

Parameters Affecting the Formation of Bromate Ion During Ozonation

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Abstract

Batch type ozone experiments conducted on aquatic humic substances solutions spiked with bromide ion were developed to evaluate the importance of various parameters that may affect the formation of bromate ion during ozonation. The nature of the NOM, the alkalinity, the bromide ion content and the presence of ammonia were found to significantly affect the bromate ion production. Temperature and pH can be considered as minor factors. The ozonation of a clarified surface water using a continuous flow ozone contactor have shown that the addition of a low quantity of ammonia (0.05 to 0.1 mg/L NH_4^+) appeared to be an interesting option for controlling the bromate formation. On the contrary, the addition of hydrogen peroxide may enhance or reduce the bromate ion production, depending on the applied hydrogen peroxide/ozone ratio.

Introduction

The use of ozone as an alternative oxidant for drinking water production was developed for controlling THM formation, taste and odor problems, microorganisms contamination, while peroxone (a combination of hydrogen peroxide and ozone) is generally applied for removal of micropollutants. In spite of its efficiency for the control of various water quality parameters, the use of ozone nowadays is confronted by the bromate ion problem.

As a large number of studies have shown (Krasner et al., 1993; Kruithof and Meijers, 1993; Legube et al., 1993-1, 1995), the ozonation of natural waters containing bromide ion may produce bromate ion, a brominated by-product that was found to be possibly carcinogenic (Kurokawa et al., 1986, 1990, Kurata et al., 1992). Bench-scale and pilot-plant experiments have demonstrated that the formation of bromate ion depends on many parameters, such as bromide ion concentration, DOC content, applied ozone dose or Ct criteria, ozonation mode (addition of hydrogen peroxide), pH, presence of ammonia. (Haag and Hoigné, 1983; Siddiqui and Amy, 1993; Legube et al., 1993-2; Koudjonou et al., 1994; von Gunten and Hoigné, 1994).

Despite the important research activity that already has been developed in this specific field, more information is needed to control the formation of bromate ion during ozonation of natural waters. The objective of our work was first to evaluate the influence of various parameters on bromate ion production during bench-scale ozonation of aquatic humic substances. The second phase of this work was focused on the effect of ammonia using pilot-scale experiments conducted on a clarified surface water.

Experimental Methods And Procedures

The ozone experiments were performed using two types of reactor, batch and continuous flow contactors.

EXPERIMENTAL CONDITIONS

Batch Reactor Experiments

Batch type experiments primarily were carried out with 125 mL flasks (BOD vessel) for aquatic humic substances isolated using an XAD resin procedure (Croué et al., 1993). A few experiments also were conducted with tripeptide solutions (tyrosine-glycine-glycine). Solutions were prepared with high purity water (Milli-Q water) buffered with phosphate ($I = 10^{-2}$ or 10^{-3} M). Most of the experiments were conducted using the following conditions: 2.5 mg/L of carbon, 200 $\mu\text{g/L}$ of bromide ion (sodium bromide), pH 6.4 or 8.4, temperature 20°C.

Ozone stock solutions were prepared by bubbling an ozone-oxygen mixture through high purity water until equilibrium was reached. Once aqueous ozone concentration was established, adequate volumes of ozonated water were added quickly to humic substance solutions to obtain the desired experimental conditions. After a given reaction time (a few minutes to one day), a few milliliters of the solution were sampled for residual ozone determination while the rest of the solution was quenched using a slight excess of indigo carmine prior bromate analysis. A reaction flask was used for each corresponding reaction time studied.

Continuous Flow Ozone Contactor

Pilot-scale experiments were conducted with a clarified water sampled at the Poitiers (France) water treatment plant using a two-liter open column (without recirculation) 1.5-m high in which ozone gas and aqueous solution were both added continuously at the bottom (cocurrent mode). The main characteristics of the studied water were:

pH = 7.9;
Dissolved organic carbon (DOC) = 2.5 mg C/L
Bromide ion (Br^-) = 0.06 mg/L
Bicarbonate ion (HCO_3^-) = 227 mg/L
Nitrate ion (NO_3^-) = 29 mg/L
Chloride ion (Cl^-) = 34 mg/L
Sulfate ion (SO_4^{2-}) = 18 mg/L

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Ozone was generated from high purity oxygen or air in a Trailigaz ozone generator equipped with a massic flow controller (Brooks, 5850 E) and a continuous flow ozone analyzer (AFX, model H1). The experimental conditions were the following:

- Gas production and flow : 10 to 80 g/m³ at 8 L/h
- Aqueous flow : 10 to 20 L/h

Using these conditions, the residence time of the treated water in the column varied from 6 to 12 minutes, depending on the experiment. Samples were collected in duplicate at the top of the column at various times until equilibrium was reached. One set of samples was purged immediately with pure nitrogen for a few minutes to remove residual ozone in solution in order to stop the reaction prior to bromate ion analysis. The second set was used for the determination of residual ozone in solution.

In the combined H₂O₂/O₃ system, hydrogen peroxide was injected in the water circuit upstream of the ozone contactor.

The Ct value for a given experiment was determined after stabilization of the solution (when the residual ozone in solution become constant) by simply multiplying the residence time by the residual ozone concentration determined in the effluent.

ANALYTICAL METHODS

Bromate and bromide ions were analyzed by ion chromatography (DIONEX DX 300) equipped with a pulsed electrochemical detector (PED), a gradient pump and an anion micromembrane suppressor. The detection was carried out in the conductivity mode. Bromate ion was analyzed by the use of AG-9 /AS-9 columns with a boric acid/sodium hydroxide mobile phase, while bromide ion was analyzed using AG-IVAS-12 columns with a bicarbonate/carbonate mobile phase. The estimated detection limits were 2 µg/L for bromate ion and 30 µg/L for bromide ion.

Ozone in the liquid phase was analyzed by the indigo trisulfonate method (Bader and Hoigné, 1982).

Results And Discussion

CONDITIONS OF BROMATE ION FORMATION DURING BATCH OZONATION OF AQUATIC HUMIC SUBSTANCES IN THE PRESENCE OF BROMIDE ION

This section relates to results obtained in the batch reactor. The literature mentioned that the formation of bromate ion depends on various parameters, such as the nature of the water and the ozone mode (Krasner et al., 1993). When considering water characteristics, two different group of parameters can be distinguished. The first group corresponds to factors that can not be modified immediately before ozone treatment -- which are DOC content, temperature and bromide ion concentration. The second group is related to specific parameters that can be "more easily" controlled before ozonation, such as pH, alkalinity and ammonia concentration.

Influence Of DOC, Temperature And Bromide Ion

The formation of bromate ion as a function of DOC content, temperature and bromide ion concentration are shown in Figures 1 to 3. Note that for these specific experiments, a one day ozone contact time was chosen, results that could be then interpreted as potential formation of bromate ion.

Using a fixed applied ozone dose (5 mg O₃/L), increasing the DOC content of the solution led to the reduction in bromate ion formation. Figure 1-a also indicates that the nature of the organics plays an important role on bromate ion production; for the same DOC level a tripeptide has a more significant impact than hydrophilic acid or a fulvic acid. In Figure 1-b, the data obtained with the mixed solution of fulvic acid-hydrophilic acid-tripeptide, 60%-30%-10%, respectively, (more representative of natural surface waters) were plotted as bromate ion formation versus ozone dose expressed in mg O₃ applied per mg of carbon. A linear curve can be drawn showing that above a certain ozone dose threshold the production of bromate ion is proportional to the applied ozone dose. The following model can be proposed:

$$\text{BrO}_3^- (\mu\text{g/L}) = -0.4 + [11.56 \cdot (\text{O}_3/\text{DOC})] \text{ at pH } 6.4 \text{ with } R^2 = 0.997$$

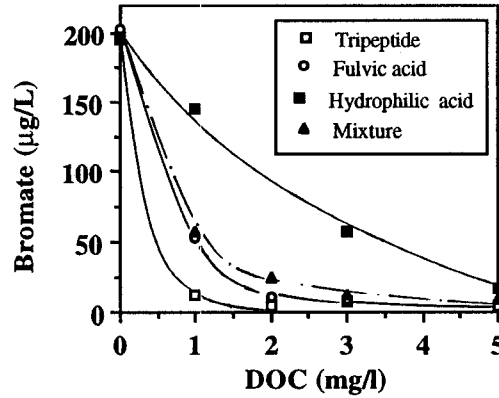
Working on different water sources, Amy et al. (1993) have seen an ozone dose threshold of 0.5 mg O₃/mg C. Based on a bromate survey conducted in different European water utilities, Legube et al. (1993-1) proposed a similar value equal to 0.7 mg O₃/mg C.

Figure 2 shows the effect of the temperature, based on the comparison of a given value with the one obtained at 20°C. As a general trend, Figure 2-a shows that the higher the water temperature, the higher the bromate ion formation. These results confirm the data of Amy et al. (1993) and Kruithof and Meijers (1993). At pH 8.4 and under our experimental conditions (2.5 mg C/L as fulvic acid, 200 µg/L of Br⁻, 2.5 mg O₃/mg C), one can observe that the bromate ion concentration obtained at 20°C is multiplied or divided by a factor of 1.1 when the temperature is increased or reduced by 10°C, respectively. Variations are less pronounced at pH 6.4. As shown in Figure 2-b, the impact of temperature can be explained by the change of the dissociation coefficient $K_{\text{H}_{\text{OBr}}/\text{BrO}^-}$ (according to the Arrhenius law) which leads to an increase in the BrO⁻/HOBr ratio (increase of hypobromite ion concentration in solution) and consequently to an increase of bromate ion formation (Haag and Hoigné, 1983). Note that the decrease of ozone stability with increasing temperature appeared to be a minor factor.

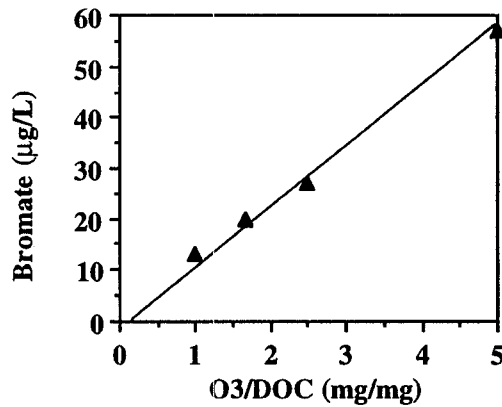
The bromide ion level also was found to be a critical parameter. Figure 3-a shows the effect of bromide ion level on the kinetic formation of bromate ion. For a given bromide ion content (especially for 200 and 500 µg/L), the data show a rapid formation of bromate ion in the first 10 minutes, followed by a slight increase of the concentration while increasing the reaction time. The ozone consumption follows the same trend with a persistence of residual ozone after 30 minutes (not presented) that can explain the higher level of bromate ion analyzed in the samples stored for 24 hours: 6, 32 and 80 µg BrO₃⁻/L for 50, 200 and 500 µg Br⁻/L, respectively. For two different pH levels and whatever the contact time, several minutes to one day (Figure 3-b plotted for a one day contact time), a linear correlation was established between bromate ion formation and bromide ion concentration, showing a straight line which seems to cross the x-axis near the origin (a few µg BrO₃⁻/L). Based on data collected from different water utilities, Krasner et al.

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(1993) mentioned that for five of the seven cases for which the bromide ion level was below 0.06 mg/L, bromate ion was not detected (the detection limit proposed at that time was 10 µg/L). Amy et al. (1993) also suggested that there is no bromide ion threshold level, an observation which seems to be more in accordance with our results.



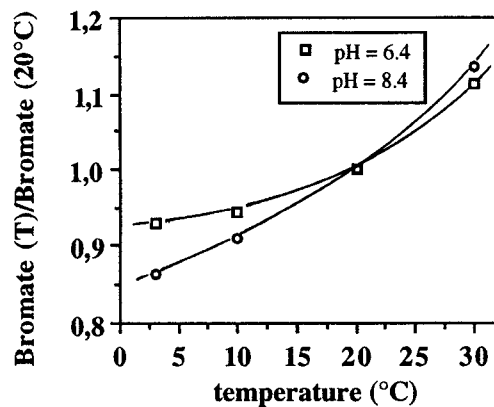
1-a: Bromate ion formation versus DOC content



1-b: Bromate ion formation versus applied ozone dose

Figure 1. Effect of DOC on bromate ion formation. (*Experimental conditions:* pH = 6.4 - phosphate buffer; initial bromide ion: 200 µg/L; ozone: 5 mg/L; analyses conducted after complete ozone consumption; temperature ≈ 20°C; mixture: 60%-30%-10% of fulvic acid, hydrophilic acid and tripeptide, respectively).

Results discussed in this section indicate that the production of bromate ion increases with increasing O₃/DOC ratio. The risk of bromate ion formation could be slightly more important during the summer time because of the increase of water temperature. The higher the bromide level, the higher is the possible formation of bromate ion.



2-a: Bromate ion formation versus temperature

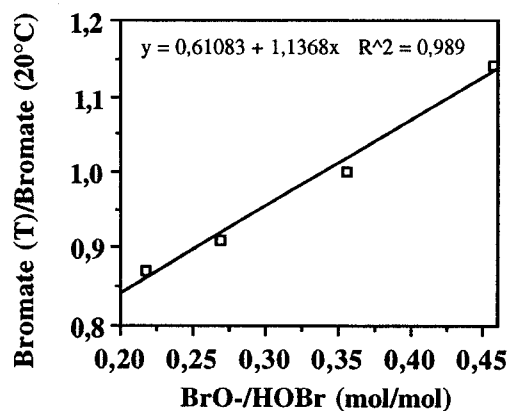
2-b: Bromate ion formation versus BrO⁻/HOBr ratio at pH = 8.4

Figure 2. Effect of temperature on bromate ion formation. (*Experimental conditions:* phosphate buffer; DOC: 2 mg/L aquatic fulvic acid; ozone: 5 mg/L; initial bromide ion: 200 µg/L; analyses conducted after complete ozone consumption).

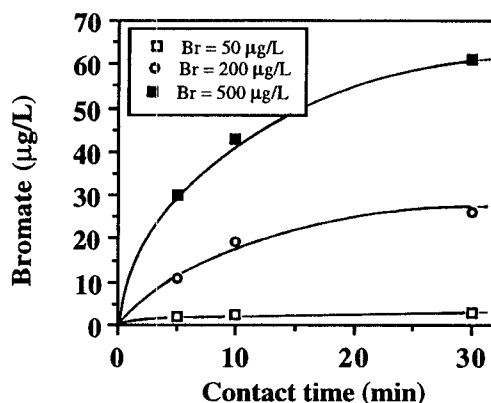
Effect Of pH, Ammonia And Alkalinity

Experiments were focused on pH, ammonia and alkalinity because the first two parameters are mentioned in the literature as possible bromate ion control strategies, while increase in alkalinity prior to ozonation (reminerzalization step) is a potential alternative that can improve the removal of THM precursors (Reckhow et al., 1986; Legube et al., 1989).

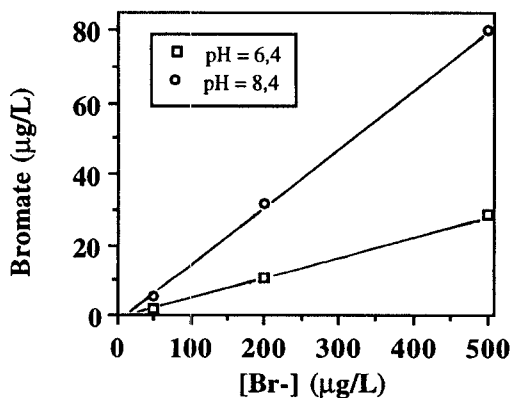
Figure 4 shows the formation of bromate ion as a function of reaction time during ozonation of a fulvic acid solution buffered at pH 6.4 or pH 8.4. Whatever the reaction time, the production of bromate ion was less important at pH 6.4 than at pH 8.4, as

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discussed in other works. However, one can see that under our experimental conditions and for contact times below 10 minutes (which may correspond to practical uses), no significant reduction of bromate ion was observed when lowering the pH from 8.4 to 6.4. The control of ozonation pH did not appear as an interesting strategy for the limitation of bromate ion production as proposed by Krasner et al. (1993) or Fielding and Hutchison (1993). Nevertheless, the reduction of alkalinity during acidification of natural waters could be partially responsible for this discordance, as we will discuss in the following paragraph.



3-a: Effect of bromide content on the kinetic formation of bromate ion at pH 8.4



3-b: Bromate ion formation versus bromide ion concentration (analyses conducted after complete ozone consumption)

Figure 3. Effect of bromide ion content on bromate ion formation (*Experimental conditions*: Temperature: $\approx 20^\circ\text{C}$; ozone: 5 mg/L; DOC: 2 mg/L aquatic fulvic acid).

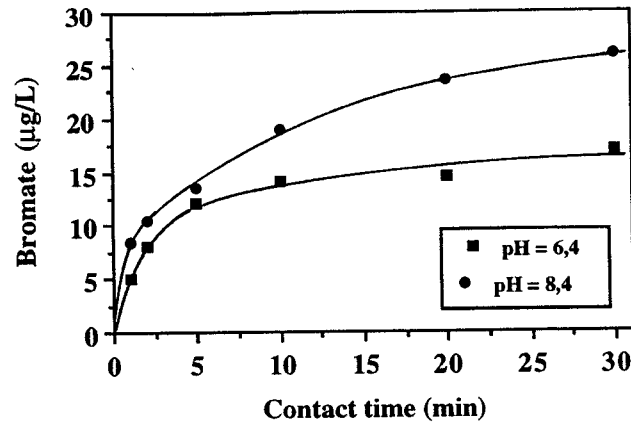


Figure 4. Kinetic formation of bromate ion at pH 6.4 and 8.4. (*Experimental conditions*: Temperature: $\approx 20^{\circ}\text{C}$; ozone: 5 mg/L; DOC: 2 mg/L aquatic fulvic acid; initial bromide ion: 200 $\mu\text{g/L}$).

The stability of molecular ozone can be optimized by the use of a remineralization step (increasing alkalinity) prior to ozonation, a technique that was found to be successful for the removal of manganese or THM precursors. Figure 5 shows that for a similar ozone dose, this procedure will favor the production of bromate ion, an observation that is more visible at pH 8.4 than at 6.4. The scavenging effect of bicarbonate ion species is, in fact, more efficient at pH 8.4 because of the higher instability of ozone to produce free radicals.

Haag and Hoigné (1983) indicated that the presence of ammonia may inhibit the formation of bromate ion by preferentially reacting with hypobromous acid and hypobromite ion to form bromamines. Results presented in Figure 6 are in accordance with that proposed mechanism. A dramatic reduction in production of bromate ion (from about 20 $\mu\text{g/L}$ to less than 10 $\mu\text{g/L}$ after 10 minutes) was observed by adding a small quantity of ammonia 0.2 mg/L as N-NH_4^+ . The use of a higher concentration of ammonia (0.5 mg/L as N-NH_4^+ , bromate ion formation after 20 minutes: 9 $\mu\text{g/L}$) did not improve these results significantly.

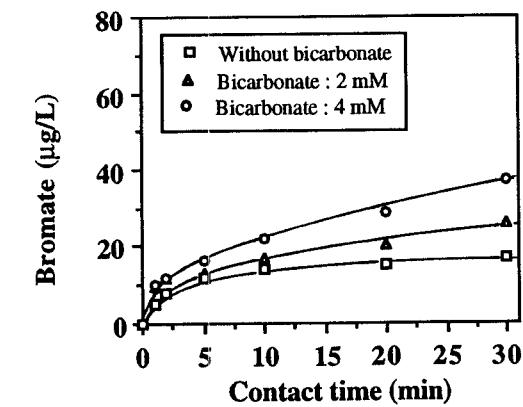
OZONATION OF A NATURAL CLARIFIED WATER: EFFECT OF THE ADDITION OF AMMONIA ON BROMATE ION FORMATION

Batch experiments discussed in the previous section and presented elsewhere (Koudjonou et al., 1994) indicated that the presence of ammonia and the addition of hydrogen peroxide are decisive control factors. In order to develop our research activity on these two important parameters, experiments were carried out on a natural clarified water (sampled at the Poitiers water treatment plant) using a continuous flow ozone contactor with a cocurrent mode.

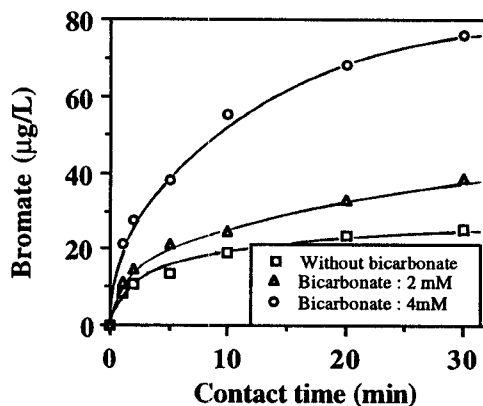
Using different Ct values, the production of bromate ion was measured in the presence or absence of ammonia and in the presence or absence of hydrogen peroxide. The determination of bromate ion level for a given Ct value was obtained following a series of residual

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aqueous ozone and bromate ion analyses conducted on five to six successive aliquots taken during the course of the reaction. Each manipulation was run for about an hour. Recirculation of the aqueous flow by use of a complementary pump from the top to the bottom of the contactor (recirculation flow rate equal to five times the feeding flow rate) had no significant effect on the ozone transfer then on the Ct value and the bromate ion production for a given experimental condition (gas flow rate, concentration of ozone in the gas). The use of a cocurrent mode without recirculation of the aqueous flow then was found to be satisfactory to obtain an homogeneous solution in the contactor.



pH = 6.4



pH = 8.4

Figure 5. Impact of alkalinity on the kinetic formation of bromate ion. *Experimental conditions:* Temperature: $\approx 20^{\circ}\text{C}$; ozone: 5 mg/L; DOC: 2 mg/L aquatic fulvic acid; initial bromide ion: 200 $\mu\text{g/L}$.

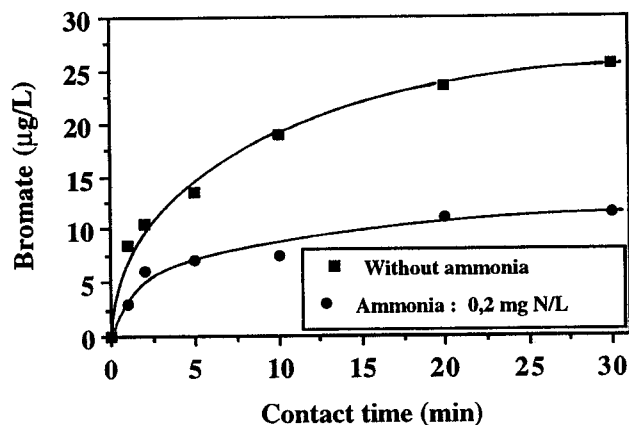


Figure 6. Effect of ammonia on the kinetic formation of bromate ion (*Experimental conditions*: Temperature: $\approx 20^{\circ}\text{C}$; pH = 8,4; ozone: 5 mg/L; DOC: 2 mg/L aquatic fulvic acid; initial bromide ion: 200 $\mu\text{g/L}$).

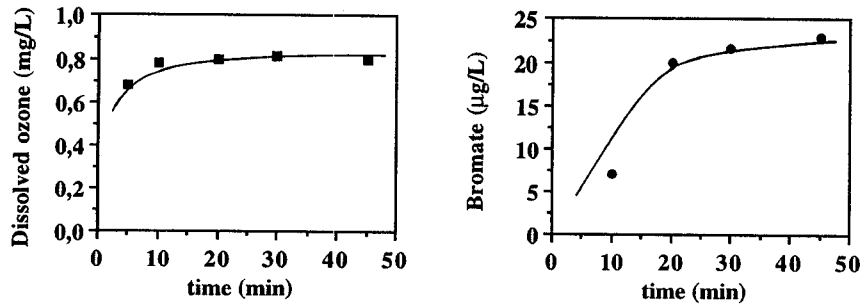
Results obtained from two different experiments are presented in Figure 7. The plotted data show a progressive increase of the two parameters until constant values are obtained. The reaction time needed to reach equilibrium was logically dependent on the chosen aqueous flow and approximately equal to the hydraulic residence time. As discussed in the experimental section, desired Ct criteria were assured by changing the aqueous flow rate or the ozone production while the gas flow rate was maintained constant. Figure 7-a indicates that for a Ct value equal to 8 (0.8 mg $\text{O}_3/\text{L} \times 10$ minutes), the formation of bromate ion for the studied water was evaluated as 22 - 23 $\mu\text{g/L}$, while Figure 7-b shows a bromate ion production of 80 $\mu\text{g/L}$ for a Ct value equal to 27.5 (2.5 mg $\text{O}_3/\text{L} \times 11$ minutes).

Bromate Ion Formation As A Function Of The Ct Criteria

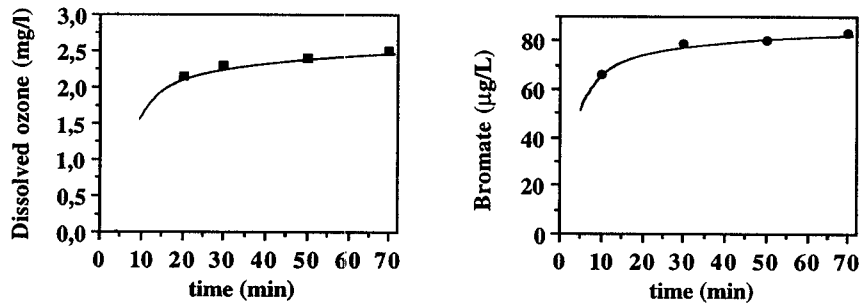
Figure 8 shows bromate ion formation as a function of the Ct value without addition of ammonia nor hydrogen peroxide. Results plotted in Figure 8-a were obtained with ozone generated from high purity oxygen. Figure 8-b compares the results obtained with ozone generated from high purity oxygen and from air.

Figure 8-a shows a linear relationship between the two parameters: the higher the Ct value, the higher the concentration of bromate ion. This observation is in accordance with data published by Krasner et al. (1993) and von Gunten and Hoigné (1994). In the following sections, the straight line presented in Figure 8-a, which corresponds to the relation $\text{BrO}_3^- = f(\text{Ct})$ which characterized the water will be used as a reference. The impact of modification of the experimental conditions, addition of ammonia, addition of hydrogen peroxide, or change in nature of the ozone-containing gas (generation with air or oxygen) will be evaluated as follows:

- parameters that will lead to data plotted above this straight line whatever the Ct value will be considered as parameters that favor the production of bromate ion



7-a: Ct = 8 (Contact time: 10 minutes; residual ozone in solution: 0.8 mg/L)
(Aqueous flow rate: 12 L/h; ozone dose: 90 mg O₃/h)

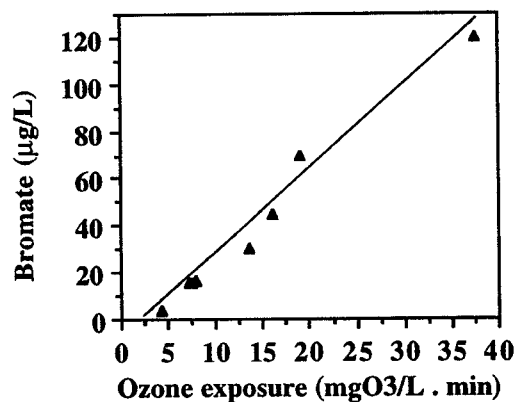


7-b: Ct = 27.5 (Contact time: 11 minutes; residual ozone in solution: 2.5 mg/L)
(Aqueous flow rate: 10.9 L/h; ozone dose: 270 mg O₃/h)

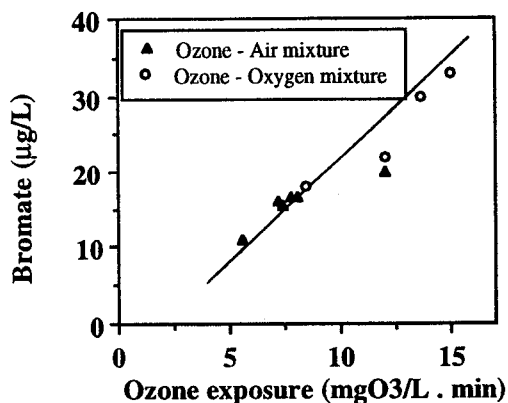
Figure 7. Evolution of residual aqueous ozone and bromate ion concentration during pilot scale ozonation of a sand-filtered water (cocurrent mode without recirculation). *Experimental conditions:* Temperature: $\approx 20^{\circ}\text{C}$; DOC: 2.5 mg/L; initial bromide ion $\approx 60 \mu\text{g/L}$; pH = 7.9.

- parameters that will lead to data plotted below this straight line whatever the Ct value will be considered as parameters that (partially) inhibit the production of bromate ion
- parameters that will lead to data plotted on the straight line whatever the Ct value will be defined as parameters that have no effect on bromate ion production.

Based on this interpretation method, Figure 8-b shows that the nature of the ozone-containing gas, ozone generated with air or oxygen, has no significant effect on the reaction mechanism of bromate ion formation (all points located on the same straight line).



8-a: Ozone generated with oxygen



8-b: Importance of the nature of the ozone-containing gas

Figure 8. Bromate ion formation as a function of the Ct criteria (*Experimental conditions*: Temperature: $\approx 20^{\circ}\text{C}$; DOC: 2.5 mg/L; initial bromide ion $\approx 60\ \mu\text{g/L}$; pH = 7.9).

Effect Of The Addition Of Ammonia

If Krasner et al. (1993) underlined that the addition of ammonia did not appear to be a control option for bromate ion, von Gunten and Hoigné (1994) noted that in the presence of organic OH radical scavengers, the presence of ammonium ion results in a lag time for bromate ion formation.

Results in Figure 9-a show that the addition of 0.05 mg/L of ammonia (expressed in mg N/L), which represents a $\text{Br}^-/\text{N-NH}_4^+$ molar ratio of 0.2, led to a decrease of bromate ion formation, except for a very low Ct condition (bromate ion concentrations were near the detection limit for the Ct value of 4 mg/L·min). Nevertheless, increasing the concentration

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of ammonia from 0.05 to 0.1 mg/L (as N) did not improve significantly the reduction of bromate ion formation.

The linear relationship between CT and bromate ion seems to be still verified in the presence of ammonia, however the slope is reduced. This underlined that the higher the ozone dose, the higher the impact of ammonia. Considering the lag time hypothesis described by von Gunten and Hoigné (1994), one would better expect that increasing CT would reduce the effect of ammonia. The difference observed between our results and those published by these authors might be related to the ozonation procedure. Von Gunten and Hoigné (1994) conducted their experiments in the presence of a radical scavenger, conditions which favor molecular ozone type reactions, while our experiments were carried without the addition of scavenger, a condition that allows both radical and molecular ozonation modes.

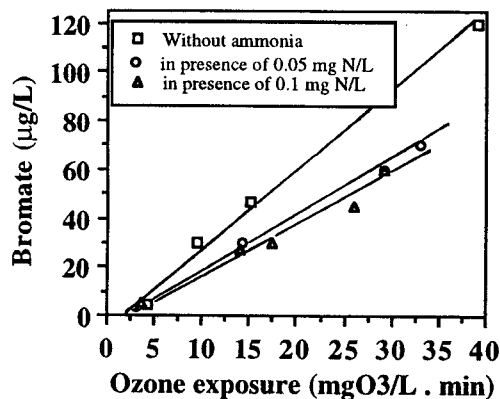
Figure 9-b) shows the formation of bromate ion as a function of ammonia concentration for a Ct value of 30 mg O₃/L.min. The data confirmed the large impact of ammonia for concentrations up to 0.05 mg N/L (32% reduction of bromate ion production), while doubling the ammonia concentration from 0.05 to 0.1 mg N/L slightly improve its efficiency (38% reduction). These results indicate that the reduction of bromate ion formation is not directly proportional to the amount of ammonia added in the water sample. Increasing the concentration of ammonia in solution increases the kinetics of the production of bromamines and consequently should accelerate the degradation of bromamines into bromide ion. The kinetics of oxidation of bromamines by ozone or radical species to produce nitrate and bromide ions might be a decisive reaction step for the role of ammonia in the bromate ion formation mechanism. More data are needed to propose a definitive explanation.

Effect Of The Addition Of Hydrogen Peroxide

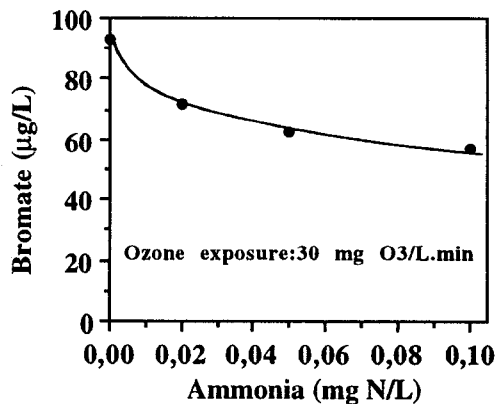
Data from ozonation experiments conducted in the presence and in the absence of hydrogen peroxide are compared in Figure 10. The interpretation of our results based on the determination of the applied Ct value confirmed, as mentioned by Krasner et al. (1993) and von Gunten and Hoigné (1994), that the addition of hydrogen peroxide increased the formation of bromate ion (Figure 10-a). The situation of the data points on Figure 10-a related to the hydrogen peroxide treatments conducted with R = 0.1; 0.2 and 0.4 (open circles) shows that the higher the H₂O₂/O₃ molar ratio, the higher the impact of the addition of H₂O₂ for a given Ct value. Increasing the H₂O₂/O₃ molar ratio from 0.1 to 0.4 led to an increase of the production of OH radicals that enhance the OH radical mechanism.

Because the experiments were carried out using a similar applied ozone dose, the addition of hydrogen peroxide led to the decrease of residual ozone in solution (without H₂O₂, residual ozone: 2.6 mg (O₃/L; R = 0.1, 0.2 and 0.4, residual ozone: 1.5, 1.0, 0.1 mg O₃/L, respectively) and, consequently, to reduction of the CT value. The results of Figure 10-a are plotted in Figure 10-b, where the x-axis corresponds to H₂O₂/O₃ (R) molar ratio. This new figure shows that whatever the reduction of the Ct value, the addition of hydrogen peroxide may increase the formation of bromate ion depending on the applied H₂O₂/O₃ molar ratio. For H₂O₂/O₃ molar ratios below 0.3 (estimated value) the formation of bromate ion was found to increase, with a maximum bromate ion concentration

obtained for $0.2 < H_2O_2/O_3 < 0.3$. A similar value could be deduced from the results published by von Gunten and Hoigné (1994).



9-a: Effect of the addition of ammonia as a function of the Ct value.



9-b: Limitation of the impact of ammonia on bromate ion formation.

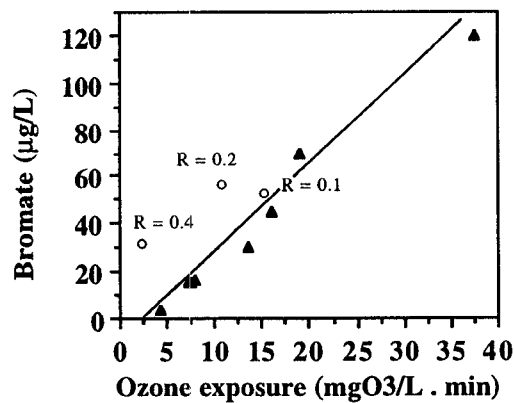
Figure 9. Impact of the addition of ammonia on the formation of bromate ion (*Experimental conditions*: Temperature: $\approx 20^\circ\text{C}$; DOC: 2.5 mg/L; initial bromide ion $\approx 60 \mu\text{g/L}$; pH = 7.9).

Summary And Conclusions

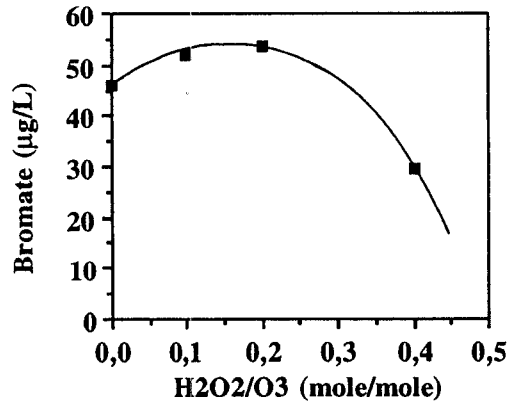
The objective of this work was to evaluate the impact of various parameters on the formation of bromate ion during ozonation. The effects of pH, bromide ion concentration, ozone dose, bicarbonate ion and ammonia were studied first using batch ozonation carried out on isolated aquatic NOM solutions. Linear relationships were established between the

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formation of bromate ion and the ozone/DOC ratio, or the formation of bromate ion and the initial concentration of bromide ion. Increasing temperature from a few degrees to 30°C was found to improve the production of bromate ion slightly, while changing pH from 6.4 to 8.4 had a minor effect using a 10 minute contact time. In the presence of high concentrations of bicarbonate ions, higher concentrations of bromate ion were obtained because of the increase of ozone stability. The effect of alkalinity was more pronounced at pH 8.4 than at pH 6.4. The addition of ammonia was considered as one of the most interesting control strategies for bromate ion production.



10-a: Bromate ion concentration versus ozone exposure (open circle: peroxone treatment with $R = \text{H}_2\text{O}_2/\text{O}_3$; black triangle: O_3 only)



10-b: Bromate ion concentration versus $\text{H}_2\text{O}_2/\text{O}_3$ molar ratio

Figure 10. Bromate ion formation during peroxone treatment: Importance of the hydrogen peroxide/ozone molar ratio (*Experimental conditions*: Temperature: $\approx 20^\circ\text{C}$; DOC: 2.5 mg/L; initial bromide ion $\approx 60 \mu\text{g/L}$; pH = 7.9).

Pilot-scale experiments (continuous flow ozone contactor) conducted with a treated water (sampled after clarification) have shown that the addition of 0.05 mg/L NNH_4^+ can lead to a significant reduction of bromate ion formation whatever the Ct value. Using a Ct value of 30, the bromate ion concentration was reduced from 92 $\mu\text{g/L}$ to about 65 $\mu\text{g/L}$ (30% reduction). However, only 38% reduction was observed in the presence of 0.1 mg/L NNH_4^+ with the same Ct value. This result indicates that the impact of ammonia is not proportional to the quantity added. The role of ammonia in the bromate ion formation mechanism remains unclear. Using the same equipment, the formation of bromate ion was found to be more important after peroxone treatment (with $\text{H}_2\text{O}_2/\text{O}_3$ molar ratios below 0.4) than after ozonation for similar Ct values. For a given applied ozone dose, the addition of hydrogen peroxide enhanced the production of bromate ion for $\text{H}_2\text{O}_2/\text{O}_3$ molar ratios up to 0.2 - 0.3, while bromate ion formation was lowered above this value.

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Key Words

Ozone; Bromate Ion Formation; Aquatic Humic Substances; Bromide Ion; Natural Organic Matter; Ammonia; Hydrogen Peroxide; Hydrogen Peroxide/Ozone Ratio; Ct Values;

Résumé

Ce travail, conduit avec des solutions de substances humiques dopées en ions bromures, a eu pour but d'évaluer l'importance des principaux paramètres pouvant intervenir dans le mécanisme de formation des ions bromate. La nature de la matière organique, la teneur en ions bromure, la présence d'espèces carbonatées ou d'ammoniac se vent révélées comme les paramètres importants de la réaction. En revanche, la variation du pH ou de la température (dans des limites cohérentes avec le traitement de l'eau) n'a qu'un impact mineur sur la formation de bromates. L'ozonation d'une eau clarifiée prélevée sur un site de production. Effectuée avec un réacteur ouvert (colonne à bulles) alimenté en continu a montré que la production de bromates est directement proportionnelle au critère Ct (concentration résiduelle en ozone dissous, C; temps de contact, t) et indépendante de la nature du gaz ozoné injecté (gaz ozoné produit à partir d'air ou d'oxygène). La présence

d'ammoniac (0,05 à 0,1 mg/L de N_{NH_4} permet de réduire la production de bromates même pour des valeurs de Ct élevées. À Ct constant l'addition de peroxyde d'hydrogène favorise la formation de bromates. En revanche, à taux d'ozone appliqué constant (mg O_3 /mg C) celle-ci n'est accentuée que pour des ratios H_2O_2/O_3 inférieurs à 0,25 - 0,3 mole/mole.

Zusammenfassung

Batchversuche wurden durchgeführt mit wässrigen Huminstofflösungen, denen Bromid zugesetzt wurde, um den Einfluß unterschiedlicher Parameter auf die Bildung von Bromat bei der Ozonung zu untersuchen. Die Art der NOM (natural organic matter), die Alkalinität, die Bromidkonzentration und die Anwesenheit von Ammonium hatten einen maßgeblichen Einfluß auf die Bildung von Bromat. Temperatur und pH hatten einen geringeren Einfluß. Die Ozonungsversuche von vorgeklärtem Oberflächenwasser in einem kontinuierlich durchströmten Ozonkontaktbecken haben gezeigt, daß der Zusatz von geringen Ammoniummengen (0,05 bis 0,1 mg NH_4^+/L) eine interessante Variante darstellen, um die Bromatbildung unter Kontrolle zu halten. Im Gegensatz dazu kann die Zugabe von Wasserstoffperoxid die Bromatbildung vergrößern oder verringern, je nachdem welches Wasserstoffperoxid/Ozonverhältnis gewählt wird.