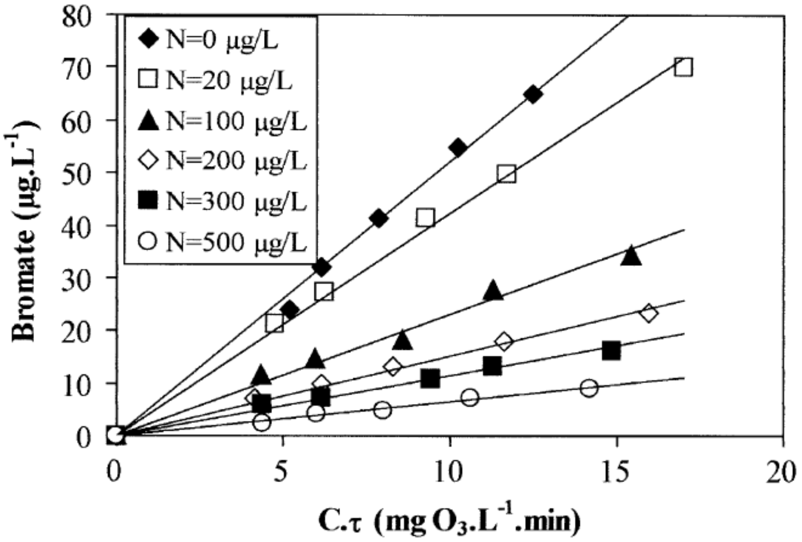


Figure 6. Effect of ammonium concentration on bromate formation versus Ct-value (sand filtrated water; bubble diffuser ozone contactor; [Br-] = 80 µg/L; pH=7.5; DOC=1.4mg/L; initial N-NH_4^+ <10 µg/L, 25°C) (Legube et al., 2004).

2.5 Model for bromate formation

Van der Helm and Smeets et al. (2007) developed a model for bromate formation in a DOPFR. Bromate formation was modeled as a linear function of the CT-value after an initial fast bromate formation. From fitting a linear equation on the experimental data, the amount of bromate formed in the DOPFR in the initial phase, $\Delta c_{BrO3,ini}$, and the amount of bromate formed in the linear phase, $\Delta c_{BrO3,lin}$, were determined. Equations were determined for prediction of the initial fast bromate formation and the bromate formation in the linear phase based on the total CT after ozonation:

$\Delta c_{BrO3,ini} = 1.5\ CT_{TOT} + 0.5$

$\Delta c_{BrO3,lin} = 1.4\ CT_{TOT} + 0.2$

The highest CT-value applied was 2.07 (mg O_3/L) × min. resulting in a total bromate concentration of 6.7 µg/L. The initial bromide concentration was 158 µg/L (Table 3).
The relation between CT-value and bromate formation will depend on the OH radical reaction and will be different for different water types. After establishing the relation for a certain type of water the CT can be used as a good indicator for on-line control of bromate formation. With the model it can be calculated that for these experimental conditions the level of 10 µg/L bromate will be reached at CT = 3.2 (mg O_3/L) × min.

In comparison, a model calculation of von Gunten and Hoigné (1992) (in: von Gunten and Hoigné, 1994) showed 10 µg/L bromate formation at 20-30 mg/L O_3 × min. exposure from 100 µg/L bromide (pH 7.5, no OH radical reactions).

2.6 Bromate reduction by UV irradiation

UV irradiation in the wavelength range of 180-300 nm provides energy sufficient for producing intermolecular changes of the irradiated molecules. The decomposition of BrO_3^- leads to the production of bromite ion (BrO_2^-):

$2\ BrO_3^- + h\nu \rightarrow 2\ BrO_2^- + O_2$

The bromite ion (BrO_2^-) is further decomposed to the hypobromite ion (BrO^-) and the bromide ion (Br^-):

$2\ BrO_2^- + h\nu \rightarrow 2\ BrO^- + O_2$
$2\ BrO^- + h\nu \rightarrow 2\ Br^- + O_2$

The decomposition of BrO_3^- proceeds through internal transition (intramolecular bond cleavage). The peak effectiveness for BrO_3^- destruction is around 195 nm. BrO_3^- has virtually no absorbance above 250 nm and negligible absorbance (< 0.05 $mole^{-1}cm^{-1}$) between 240 and 250 nm. These reactions indicate that the photodecomposition of bromate leads to the production of Br^- and oxygen as end products and of bromite (BrO_2^-) and bromine ($HOBr/BrO^-$) as intermediates. The reduction of BrO_2^- and BrO^- is most effective at λ = 260 and 330 nm, respectively (Siddiqui et al. 1996).

Siddiqui et al. (1996) investigated bromate destruction by UV irradiation using low pressure mercury lamps and a medium pressure mercury lamp (Table 3). The UV-1 LP lamp, emitting mainly at a wavelength of 254 nm, reduced bromate to bromide (Br^-) with bromine ($HOBr/BrO^-$) as an intermediate. The bromate ion seemed to have a peak absorbance around 195 nm.
The MP lamp achieved 7-46% bromate reduction at initial bromate ion concentrations of 11-38 µg/L and UV doses ranging from 60 to 550 mJ/cm^2.

The presence of organic matter (DOC) lowered the reduction of BrO_3^- levels in natural waters somewhat, presumably due to some absorption of UV energy and the consumption of free radical species by organic carbon (Siddiqui et al., 1996).

Changes in pH (6.5 – 8.5) and ionic strength had no significant effect on BrO_3^- reduction by UV irradiation. This is possibly because the $HBrO_3/BrO_3^-$ system has a very low pKa value (< 2.0) and for the pH levels investigated, hypobromic acid ($HBrO_3$) was present entirely in its deprotonated form (BrO_3^-). Temperature was found to affect the decomposition rate of bromate ion; upon decreasing the water temperature to 10˚C from 26˚C, the destruction efficiency was reduced by 28% (Siddiqui et al., 1996).

Collivignarelli and Sorlini (2004) investigated bromate formation in surface water by ozone and UV radiation with two different low pressure UV lamps (maximum light intensity at 254 and 185 nm, respectively; Table 3). Batch tests were performed with ozone concentrations up to 10 mg/L, UV doses up to 14,000 J/m^2 and a maximum contact time of 14 minutes. The combination of ozonation with UV irradiation lowered the bromate formation compared to ozone treatment alone (Figure 7): at 185 nm the reduction was about 10–20% compared to ozone alone, at 254 nm this was 40–50%. This result is surprising, because the bromate ion has a peak absorbance around 195 nm and virtually no absorbance above 250 nm.
However, the bromite ion (BrO_2^-), one of the intermediates in bromate formation, is reduced most effectively at 260 nm. The LP lamp emitting at 254 nm could have prevented bromate formation by reducing BrO_2^-. The UV irradiation seems only effective at ozone exposures below 10 mg min/L and/or UV doses below about 800 mJ/cm^2 (Figure 7). Above these values the LP lamp (185 nm) seems to enhance the bromate formation compared to the situation with ozone alone. This might be due to the increased OH radical formation at higher ozone concentrations and UV doses. Thus, ozone and UV doses should be carefully chosen.

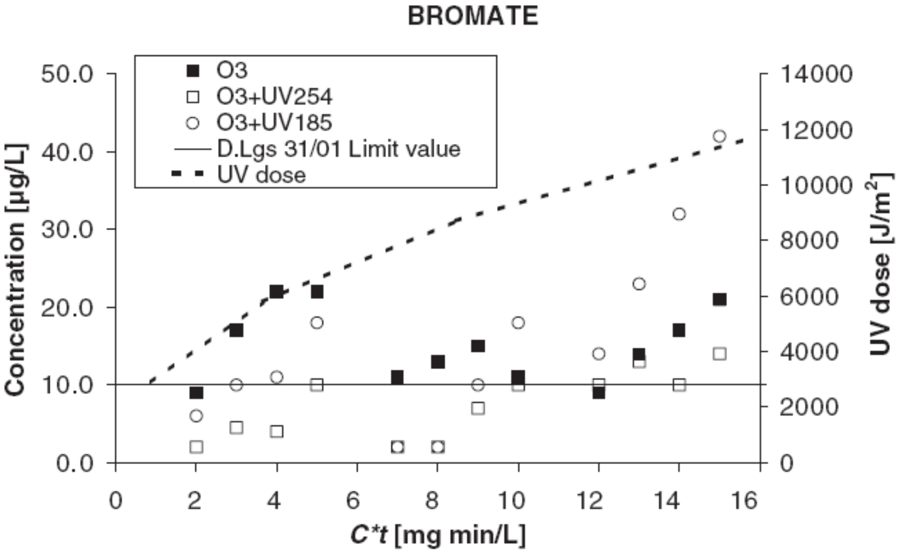


Figure 7. Bromate formation during ozone, ozone/UV 254 nm and ozone/UV 185 nm

Recommendation

To reduce bromate formation in ozone systems LP or MP lamps emitting at 195 nm (bromate reduction), 260 nm (bromite, BrO_2^- reduction) or 330 nm (BrO^-) should be tested. For the reduction of bromate (with no ozone present) an LP lamp emitting around 195 nm should be most efficient. At high ozone exposures (> 10 mg min/L) UV irradiation at 195 nm could work contra productive (Collivignarelli and Sorlini 2004).

Meunier et al. (2006) reduced ozone doses while implementing an additional UV disinfection step for an actual drinking water treatment plant. Ozonation was performed at low ozone doses in bench-scale experiments with pretreated river water from the Paris area (France). At the low ozone dose of 0.5 mg L^{-1}, bromate formation could be kept below 0.4 µg L^{-1}. Table 3 gives an overview of the referred bromate formation and reduction experiments.

Table 3 *Overview of ozone and UV process conditions and bromate formation in water treatment processes.*

Ozonation		UV process		Br concentrations				conditions			
O_3 dose (mg/L)	contact time (min)	lamp	UV dose (mJ/cm^2)	initial [Br-] (µg/L)	initial [BrO3-]	[BrO3-] reduction	[BrO3-] formation (µg/L)	Water type	pH	T (°C)	ref
0.5	20	-	-	73	-	-	0.4	Treatment plant, after sand filtration	8	16.5	[1]
1	20	-	-	73	-	-	8	Treatment plant, after sand filtration	8	16.5	[1]
-	-	LP lamp (UV-1)	630	-	1 mg/L	50%	-	MQW	6	? 10-26	[2]
-	-	LP lamp with quartz A (UV-2)	245	-	50 µg/L	50%	-	MQW	6	? 10-26	[2]
-	-	LP lamp with quartz B (UV-2)	500	-	50 µg/L	50%	-	MQW	6	? 10-26	[2]
-	-	MP lamp (UV-3)	550	-	11µg/L	46%	-	MQW	6	20	[2]
0.3	?	-	-	220	-	-	10	Raw Costa Mesa water	6.9	14	[4]
0.55	?	-	-	56	-	-	10	MIEX pretreated	6.6	14	[4]
6.4	?	-	-	300	-	-	11	Settled Occoquan reservoir water	6	?	[6]

Ozonation	UV process		Br concentrations				Conditions			
Ct (mg min/L)	lamp	UV dose (mJ/cm^2)	initial [Br-] (µg/L)	initial [BrO3-]	[BrO3-] reduction	[BrO3-] formation (µg/L)	Water type	pH	T (°C)	ref
5	-	625	30	-	-	21.5	raw river water	8		[3]
5	LP lamp (185 nm)	625	30	-	3.8	17.7	raw river water	8		[3]
5	LP lamp (254 nm)	625	30	-	11.5	10	raw river water	8		[3]
2.07	-	-	158	-	-	6.7	MQW	8	12	[5]
10	-	-	80	-	-	12	Sand filtered water	7.6	21	[7]
10	-	-	110	-	-	25	Sand filtered water	7.6	21	[7]

1 Meunier et al. 2006; 2 Siddiqui et al.1996; 3 Collivignarelli and Sorlini 2004; 4 Johnson and Singer, 2004; 5 van der Helm and Smeets et al., 2007; 6 Bonacquisti et al., 2006; 7 Legube et al., 2004

2.7 Conclusions/Summary of literature search

2.7.1 Summary

Bromate formation with ozonation
The bromate ion (BrO_3^-) is formed through a complex web of pathways with several bromine-containing intermediates that undergo reactions with both molecular ozone and hydroxyl radicals. Pathway molecular ozone (O_3): $Br^- \rightarrow OBr^- \rightarrow BrO_2^- \rightarrow BrO_3^-$. The reactions of molecular ozone with bromide and hypobromite ions are relatively slow compared to indirect oxidation of bromide by radicals. In the absence of scavengers, OH radical reactions contribute significantly to bromate formation.

Presently, there is no evidence of bromate formation in a system where bromide and hydroxyl radicals are the only initial reactants. Hypobromite (BrO^-) is a decisive intermediate in bromate formation through the OH radical mechanism: as soon as hypobromite is formed by molecular ozone, it can be rapidly transformed into bromate by OH radicals.

Generally, more than 90% of the oxidation of bromide occurs with molecular ozone. Only during the initial phase of an ozonation process (higher $OH^\cdot/O_3$ ratio) the fraction of bromide oxidized by OH radicals can make up for as much as 50% of the total bromide oxidation. The bromate formation mechanism cannot simply be divided into a “radical” and “molecular pathway” because both oxidants can react simultaneously or in sequence.

Bromate formation with ozonation
Minimizing ozone doses, especially to waters at a relatively low temperature, should lead to a low oxidation yield of bromide ions to bromate ions. Several attempts were made to model the effect of the ozone concentration/exposure on the bromate formation. Van der Helm and Smeets et al. (2007) developed a model for bromate formation in a DOPFR (milliQ, pH 8). Equations were determined for prediction of the initial fast bromate formation and the bromate formation in the linear phase based on the total CT after ozonation:

$$\Delta c_{BrO3,ini} = 1.5\ CT_{TOT} + 0.5$$

$$\Delta c_{BrO3,lin} = 1.4\ CT_{TOT} + 0.2$$

The relation between CT-value and bromate formation will depend on the OH radical reaction and will be different for different water types. With the model it can be calculated that for these experimental conditions the level of 10 µg/L bromate will be reached at CT = 3.2 (mg O_3/L) × min.
A model calculation of von Gunten and Hoigné (1992) showed 10 µg/L bromate formation at 20-30 mg/L O_3 × min. exposure from 100 µg/L bromide (pH 7.5, no OH radical reactions).

Bromate formation was a linear function of Ct-value (ozone concentration * time) in sand filtrated water at pH 7.6 (only molecular ozone reactions).

Bromate reduction with UV irradiation
UV irradiation in the wavelength range of 180-300 nm provides sufficient energy for producing intermolecular changes of irradiated molecules. The decomposition of BrO_3^- leads to the production of bromite ions (BrO_2^-):

$$2\ BrO_3^- + h\nu \rightarrow 2\ BrO_2^- + O_2$$

The bromite ion (BrO_2^-) is further decomposed to the hypobromite ion (BrO^-) and the bromide ion (Br^-):

$$2\ BrO_2^- + h\nu \rightarrow 2\ BrO^- + O_2$$
$$2\ BrO^- + h\nu \rightarrow 2\ Br^- + O_2$$

The peak effectiveness for BrO_3^- destruction is around 195 nm. BrO_3^- has virtually no absorbance above 250 nm. The reduction of BrO_2^- and BrO^- is most effective at $\lambda = 260$ and 330 nm, respectively. A low pressure lamp which emits radiation predominantly at < 200 nm is more effective for bromate destruction than the UV lamp which emits radiation at 254 nm, because the bromate ion has a peak absorbance around 195 nm.

Influence of other water quality parameters (DOC, Alkalinity, and pH) on bromate formation
Several water quality parameters are described in literature with respect to bromate formation:

Ionic strength. The rate of bromate formation (initial bromide 0.2 - 1 mg/L) by molecular ozone increased by a factor 1.5 by increasing the ionic strength from 1 to 50 mM (Na_2SO_4). This can be fully accounted for by considering the dependence of the dissociation constant of HOBr on ionic strength.

Effect of alkalinity. Carbonate radicals, which are formed through OH radical scavenging, react as secondary oxidants for hypobromite. $HOBr/BrO^-$ can react either with OH or carbonate radicals. The bromate formed through the OH radical mechanism is nearly independent of total carbonate concentration.

Effect of organic matter. The concentration and nature of NOM affect bromate formation, as consumer of molecular ozone, hydroxyl radicals, or bromine. NOM accelerates the transformation of ozone into OH radicals but also scavenges them. The hydrophobic or hydrophilic nature of the organic matter is an important parameter. Hydrophobic NOM (humic substances) is a poorer ''scavenger'' of hypobromite than hydrophilic NOM, probably because hydrophilic fractions of NOM includes more amino groups in their structure than hydrophobic fractions.

Effect of pH. A decrease in pH influences and normally lowers bromate formation by (i) shifting the $HOBr/OBr^-$ equilibrium to HOBr or (ii) altering the oxidant exposures (more ozone and less OH radicals). A pH increase generally leads to an increase in bromate formation.

Effect of temperature. Temperature influences the (i) reaction kinetics: decrease of reaction rate at decreased temperatures, (ii) $HOBr/BrO^-$ ratio: decrease of acidity constant when temperature decreases These cumulated effects lead to a decrease of bromate formation as temperature decreases.

Ammonia concentration. Ammonia reacts quickly with bromine to give bromamine ($HOBr + NH_3 \rightarrow NH_2Br + H_2O$) that can react further with ozone to give bromide and nitrate. This leads to lower bromate formation for a given Ct-value.

Integration: influence of time between ozone dosing and applying UV light
Both UV irradiation and the ozone concentration influence the pathway of bromide formation ($Br^- \leftrightarrow OBr^- \leftrightarrow BrO_2^- \leftrightarrow BrO_3^-$).

From the description of the experimental set-up of Collivignarelli and Sorlini (2004) which use both UV and ozone in the presence of bromide (see Annex 1) it can only be concluded that the time between ozone dosing and UV light application in the system is less than 2 minutes. Water is continuously recycled in the reactor system. During a complete cycle in the system (2 minutes) the UV irradiation time is 20 seconds. It is not clear whether ozone is still present at the UV lamp or has already reacted away completely.

To prevent bromate formation in ozone systems LP or MP lamps emitting at 195 nm (bromate reduction), 260 nm (bromite, BrO_2^- reduction) or 330 nm (BrO^- reduction) have been tested. The drawback of using a wavelength of 195 is that NOM also strongly absorbs at this wavelength, making the bromate reduction less efficient.

The energy supplied by UV radiation interacts with O_3, the overall reaction being:

$$O_3 + H_2O \xrightarrow{h\upsilon} 2\,OH\cdot + O_2$$

These OH radicals too can be involved in processes resulting in the formation of bromate. To prevent additional OH radical formation by UV radiation via the above reaction it might be recommended to apply the UV irradiation after most of the ozone has reacted away.
On the other hand, UV radiation (260 nm , 330 nm) could prevent bromate formation in an early stage by reduction of intermediates when the UV lamp is placed shortly after the ozone dosing. Experimental research must answer the question what is the optimal contact time between ozone dosing and UV irradiation.

2.7.2 Conclusion

Can bromate concentrations be kept below the water quality norm in UV-O_3 systems?
Bromate formation depends on:

- incoming Br^-
- ozone concentration en contact time (c*t)
- UV dose and wavelength of UV radiation
- Matrix effects (DOC, pH, alkalinity, ionic strength, ammonium)
- temperature

Von Gunten and Hoigné (1994) mention ozone exposure, pH and bromide concentration as the decisive input parameters to determine the bromate concentration.

The most effective UV wavelength for bromate reduction is about 195 nm. However, as at this wavelength the UV absorbance by water is very high, it is unlikely that we can use UV to directly reduce bromate formed. On the other hand: the processes involved in bromate formation are very complex, and thus it still is possible that another wavelength may be effective in preventing the formation of bromate.

From literature no clear conclusions can be drawn, whether or not the combination of ozone and UV results in a decrease in the final bromate concentration).

3 Materials and methods

3.1 Introduction

In the project TTI DOPFR-UV the bromate formation in the DOPFR-UV reactor (Dissolved Ozone Plug Flow Reactor, Figure 1) will be studied. In this system, depending on the distance between the ozone dosing point and the UV reactor, and the UV dose, the ozone is converted to hydroxyl radicals (HO•). Thus, the DOPFR-UV system may provide flexibility with regard to oxidation and disinfection. However, at the moment it is not clear whether the bromate formation rate in the DOPFR-UV concept is higher or lower compared with conventional ozone systems.

From the literature search (chapter 2), it was concluded that the reaction schemes involved are very complicated, and strongly depend on conditions like pH, temperature and NOM (natural organic matter). From this literature study no conclusions could be drawn, whether or not UV irradiation can be applied to prevent or decrease bromate formation in our system. It seemed unlikely that UV irradiation will reduce the bromate (as for this purpose about 195 nm would be required, which is the wavelength which is strongly absorbed by the water matrix itself). On the other hand, the UV irradiation applied may interfere with some intermediates of the bromate formation. Furthermore, the process may be influenced by the time between ozone dosing and UV irradiation.

In a subsequent feasibility study the combined effect of ozone and UV treatment on the bromate formation in pre-treated water from ps. Soestduinen and from ps Leiduin was studied. The goal of this study was to find out whether bromate formation can be reduced in an ozone system by applying UV irradiation. Based on the results obtained a go/no go decision is to be taken for this project.
Five tests were designed:

Test 1:	Ozone half-life and stability, to be able to control the experimental conditions during the following tests.
Test 2:	Determination of bromate reduction by UV irradiation, in order to check whether UV irradiation can reduce the bromate content under these circumstances.
Test 3:	Determination of bromate formation due to ozone, to determine the maximum concentration that will be formed in this system.
Test 4:	Determination of bromate formation in a combined system of UV and ozone, using Soestduinen water (with low NOM content).
Test 5:	Determination of bromate formation in a combined system of UV and ozone, using Leiduin water (with “normal” NOM content).

3.2 Materials

3.2.1 Ozone set-up

For the conducted tests, ozone saturated water was used. Ozone was produced using an ozone set-up which was available at KWR. The set-up is depicted in Figure 8.

Ozone gas was generated using a Fisher PH310 Ozone generator (PH310 OZ 503 20 g/h). Ozone was bubbled through a solution of ‘drinking water from WTP. Soestduinen’. Due to the fact that not all ozone will dissolve into the water the remaining ozone gas was lead through an ozone killer (Trailgaz). In order to determine the concentration of the ozonated water solution, the milli Q water was circulated (flow 22 L/h) and measured by means of an ozone in water sensor (Orbisphere MK309 model 26505, with a 2301 sensor), after the ozone concentration in the solution had become stable (saturated). The amount of solution necessary for the tests was taken at the sample point.

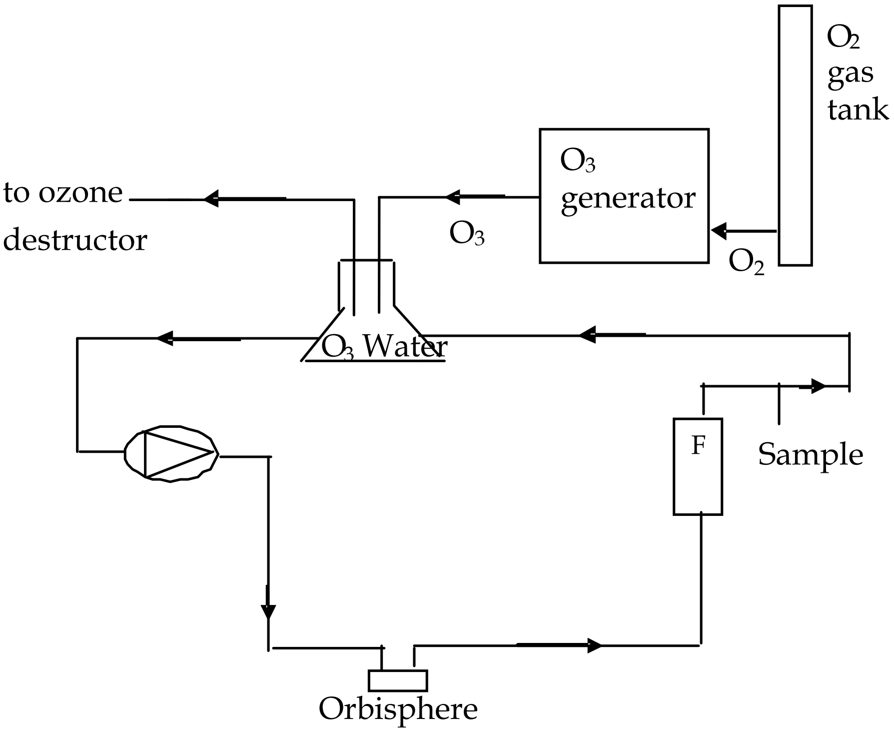


Figure 8 Ozone set-up to produce ozone saturated water

3.2.2 Collimated beam set-up

All collimated beam tests were performed with the collimated beam apparatus of KWR [Harmsen, 2004]. A collimated beam apparatus is a UV-apparatus which can, under accurately defined circumstances, determine dose effect relations on a laboratory scale.

With the collimated beam apparatus of KWR, different kinds of UV-lamps can be tested. The height and the shape of the collimated beam can be varied. During the tests the irradiated solutions are stirred. The collimated beam apparatus is schematically shown in Figure 9.

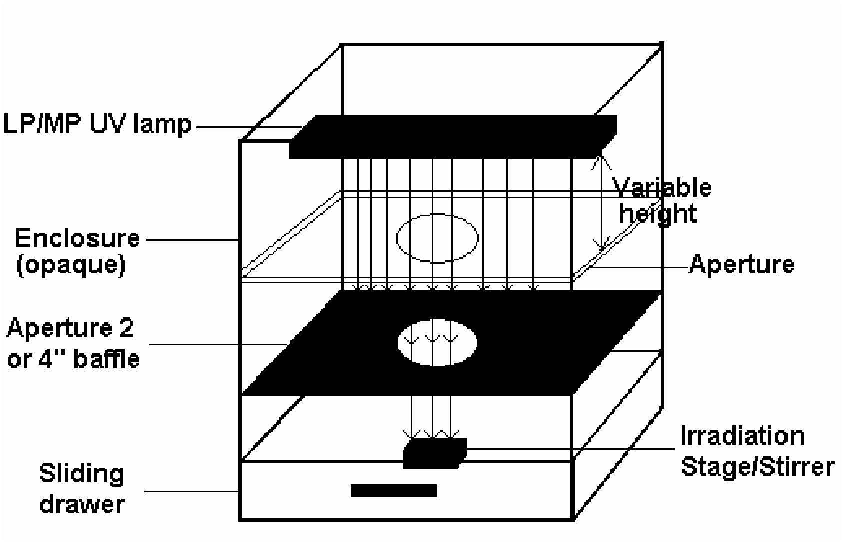


Figure 9 Drawing of the collimated beam apparatus

During the collimated beam tests two types of lamps were applied. A low pressure (LP) lamp (Philips TUV PL-L95/4P; 95 W HO) and a medium pressure (MP) lamp (Philips HOK 20/100; 2 kW).To obtain a certain dose, the sample was exposed to UV light during a certain time (exposure time). To calculate the exposure time corresponding to a certain dose, a spreadsheet from Bolton was used (Bolton *et al.*, 2003). In order to calculate the exposure time, the UV-absorbance of the solution [254 nm using the LP lamp and from 200 to 300nm using the MP lamp], the Petri factor, the Sensor factor, the distance between lamp and irradiance surface, the water depth, the irradiated water volume and the intensity of the lamp in the middle of the Petri dish were measured and used as input for the Bolton spreadsheet [Bolton, 2003].

The intensity of the lamp was measured with an IL 1700 Research Radiometer and SED240W detector from International Light.

3.3 Solutions

Test water
At first it was tried to use milliQ water (Millipore Academic A10) for the experiments. However, these solutions had to be buffered (with K_2PO_4/NaOH), and this appeared to interfere with the bromate analysis. Therefore, it was decided to use drinking water from ps. Soestduinen, Vitens (pH =7.9; NPOC = 0.24 C/L), as this water is known for its low TOC (less scavenging of OH radicals). The natural Br^- concentration is 53 μg/L and 130 μg/L is added (total 170-180 μg/L Br^-).

An additional test was carried out with pre-treated water before ozonation from ps. Leiduin, Waternet (pH =7.8; NPOC = 1.75 C/L). The initial Br^- concentration is unknown and 30 μg/L is added (to a total of 160-170 μg/L Br^-, as was determined after addition of the extra amount of bromide).

Chemicals
Potassium bromide from J.T. Baker was used (J.T Baker 0202; lot no: T 38627; 100g; FW=119 g/mol; baker analyzed).

Potassium bromate from Aldrich was used (Aldrich; 99.8%, ACS reagent; FW=167.01 g/mol).

Sodium sulfite Na_2SO_3 (J.T Baker 0316; lot no: Y46622; 250g; FW=126.04g/mol; baker analyzed) to quench the ozonated samples.

3.4 Analyses

Ozone

The analyses were carried out by KWR using the indigo solution from HWL (detection limit 0.01 mg O_3\L).
The absorption of the analyzed ozone solution was measured using a Thermo Spectronic Unicam UV500 spectrophotometer available at KWR. The solutions were measured applying a 1 cm quartz cell at a wavelength of 600 nm. The ozone concentration was calculated by HWL using the input data (absorbance, amount of solution) from KWR.

Bromate

Analyses were conducted by HWL.

Bromide

Analyses were conducted by HWL.

pH

pH was measured using an Orion pH meter, model 720A with a pt100 electrode.

Hydrogen carbonate (HCO_3)

Methods LAM-042, according to NEN 6531 and 6532
Hydrogen carbonate was titrated with hydrochloric acid to a pH of 4.35. The pH was measured with a PHM 83 autocal pH meter from Radiometer Copenhagen.

NPOC

Methods LAM-041, according to ISO 8245 and NEN-EN 1484
The non-volatile organic carbon has been analyzed using infrared gas analyzer. The analyzer is a Schimadzu TOC-5000A with TOC-control and an ASI-5000A autosampler.

3.5 Experimental Set-up

In order to determine the feasibility of DOPFR-UV the following tests were conducted:

1. Ozone half-life and stability.
2. Determination of bromate reduction by UV irradiation.
3. Determination of bromate formation due to ozone.
4. Determination of bromate formation in a combined system of UV and ozone in water from WTP Soestduinen.
5. Determination of bromate formation in a combined system of UV and ozone in water from WTP Leiduin.

3.5.1 Test 1: Ozone half life and stability

For the tests with ozone, it is necessary to be able to prepare solutions containing a constant and reproducible ozone concentration. Ozone decomposes, but in order to carry out reactions at a certain ozone concentration, this concentration should not notably decrease within the period required to do the testing. Therefore, the ozone half-life and stability were studied. In order to determine the ozone half-life and stability, water was saturated with ozone using the ozone set-up (see paragraph 3.2.1). First water was ozonated till saturation. At the saturation point the ozone supply was stopped and the decay of ozone was determined. The test was carried out with milliQ and Soestduinen water. The ozone concentration in water was measured with the sensor (Orbisphere) or analyzed using the indigo method.

Table 4 Set-up test 1

Experiment	Water	Method
1	Soestduinen Water	sensor
2	Soestduinen Water	Analyzed
3	MilliQ	Sensor

3.5.2 Test 2: determination of bromate reduction by UV irradiation

In order to determine the bromate reduction by UV irradiation a test was conducted using the collimated beam apparatus available at KWR (see paragraph 3.2.2).

Potassium bromate (10 µg/L) was dissolved in Soestduinen water, and treated with UV in the collimated beam apparatus. The tests were conducted both with LP and MP lamps. After each irradiation samples were taken and analyzed for bromate. Also the pH and NPOC from the Soestduinen water were analyzed. The conditions of test 2 are shown in table 5.

Table 5 Conditions test 2

Lamp type	MP	LP
Irradiated Solution	Soestduinen DW + 10 µg/L BrO_3^-	Soestduinen DW + 10 µg/L BrO_3^-
Distance lamp irradiance surface	80 cm	30 cm
Irradiate volume	100 mL	100 mL
UV-dose (mJ/cm^2)	0-40-300-600*	0-40-300-600

*All doses were conducted in duplo and the UV doses for one test were irradiated at random.

3.5.3 Test 3: Determination of bromate formation due to ozone

In order to determine the bromate formation, due to ozone, milliQ water was saturated with ozone using the ozone set-up (see paragraph 3.2.1). Also Soestduinen water with addition of 130 µg/L bromide was prepared. The concentration of the saturated ozone solution was determined using the orbisphere sensor. Different amounts of the saturated ozonated milliQ water were added to the Soestduinen water. During the test the solution was stirred. Directly after every test the solution was quenched with sodium sulfite (Na_2SO_3). Solutions (100 mL) containing 2 mg O_3/L at the beginning of the test were quenched with 100 µl of a solution of 0.8269 g Na_2SO_3/100mL in order to neutralize the remaining ozone (except for the ozone samples). Solutions containing less ozone were quenched by ratio.

Samples for ozone and bromate analysis were taken after different contact times between the ozone and the Soestduinen water in order to study the influence of the contact time on the bromate formation in Soestduinen water containing bromide. Also the ozone concentration at the beginning of the tests was analyzed (due to practical circumstances a few seconds after addition of the ozone to the Soestduinen water). Also the pH and NPOC from the Soestduinen water were analyzed. The conditions of test 3 are given in table 6.

Table 6: Conditions test 3 with test water = Soestduinen water + 130 μg/L bromide (total 170-180 μg/L bromide)

Experiment	Initial Ozone dose (mg/L)	contact time (s)
1	2	10
2	2	30
3	2	60
4	2	1800
5	1	10
6	1	30
7	1	60
8	0.5	10
9	0.5	30
10	0.5	60

3.5.4 Test 4: Determination of bromate formation in a combined system of UV and ozone

In order to determine the bromate formation in a combined system of UV and ozone an experimental set-up was used which combines tests 2 and 3.

At the start of the test milliQ water was saturated with ozone using the ozone set-up (see paragraph 3.2.1). Also Soestduinen water with addition of 130 μg/L bromide was prepared. The concentration of the saturated ozone solution was determined using the orbisphere sensor. The saturated ozonated milliQ water was added to the Soestduinen water to obtain an initial ozone concentration of 2 mg/L. After a certain contact time between ozone and the Soestduinen water the water was irradiated with UV using the collimated beam apparatus (see paragraph 3.2.2) at different UV doses. After a test the samples were quenched with 100 μl of a solution of 0.8269 g Na_2SO_3/100mL to neutralize the remaining ozone (except for the ozone samples). Quenching took place at different times after irradiation in order to investigate the influence of the remaining ozone on the UV treated water. During a test the solution was stirred.

Samples for ozone and bromate (duplo) analyses were taken at the end of a conducted test. For each sample a separate test was conducted, this means that each test was conducted in triplo (2x bromate, 1x ozone). Also the pH, HCO_3, NPOC and bromide contents from the Soestduinen water were analyzed. The conditions of test 4 are given in Table 7.

Table 7 Conditions test 4 (test water = Soestduinen water + 130 µg/L bromide)

Experiment	Initial Ozone dose (mg/L)	contact time before UV (s)	UV-dose (mJ/cm^2)	Contact time after UV (s)
1	2	30	0	0
2	2	0	300	0
3	2	0	600	0
4	2	0	600	600
5	2	0	600	1800
6	2	30	600	0

3.5.5 Test 5 Determination of bromate formation in a combined system of UV and ozonewith a different water composition

In order to determine the influence of the water composition on the bromate formation in a combined system of UV and ozone, test 4 was repeated with a different water composition (pre-treated water ps. Leiduin, Waternet before ozonation).

At the start of the test milliQ water was saturated with ozone using the ozone set-up (see paragraph 3.2.1). Instead of Soestduinen water, water of Leiduin (Waternet) before ozonation was tested. Water of Leiduin with addition of 30 µg/L bromide was prepared. The concentration of the saturated ozone solution was determined using the orbisphere sensor. The saturated ozonated milliQ water was added to the Leiduin water to obtain an initial ozone concentration of 2 mg/L. After a certain contact time between ozone and the test water the water was irradiated with UV using the collimated beam apparatus (see paragraph 3.2.2) at different UV doses. After a test the samples were quenched with 100 µl of a solution of 0.8269 g Na_2SO_3/100mL to neutralize the remaining ozone (except for the ozone samples). Quenching took place at different times after irradiation in order to investigate the influence of the remaining ozone on the UV treated water. During a test the solution was stirred.

Samples for ozone and bromate (duplo) analyses were taken at the end of a conducted test. For each sample a separate test was conducted, this means that each sample three analyses were carried out (2x bromate, 1x ozone). Also the pH, HCO_3, NPOC and bromide contents from the Leiduin water after addition of bromide were analysed in duplo. The conditions of test 5 are given in Tables 8 and 9.

Table 8: Analytical details of Leiduin water before O3 addition (+ 30 µg Bromide)

pH	temp (pH)	pH (lab)	temp (lab)	HCO_3	NPOC	Bromide	temp (ambient)
	^0C		^0C	mg/L	mg/L	µg/L	^0C
7,81	21,4	7,9	20,6	202	1,7	170	23,1 (begin test)
7,86	20,4	8,0	20,7	201	1,8	160	24,0 (end test)
7,83	21,5						

Table 9: Conditions test 5 (test water = Leiduin water + 30 µg/L bromide)

Experiment	Initial Ozone dose (mg/L)	contact time before UV (s)	UV-dose (mJ/cm^2)	Contact time after UV (s)
1	2	10	0	0
2	2	30	0	0
3	2	60	0	0
4	2	0	300	0
5	2	0	600	0
6	2	0	600	600
7	2	0	600	1800
8	2	30	600	0

4 Results and discussion

4.1 Test 1: Ozone half life and stability

The ozone stability and half life in Soestduinen water were determined using both the Orbisphere sensor and the "indigo test". In appendix II all raw data are shown.

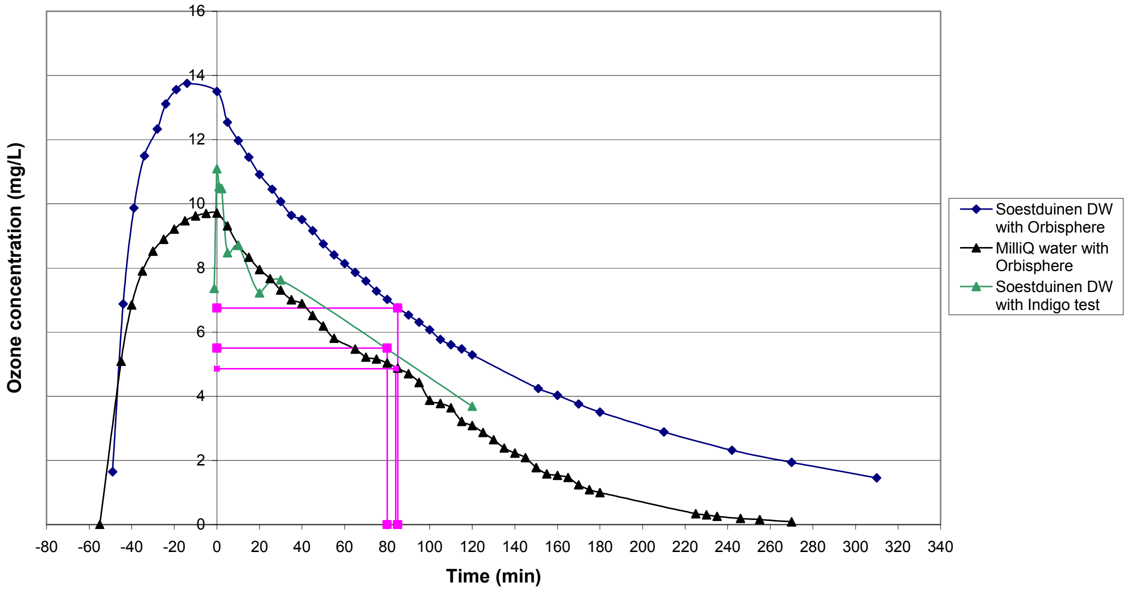


Figure 10 Ozone concentration (graphs) and half-life (pink dots)

The results are shown in table 10.

Table 10: Ozone half life time in Soestduinen water.

Experiment	Water	Temperature (ºC)	Method	Ozone half life (min)
09/03/2009	Soestduinen Water	21.7	sensor	85
24/03/2009		23.1	Analyzed	80
07/04/2009	MilliQ water KWR	23	Sensor	84

From these results it can be concluded, that solutions with a constant and reproducible ozone concentration can be made. Furthermore, the ozone half-life is long enough to have a "constant" ozone concentration during the period of the experiment.

4.2 Test 2: Determination of bromate reduction by UV irradiation

Potassium bromate was dissolved in Soestduinen water, and treated with UV in a collimated beam apparatus, using either LP or MP lamps.
The results are shown in table 11.and figure 11.

Table 11: Bromate reduction by UV irradiation in a collimated beam apparatus. pH of the solution was 7.9, NPOC concentration < 0.20 mg C/L, temperature 22.7°C, initial BrO_3^- concentration 10 µg/L.

Lamp type	UV dose (mJ/cm^2)	Bromate concentration after irradiation (µg/L) (HWL results)	Average (µg/l)	Bromate reduction
LP	0	9,8	9,8	/
	40	9,9	9,85	0%
	40	9,8		
	300	9,7	9,65	1.50%
	300	9,6		
	600	9,7	9,7	1%
	600	9,7		
MP	0	9,8	9,8	/
	40	9,8	9,75	0.50%
	40	9,7		
	300	9,3	9,2	6.10%
	300	9,1		
	600	8,4	8,5	13.30%

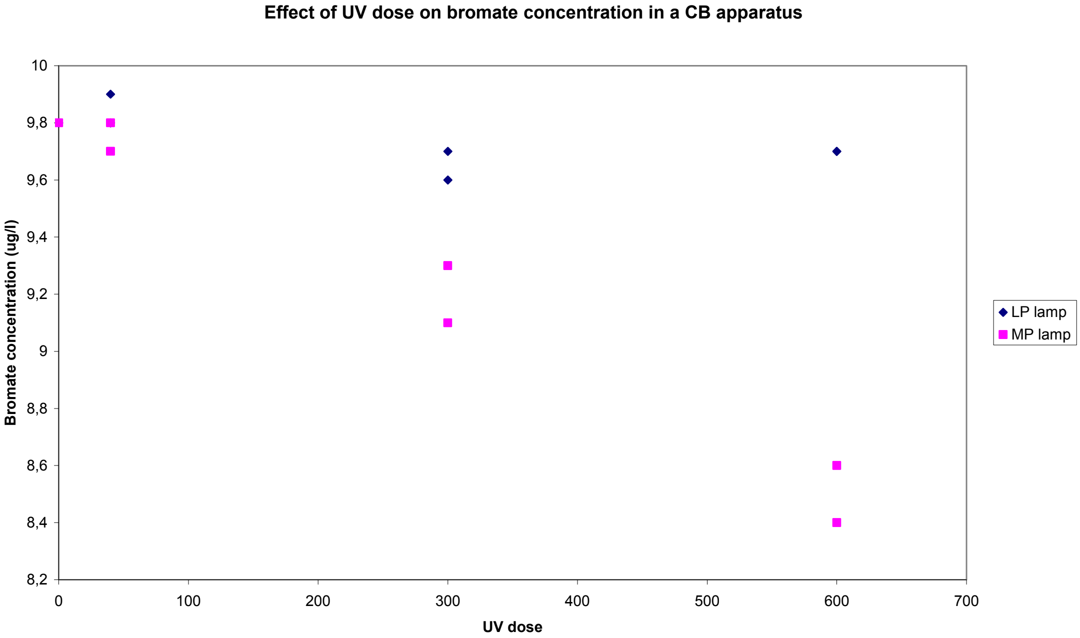


Figure 11: bromate reduction by UV irradiation in a CB apparatus; Effect of lamp type and UV dose (in mJ/cm²).

From these results it can be concluded that the LP lamp (emitting UV with a wavelength of 253.7 nm) didn't show a significant bromate reduction, whereas the MP lamp was more effective. This is in accordance with literature (see chapter 2), as the peak effectiveness for BrO_3^- destruction is around 195 nm, and BrO_3^- has virtually no absorbance above 250 nm. For the MP lamp used, the bromate reduction strongly depends on the UV dose applied. There seems to be a more or less linear relation between UV dose and bromate reduction. We didn't use a LP lamp with a wavelength of 180-200 nm, as the UV absorption of water at this wavelength is too high. As a result, in drinking water technology LP lamps with an emittance at 254 nm are used.

4.3 Test 3: Determination of bromate formation due to ozone

The Soestduinen water, used in this test, contained 53 µg/l bromide. Extra bromide was added, to a concentration of 180 or 170 µg/L. The water had a NPOC content of 0.24 mg/L and a pH of 7.9. An ozone saturated MilliQ solution was added to the bromide containing water, and the starting ozone concentration was determined. Afterwards, the bromate and remaining ozone concentrations were measured. The results are shown in table 12 and figure 12.

Table 12: Bromate formation during ozonation

Bromide concentration (µg/L)	Initial Ozone dose (mg/L)	Measured Ozone dose (mg/L)		contact time (s)	Average Bromate (µg/L)
		Initial	After contact time		
180	2	0.186	0.163	10	4
180	2	0.907	0.758	30	5.3
180	2	0.856	0.842	60	4.3
180	2	0.806	0.157	1800	5.2
180	1	0.650	0.600	10	3.2
180	1	0.503	0.493	30	2.7
180	1	0.144	0.113	60	2.2
170	0.5	0.180	0.191	10	1.1
170	0.5	0.191	0.179	30	1
170	0.5	0.190	0.018	60	1.1

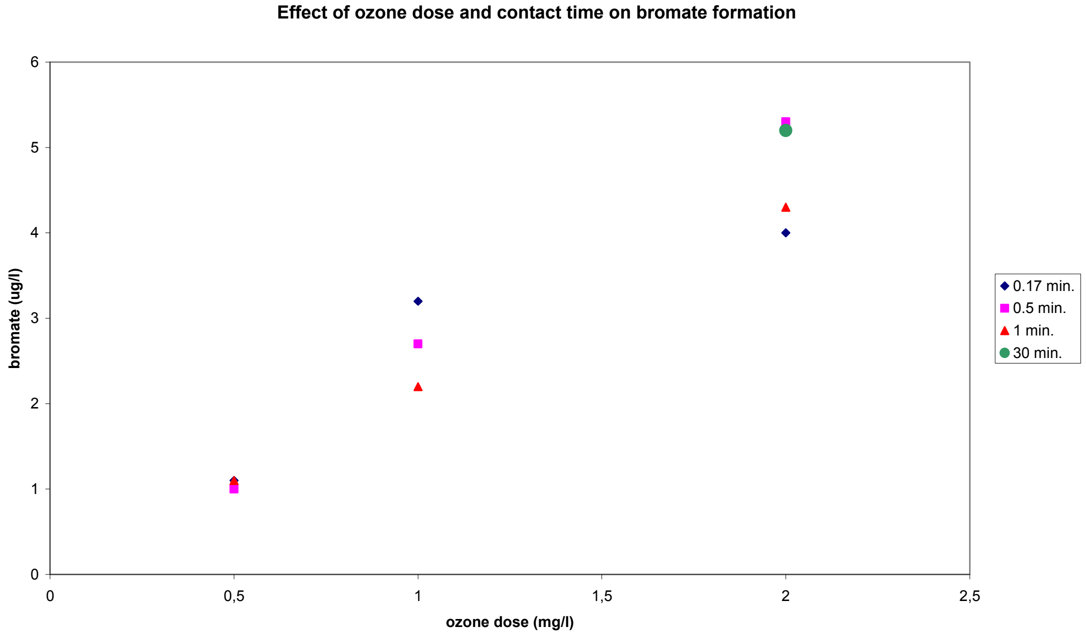


Figure 12: Effect of ozone dose and contact time on bromate formation

From these results it can be concluded that the bromate formation increases with increasing ozone dose, while the contact time does not seem to be of influence. This means that the reaction probably occurs almost instantaneously.

4.4 Tests 4 and 5: Determination of bromate formation in a combined system of UV and ozone

4.4.1 Test 4:applying Soestduinen water

In the collimated beam apparatus the combination of ozone and UV irradiation was investigated, using the MP lamp. In both series the bromate content after ozonation and irradiation was measured, and the results are shown in table 13 and figure 13.

Surprisingly, it was found that after the experiments the pH of the second series appeared to have decreased to a value of about 4-5. Although according to table 2 H^+ formation can occur during the bromate formation, the total bromide content of the original solution was too low to account for this decrease. Furthermore, the bromate concentration in these samples could not be determined, as the analysis was hindered by the presence of what seemed to be nitrate. So far we have found no explanation for this observation.

Table 13: Bromate formation after ozonation and UV irradiation; starting bromide concentration: 170 µg/l (Soestduinen water).

Initial Ozone dose (mg/l)	UV dose (mJ/cm^2)	pH after reaction	Contact time (s)*	Sample time (s)**	Bromate (µg/l)
0	0	7	0	0	<0.5
2	0	7	30	0	28
2	300	7	0	0	46
2	600	7	0	10	56
2	600	7	0	30	55
/	600	7	0	0	51
2	600	7	30	0	69
2	0	4-5	30	0	
2	300	4-5	0	0	
2	600	4-5	0	0	
2	600	7	0	10	45
2	600	4-5	0	30	54
2	600	4-5	30	0	

*: time between the ozone addition and the start of UV irradiation

**: time before quenching after UV irradiation

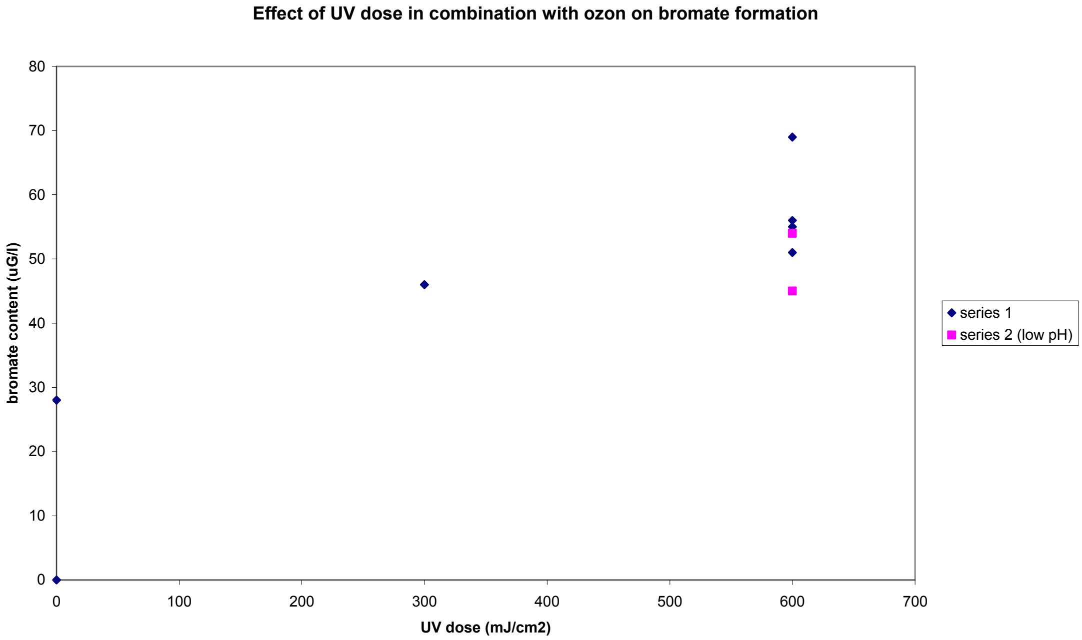


Figure 13: Effect of UV dose in combination with ozone on the bromate formation in a solution of 170 µg/l bromide in Soestduinen water.

From the results shown above it can be seen that the concentration of bromate, formed by the combination of ozone and UV irradiation in this case seems to be about the tenfold of the concentration observed with only ozone. This may be explained from the fact that Soestduinen water has a very low TOC (NPOC 0.25 mg/L, pH = 8.1, HCO: 105 mg/l), and thus there is hardly any scavenging of the OH· radicals in this water. In systems where OH radicals are not scavenged by organic compounds, according to Von Gunten (1994) considerably higher amounts of bromate can be formed, resulting in a bromate concentration that may be 30-70% higher than in systems where only reactions with molecular ozone occur.

N.B. Even the bromate concentration in case of a UV dose of 0 mJ/cm^2 appears to be much higher than in the previous experiment. This may be due to an analytical uncertainty. Another explanation may be that we used water from Soestduinen with a very low NOM content. There are hardly any radical scavengers present in this type of water, as a result of which small changes in NOM content may cause a relatively large effect. It might be better to use water with a higher, more common NOM content. Therefore, it was decided to repeat this test with water from ps. Leiduin.

Table 14: Ozone concentration after ozonation and UV irradiation; starting bromide concentration: 170 µg/l (Soestduinen water).

Initial Ozone dose (mg/L)	UV dose (mJ/cm^2)	Contact time (s)*	Sample time (s)**	Measured Ozone dose after test (mg/L)
0	0	0	0	0.010
2	0	30	0	1.237
/	300	0	0	0.055
/	600	0	10	0.068

2	600	0	30	0.020
/	600	0	0	0.029
2	600	30	0	0.052

*: time between the ozone addition and the start of UV irradiation
**: time before quenching after UV irradiation

Comparing the ozone concentrations in tests 3 and 4 shows that in both tests the ozone concentration at the start of the test was only half the original concentration. This can be explained from the fact that ozone seems to immediately react with the test solution (Soestduinen water + 170 – 180 µg/L bromide), and that a few seconds are required to take a sample. When UV irradiation is applied, the ozone concentration further decreases, indicating that as a result of the UV irradiation reactions involving ozone are taking place. This may account for the increase in bromate content found in test four. Furthermore, the fact that Soestduinen water has a very low NOM content means that there are only few radical scavengers present, which may also account for the large bromate content measured.

4.4.2 Test 5: applying Leiduin water

The results obtained in test 4 may be strongly influenced by the fact that the Soestduinen water has a very low NOM content. At PS Leiduin, ozonation actually is applied in the purification process. The water from PS Leiduin contains more NOM, and has a natural bromide content of about 140-150 µg/L. It was decided to repeat test 4 (applying MP-lamps), using Leiduin water instead of Soestduinen water. An extra amount of 30 µg/L bromide was added, resulting in a total bromide content of 170 µg/L. The results are shown in tables 15 and 16. The desired ozone dose for test 5 was 2 µg/L

Table 15 Ozone concentration after ozonation and UV irradiation; starting bromide concentration: 170 µg/l Leiduin water).

Initial ozone dose	Contact time before UV	UV dose	Time after UV	Ozone conc. After test
(mg/L)	s	mJ/cm^2	Min.	(µg/L)
1.84	10	0	0	0.52
1.84	30	0	0	0.40
--	60	0	0	0.33
1.84	0	300	0	0
1.82	0	600	0	0.01
1.82	0	600	10	0
1.82	0	600	30	0
1.82	30	600	0	0.01

Table 16 *bromate formation after ozonation and UV irradiation; starting bromide concentration about 170 µg/L.*

Initial ozone dose (sensor reading)		Contact time before UV	UV dose	Time after UV	Bromate concentration after test (duplo)	
A	B				A	B
(mg/L)	(mg/L)	(s)	mJ/cm^2	(min.)	(µg/L)	(µg/L)
0	0	0	0	0	<0.5	0
2.13	1.86	10	0	0	83	130
2.11	1.89	30	0	0	89	130
2.11	2.13	60	0	0	82	130
2.14	2.02	0	300	0	91	140
2.11	1.89	0	600	0	120	130
2.08	2.00	0	600	10	120	120
2.06	1.86	0	600	30	130	130
2.11	1.97	30	600	0	120	130

The results obtained with Leiduin water in table 15 are comparable to the results obtained with Soestduinen water (table 14). The ozone concentration decreases upon reaction with the compounds present in the water. As Leiduin water contains more NOM than Soestduinen water, the ozone concentration here becomes lower. In both cases it can be seen that application of UV irradiation results in complete reduction of the ozone.

Two tests were carried out to determine the bromate concentration in Leiduin water after ozonation combined with UV irradiation. The bromate concentration in test A seems to be lower than the bromate concentration in test B. This may be due to experimental uncertainties in the experiments and the analyses. From these results it cannot clearly be concluded that application of UV irradiation results in a higher bromate concentration, as was found in table 13. Considering only series A might also give the impression that UV-irradiation may increase the bromate content, but considering all results it can only be concluded that the differences are within the experimental uncertainty. The bromate concentration as measured after ozonation (without UV) is in good accordance with data in literature (Orlandini 1997). Orlandini carried out ozonation experiments with Leiduin water (with a bromide content of about 170 µg/L), and found that the bromate concentration strongly depends on the ozone dose applied. At ozone doses below 0.8 mg/L, the resulting bromate concentration was found to be < 10 µg/L, but with increasing ozone doses a sharp increase in the resulting bromate concentration was observed. At an ozone dose of 2 mg/L the bromate concentration was found to be about 100 µg/L, which is in good accordance with the results we found. Later, van der Helm carried out ozonation experiments with Leiduin water (van der Helm 2007). In general he used low ozone concentrations (<1 mg/L) in order to obtain low bromate concentrations. He too found that ozone reacts very fast. In our case, with Leiduin water the application of UV irradiation does not seem to be of any influence on the final bromate concentration. As was shown in test 2, UV can only decrease the bromate concentration to a small extend. Obviously, the formation of bromate is so fast, that the intermediates that might interact with UV had already disappeared when UV irradiation was applied.

It may seem strange that in Leiduin water, containing more NOM than Soestduinen water, a higher bromate concentration is obtained, although there were more radical scavengers present. However, as was pointed out in section 2.4.2, not only the NOM concentration but also the hydrophobic or hydrophilic nature of the organic matter is a very important parameter. At the moment we do not have information on the characteristics of NOM in Soestduinen and Leiduin water.

The conclusion from Collivignarelli and Sorlini (Collivignarelli 2004) here too is valid: for a process with combined ozone and UV irradiation, the doses should be carefully chosen.

5 Conclusions

Ozonation of water containing bromide results in the formation of bromate, the amount of bromate increasing with increasing ozone content. This is independent of the contact time of the ozone, indicating a very fast or even instantaneous reaction.
UV irradiation of an aqueous solution containing bromate using a MP lamp results in a small decrease in bromate concentration. There seems to be a more or less linear relation between the UV-dose applied, and the bromate reduction observed.

Combination of ozonation and UV irradiation in water with a very low TOC (and thus little scavenging of the $OH\cdot$ radicals) seemed to result in an enhanced bromate formation. When the experiment was carried out using water with a higher NOM content, it was found that UV irradiation hardly affects the bromate concentration. The bromate reduction by UV is small, and obviously the bromate formation by ozone is a very fast reaction, as a result of which UV irradiation was applied too late to be of any influence on the intermediates. There is a chance that simultaneous application of ozone and UV may result in a lower bromate concentration, but even if this can be achieved practically, it is uncertain whether a sufficient UV dose can be obtained fast enough to compete with the bromate formation.

Considering the conclusions described above, the conclusion of our experiments is that application of DOPFR-UV probably will not contribute to a lower bromate concentration than applying ozonation in a DOPFR reactor without UV irradiation.

6 Literature

R. v.d. Aa; Waternet; personal communication (2010)

Almendral-Parra MJ, Alonso-Mateos A, Fuentes-Prieto, MS, Online Monitoring of Bromate in Ozonized Water Without a Previous Separation Process, J Fluoresc (2008) 18:1169–1179

Bolton J.R., Linden K.G.; *"Standardization of Methods for fluence (UV Dose) Determination in Bench-scale UV Experiments"*; J. Environ Engineering, 2003

Thomas P. Bonacquisti, A drinking water utility's perspective on bromide,
bromate and ozonation. Toxicology 221 (2006) 145–148

Daniel Clifford and D. J. Donaldson
Direct Experimental Evidence for a Heterogeneous Reaction of Ozone with Bromide at the Air−Aqueous Interface *J. Phys. Chem. A* 2007, *111,* 9809-9814

Collivignarelli, C.; Sorlini, S. AOPs with ozone and UV radiation in drinking water: contaminants removal and effects on disinfection byproducts formation, Water Science and Technology (2004), 49(4, Oxidation Technologies for Water and Wastewater Treatment III), 51-56

Von Gunten, U. and Hoigné, J. Factors controlling the formation of bromate during ozonation of bromide-containing waters. J. Water SRT - Aqua, 41: 299-304 (1992).

Von Gunten, U and Jurg Hoigné, Bromate Formation during Ozonation of Bromide-Containing Waters: Interaction of Ozone and Hydroxyl Radical Reactions, *Environ. Sci. Technol.* 1994, 28, 1234-1242

Von Gunten, U and Oliveras, Y; Advanced oxidation of bromide containing waters: bromate formation mechanisms; Environm. Sci. Techn., 32, 63-70 (1998)

Von Gunten, U. Ozonation of drinkingwater: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine Water Research 37 (2003) 1469–1487

Harmsen D; *"Protocol Collimated Beam UV"*; Kiwa Water Research, BTO 04.014 Nieuwegein, 2004.

van der Helm, A. W. C.; Smeets, P. W. M. H.; Baars, E. T.; Rietveld, L. C.; van Dijk, J. C., Modeling of ozonation for dissolved ozone dosing, Ozone: Science & Engineering (2007), 29(5), 379-389

Van der Helm, A.W.C.; Integrated modeling of ozonation for optimization of drinking water treatment; Thesis Delft University of Technology, 2007.

Hofman, J. Project plan "New reactor concepts for chemical degradation of trace organic compounds and disinfection", KWR Watercycle Research Institute, 19 May 2008 (project number B111661-001)

Huang X, Gao NY, Zhao JF, Zhu ZL, Bromate ions formation in UV/chlorination processes for bromide-containing solutions Huan Jing Ke Xue. 2007 Nov; 28(11):2526-32

Johnson, CJ; Singer, PC, Impact of a magnetic ion exchange resin on ozone demand and bromate formation during drinking water treatment, Water Research 38, 17, 3738-3750. 2004

Kruithof, IOA/EA$_3$G Conference Proceedings Moscow (1998)

Kurokawa, Y; Maekawa, A; Takahashi, M; Hayashi, Y (1990) Toxicity and carcinogenicity of potassium bromate – a new renal carcinogen, Environ. Health Persp., 87, 309-335.

Bernard Legube, Bernard Parinet, Karine Gelinet, Florence Berne, Jean-Philippe Croue, Modeling of bromate formation by ozonation of surface waters in drinking water treatment Water Research 38 (2004) 2185–2195

Qian Liu, Lynn M. Schurter, Charles E. Muller, Simone Aloisio, Joseph S. Francisco, and Dale W. Margerum, Kinetics and Mechanisms of Aqueous Ozone Reactions with Bromide, Sulfite, Hydrogen Sulfite, Iodide, and Nitrite Ions
Inorg. Chem. 2001, *40,* 4436-4442

Meunier, Laurence; Canonica, Silvio; Von Gunten, Urs, Implications of sequential use of UV and ozone for drinking water quality, Water Research Vol. 40, no. 9, pp. 1864-1876. 2006

Orlandini, E; Kruithof, J.C.; Van der Hoek, J.P.; Siebel, M.A.; Schippers, J.C.; Impact of ozonation on disinfection and formation of biodegradable organic matter and bromate; J. Watger SRT – Aqua Vol. 46 (1) 1997, 20-30

Siddiqui, Mohamed S., Amy, GL, McCollum LJ
Bromate destruction by UV irradiation and electric arc discharge
Ozone Science & Engineering Vol. 18 pp 271-290 1996

Pinkernell U, Von Gunten U, Bromate Minimization during Ozonation: Mechanistic Considerations, Environ. Sci. Technol. 2001, 35, 2525-2531

Rodriguez, A; Rosal, R.; Perdigòn-Melón, J.A.; Mezcua, M.; Agüera, A.; Hernando, M.D.; Letón, P.; Fernández-Alba, A.R.; García_Calvo, E.; Ozone-based technologies in water and wastewater treatment; Env. Chem. (2008), 5, part S/2; 127-175

Wert, Eric; Edwards-Brandt, Jessica; Singer, Philip; Budd, George, Evaluating Magnetic Ion Exchange Resin (MIEX) Pretreatment to Increase Ozone Disinfection and Reduce Bromate Formation Ozone: Science & Engineering (2005), 27(5), 371-379

Tao Zhang, Weipeng Chen, Jun Ma, Zhimin Qiang, Minimizing bromate formation with cerium dioxide during ozonation of bromide-containing water, water research 42 (2008) 3651 – 3658

I Experimental set-up Collivignarelli and Sorlini (2004)

Tests were performed in batch conditions on a laboratory-scale plant (Figure 14) (Q = 10 L/min) formed by a stainless steel feed tank (volume of 20 L), a pump, an in-line ozone injection followed by a static mixer and a low pressure mercury-vapor UV lamp. Ozone was generated by means of an "Ozonia Triogen Compact Ozone Generator" (Model TOGC2) with a capacity of 8 g O_3/h. Two UV lamps (model TR-65) were applied separately with different nominal wavelengths of maximum light intensity of 254 and 185 nm. Each lamp had about 80% of the radiation around the maximum wavelength and the intensity was about 25 W/m^2. The experimental conditions tested on water samples were: ozone concentrations = 0–15 mg/L; ozone contact time = 0–14 min; UV dose = 0–14,000 J/m^2. During each experimental test water was recirculated in the plant (the time required for one complete cycle in the system is 2 minutes) and after each recirculation water samples were collected at the UV chamber outlet at 2, 4, 6, 8, 10, 12 and 14 minutes from the beginning of the test. During each recirculation water received an ozone dose of about 0.3 mg/L and an UV dose of 2,700 J/m^2. Consequently, water samples have different applied ozone concentrations (C), ozone/water contact times (t) and UV doses. The UV irradiation time is the time of contact between water and UV light in the UV chamber and is 20 seconds for each recirculation.

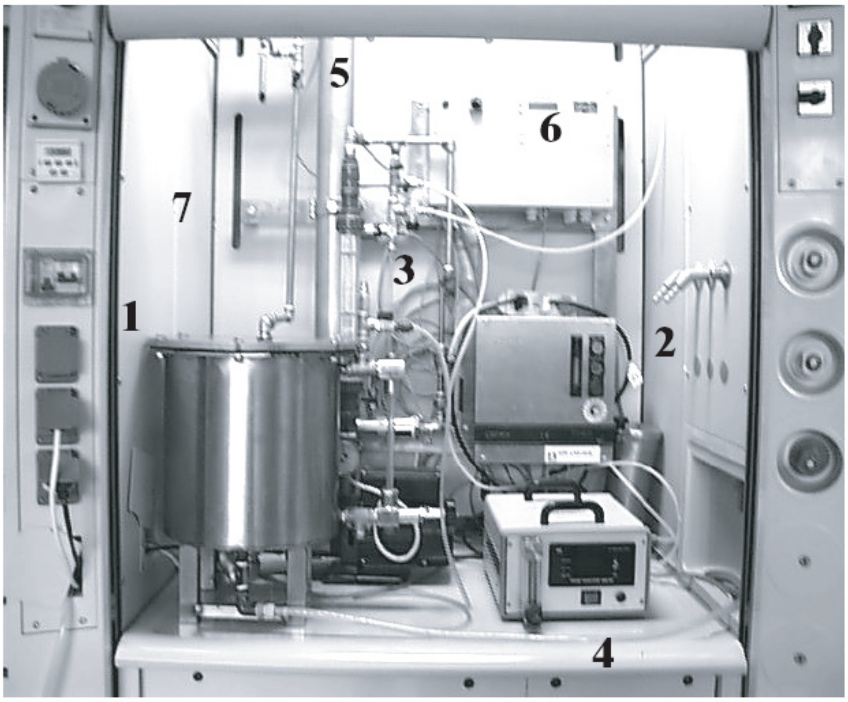


Figure 14: Experimental set-up; 1 steel feed tank; 2 ozone generator; 3 static mixer; 4 BMT 961; 5 UV lamp; 6 UV generator; 7 sampling point

II Results tests 1-4

Table 17 Ozone production and decay given by the Orbisphere sensor

Time (min)	Ozone concentration (mg/L) Orbisphere
-49	1,65
-44	6,88
-39	9,87
-34	11,49
-28	12,33
-24	13,11
-19	13,56
-14	13,75
0	13,5
5	12,54
10	11,97
15	11,45
20	10,91
26	10,45
30	10,07
35	9,64
40	9,51
45	9,16
50	8,75
55	8,41
60	8,14
65	7,86
70	7,59
75	7,28
80	7,02
85	6,76
90	6,53
95	6,31
100	6,07
105	5,77
110	5,61
115	5,48
120	5,29
151	4,24
160	4,03
170	3,76
180	3,51
210	2,89
242	2,32
270	1,94
310	1,46

Table 18: Ozone concentration given by Indigo test in the production and decay of ozone saturated Soestduinen water (24/03/09)

Time (min)	Ozone concentration given by the indigo test (mg/L)
-21.23	/
-11.23	/
-1.23	7.361
0	11.093
1	10.531
2.25	10.474
5	8.475
10	8.706
20	7.223
30	7.625
60	/
120	3.688

Table 19: Ozone production and decay in MilliQ water

Time (min)	Orbisphere ozone concentration (mg/L)
-55	0
-45	5,09
-40	6,85
-35	7,9
-30	8,52
-25	8,89
-20	9,21
-15	9,47
-10	9,62
-5	9,7
0	9,71
5	9,31
10	8,71
15	8,33
20	7,95
25	7,67
30	7,31
35	7,01
40	6,89
45	6,52
50	6,19
55	5,81
65	5,47
70	5,22
75	5,16
80	5,04
85	4,88
90	4,7
95	4,43
100	3,88
105	3,78
110	3,64
115	3,22
120	3,09
125	2,87
130	2,65
135	2,39
140	2,23
145	2,09
150	1,78
155	1,58
160	1,537
165	1,47
170	1,243
175	1,087
180	1
225	0,343
230	0,304
235	0,259
246	0,194
255	0,157
270	0,086

All ozone reactions were carried out in a solution containing 2 mg/L. However, the ozone concentrations also were measured by means of a sensor, and corrected for the dilution of the sample. This resulted in the data as shown below in tables 20 and 21.

Table 20: Bromate formation after ozonation and UV irradiation; starting bromide concentration: 170 µg/l (143 µg/l was added).

Initial Ozone dose (mg/l)	UV dose (mJ/cm^2)	pH after reaction	Contact time (s)*	Sample time (s)**	Bromate (µg/l)
0	0	7	0	0	<0.5
1.88	0	7	30	0	28
1.93	300	7	0	0	46
1.81	600	7	0	10	56
2.16	600	7	0	30	55
/	600	7	0	0	51
1.87	600	7	30	0	69
2.14	0	4-5	30	0	
2.02	300	4-5	0	0	
2.02	600	4-5	0	0	
2.11	600	7	0	10	45
2.08	600	4-5	0	30	54
2.06	600	4-5	30	0	

*: time between the ozone addition and the start of UV irradiation

**: time before quenching after UV irradiation

Table 21: Ozone concentration after ozonation and UV irradiation; starting bromide concentration: 143 µg/l.

Initial Ozone dose (mg/L)	UV dose (mJ/cm^2)	Contact time (s)*	Sample time (s)**	Measured Ozone dose after test (mg/L)
0	0	0	0	0.010
2.16	0	30	0	1.237
/	300	0	0	0.055
/	600	0	10	0.068
2.17	600	0	30	0.020
/	600	0	0	0.029
2.10	600	30	0	0.052

*: time between the ozone addition and the start of UV irradiation

**: time before quenching after UV irradiation

Postbus 1072 3430 BB Nieuwegein T 030 606 95 11 F 030 606 11 65 E info@kwrwater.nl I www.kwrwater.nl