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# **The Formation of Bromate during Drinking Water Disinfection (DWE 7101)**

*Final Report to the Department of the Environment*



# **THE FORMATION OF BROMATE DURING DRINKING WATER DISINFECTION (DWE 7101)**

Final Report to the Department of the Environment

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## **PREFACE**

The formation of bromate from the ozonation of raw waters containing bromide is of concern since it is a suspected carcinogen. It is also possible that bromate could be present in chlorinated waters (via the use of hypochlorite for disinfection). Few data are available on the formation and occurrence of bromate in UK drinking waters.

The Department of the Environment placed a contract with WRc in November 1992 to review the current knowledge concerning bromate formation during drinking water disinfection, to assess possible control options from recent literature findings and to carry out a limited survey of bromide and bromate concentrations in UK treated waters.

This final report presents the work undertaken.

## SUMMARY

An increase in interest in the use of ozone in drinking water treatment has led to concern over the formation of ozonation by-products. Of particular concern is bromate which can be formed from the ozonation of raw waters containing bromide. In addition it is possible that bromate could be present in chlorinated waters (via the use of hypochlorite for disinfection).

Bromate has been classified by the International Agency for Research on Cancer (IARC) as having sufficient evidence of carcinogenicity in laboratory animals. The World Health Organization have set a provisional guideline value of  $25 \mu\text{g l}^{-1}$  in their forthcoming revision of the drinking water guidelines. This value was set to take account of analytical problems associated with measuring bromate - the value obtained from low dose extrapolation models is  $3 \mu\text{g l}^{-1}$  (at an upper 95% confidence limit risk of 1 in  $10^5$  of the population). There are few data available on the formation and occurrence of bromate in UK waters. Consequently, a review of current knowledge concerning bromate formation during drinking water disinfection was undertaken. Possible control options for minimising bromate formation were assessed from recent literature findings. In addition, a limited survey of bromide and bromate concentrations in UK treated waters (both chlorinated and ozonated) was carried out.

The literature review revealed that bromate could readily be formed from the ozonation of waters containing bromide under typical water treatment conditions. There is some evidence that, under certain conditions, chlorine can oxidise bromide to bromate. However, there have been no reports of bromate formation from chlorination under realistic treatment conditions. Commercial sodium hypochlorite has been found to contain bromate as a contaminant (probably produced from the bromide present in the brine used in hypochlorite production) and this could give rise to low  $\mu\text{g l}^{-1}$  levels of bromate in chlorinated drinking water. There seems to be some scope for minimising bromate formation by modifying treatment processes (e.g. ozone dose, ozone residual, pH). However, limiting bromate formation could result in increased levels of brominated organic by-products.

The survey of treated drinking waters revealed that bromate was produced from ozonation. Concentrations of  $10 - 20 \mu\text{g l}^{-1}$  were detected at two of the four sites sampled, with bromide concentrations in the corresponding raw waters of  $>100 \mu\text{g l}^{-1}$ . At two other sites the raw waters contained very low levels of bromide ( $<20 \mu\text{g l}^{-1}$ ) and no bromate was detected after ozonation. Bromate was only detected in one of the chlorinated samples analysed - from a treatment works using hypochlorite for disinfection. Bromate was also detected in samples of hypochlorite produced by on-site electrolytic generation, although no bromate was detected in final waters disinfected using hypochlorite generated in this way. The use of hypochlorite for disinfection would seem to be the most likely source of bromate in chlorinated drinking water - the formation of bromate from the oxidation of bromide by chlorine would appear unlikely under normal drinking water treatment conditions.

# 1. INTRODUCTION

The use of chemical disinfectants/oxidants, such as chlorine and ozone, in the treatment of drinking water can give rise to unwanted by-products. Some of these are potentially harmful and this has been the stimulus for much research, particularly with chlorine. Ozone by-products are less well studied, but one of particular concern is bromate which can be formed from the ozonation of water containing bromide.

Bromate has been shown to induce a high incidence of tumours in kidneys of both male and female rats in two studies and of peritoneal mesotheliomas in males in one study (Kurokawa *et al.*, 1986, 1987). Bromate was not carcinogenic in mice, but was shown to increase kidney tumours in a single study in hamsters (Takamura *et al.*, 1985). There is also evidence that bromate is genotoxic, causing mutations in bacteria and chromosome damage *in vitro* and *in vivo* (Ishidate *et al.*, 1984). Bromate has been classified by the International Agency for Research on Cancer (IARC) as having sufficient evidence of carcinogenicity in laboratory animals.

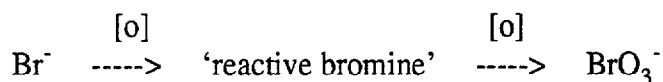
WHO have proposed a provisional guideline value of  $25 \mu\text{g l}^{-1}$  in drinking water as a practical quantitation limit. However, the value giving rise to a theoretical excess cancer risk of  $10^{-5}$ , a factor commonly used in setting standards, is  $3 \mu\text{g l}^{-1}$  for lifetime exposure. Since bromide is ubiquitous in natural waters and bromate has been shown to occur above these values following ozonation, development of methods for controlling bromate formation requires an understanding of the factors that influence its formation during water treatment.

This report reviews current knowledge concerning the formation of bromate from drinking water disinfection and assesses possible control options for minimising its production during drinking water treatment. In addition, the results from a limited survey of bromide and bromate concentrations in UK treated waters (both chlorinated and ozonated) are reported.

## 2. DISINFECTION CHEMISTRY

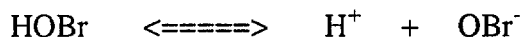
### 2.1 Oxidation mechanism

It is accepted that the oxidation of bromide to bromate proceeds via an intermediate 'reactive bromine' species.



The 'reactive bromine' can comprise three different species (dibromine, hypobromous acid and hypobromite ion) depending on the pH of the system.

Dibromine ( $\text{Br}_2$ ) only becomes significant at  $\text{pH} < 5.5$ . Therefore under normal water treatment conditions the important equilibrium is between hypobromous acid and the hypobromite ion.



The understanding of this equilibrium is essential in controlling bromate formation, since it is generally accepted that further oxidation of the ionised form, hypobromite, is the dominant pathway for bromate formation, whereas the unionised form can react with organics to form brominated organic compounds such as bromoform (Haag and Hoigné 1983).

Figure 2.1 (from Haag and Hoigné 1983) shows this equilibrium at 20 °C and at pH values typically encountered during water treatment.

Other general water quality parameters (e.g. organic content, ammonia) will influence the stability of the  $\text{HOBr}/\text{OBr}^-$  speciation. These are described in more detail in Section 3.

Most oxidising chemical disinfectants can oxidise bromide to 'reactive bromine'. Further oxidation to bromate, however is very much dependent on the mode of action of the individual disinfectant.

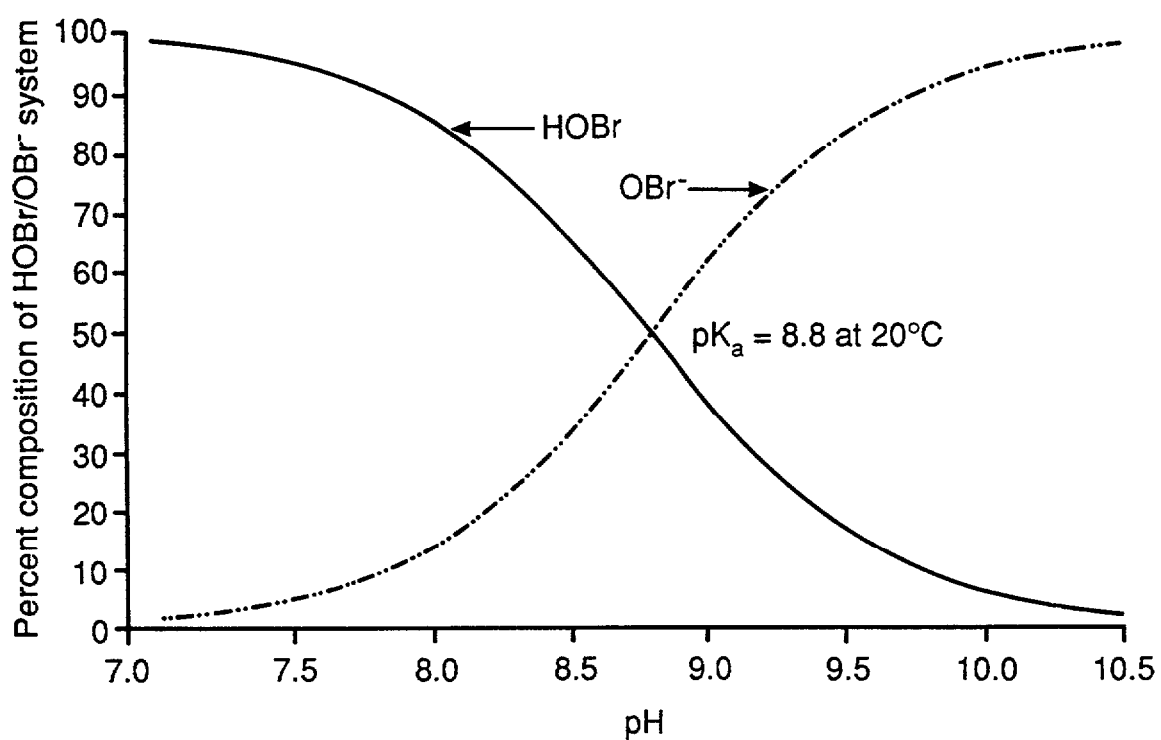
### 2.2 Action of disinfectants

#### 2.2.1 Chlorine

Several authors have demonstrated the formation of 'reactive bromine' from the chlorination of water containing bromide (White 1986a, Williams *et al.*, 1978). However, there is some disagreement over the ability of chlorine to further oxidise 'reactive bromine' to bromate under water treatment conditions.

Macalady *et al.* (1977) reported significant amounts of bromate in chlorinated sea-water samples exposed to sunlight. The levels of bromate were proportional to sunlight intensity. Richardson *et al.* (1981) confirmed that bromate was produced by photolysis in

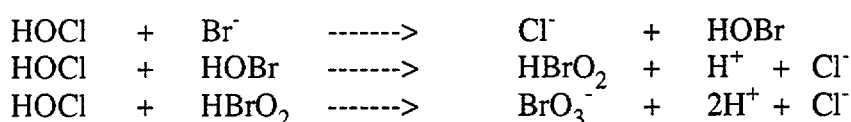




**Figure 2.1** Distribution of HOBr and OBr<sup>-</sup> in aqueous solution in relationship to pH (Krasner *et al* 1991) (adapted from Haag and Hoigné 1983)

water samples chlorinated to an initial residual oxidant level of 5 mg l<sup>-1</sup>. No bromate was detected in samples stored in the dark or in samples treated with lower chlorine doses. The photolytic production of various radical species and their reaction with 'reactive bromine' were thought to be the essential steps in the formation of bromate (Richardson *et al.*, 1981).

Haag (1981) reported that bromate could be formed from chlorination without the action of sunlight. Small amounts of bromate were formed over a period of several days in a solution of 'reactive bromine' by auto-oxidation. Since 'reactive bromine' is formed from the action of chlorine on bromide, a similar effect might be observed upon chlorinating solutions containing bromide. In fact upon chlorinating sea-water, enhanced formation of bromate was observed. This was thought to be due to 'cross oxidation' of chlorine and bromine as well as auto-oxidation. Enhanced chlorate formation was also observed. The 'cross oxidation' reactions resulting in bromate formation were described by the following reaction scheme:



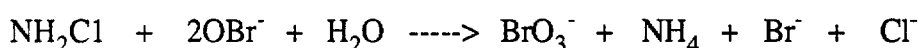
Although these reactions involve the protonated hypohalite species, and the reaction rates increase with decreasing pH, it has been suggested that the ionic species can also react via sodium hypochlorite ion pairs (Bousher *et al.*, 1986). This is one example of bromate formation from hypobromous acid rather than hypobromite.

In the Haag study, sunlight was found to dramatically increase bromate formation via a photolytically induced radical mechanism. In the dark, bromate could only be formed after several hours if there was residual chlorine present in excess of 'reactive bromine' species after the oxidant demand of the water (e.g. from organics) has been satisfied.

This study was mainly concerned with the fate of chlorine discharged to sea-water and it concluded that bromate formation was not significant without the action of light. However the study was mainly concerned with high levels (mg l<sup>-1</sup>) of bromate, measured as an oxidant and did not consider the possible importance of low levels of the bromate ion in drinking water.

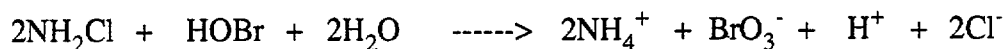
Another reaction mechanism, not involving photolysis, has been proposed for bromate formation (Bousher *et al.*, 1990). In the presence of ammonia, residual chlorine may exist as monochloramine. It was demonstrated that monochloramine could react with hypobromite to form bromate via a bromite intermediate species. The reaction mechanisms postulated were:

In excess hypobromite:

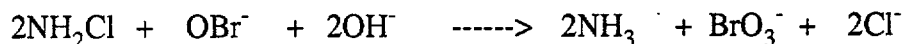


In excess monochloramine:

At low pH



At high pH



Excess bromide ions and the formation of sodium hypobromite ion pairs reduced the reaction rates.

It should be noted, however, that the validity of the Bousher *et al.* (1990) study has been questioned by Haag (1993), who tried to reproduce the experiment but was unable to produce bromate under these conditions. This highlights the disagreement on the significance of bromate production from chlorination.

It may be possible to meet the temporal and stoichiometric requirements for bromate production within a distribution system where a chlorine residual is maintained. This may result in low  $\mu\text{g l}^{-1}$  of bromate being formed which may be significant for drinking water but would not be considered significant in the context of total oxidants in marine waters.

Another possible source of bromate in drinking water is from the use of hypochlorite solutions in disinfection. Bolyard *et al.* (1992) detected bromate in hypochlorite solutions at a range of concentrations ( $<2 - 50 \text{ mg l}^{-1}$ ). No information was given as to whether the bromate was a product of the manufacture of the hypochlorite or whether it resulted from storage. None of the final waters examined in the study contained bromate at concentrations above the  $10 \mu\text{g l}^{-1}$  detection limit, but data on the chlorine doses employed were not given. It is possible that under certain conditions final waters treated with hypochlorite could contain a few  $\mu\text{g l}^{-1}$  bromate.

Bromate could also be produced during on-site electrolytic chlorine generation. Brine, used as a starting material, will contain bromide at a concentration of several  $\text{mg l}^{-1}$ . This will be readily oxidised to bromine and probably onto bromate during electrolysis. In theory, treating water with electrolytically generated chlorine may result in a concentration of several  $\mu\text{g l}^{-1}$  bromate in the final water. However, at the current time, there is no practical evidence to confirm this.

There is very limited information on the production of bromate from chlorination under conditions typical of drinking water treatment. It is theoretically possible for chlorination during the treatment of drinking water to result in the formation of bromate. However, the significance of this is thought to be limited.

In summary:

- Photolysis of chlorinated sea-water can result in bromate formation.

- Excess chlorine can slowly oxidise 'reactive bromine' to bromate, under certain conditions.
- Bromate can be present as a contaminant of hypochlorite used in drinking water treatment.
- Bromate formation has not been demonstrated under typical drinking water chlorination conditions.

### 2.2.2 Ozone

Before studying the specific reactions of ozone and bromide, it is necessary to examine the stability of ozone in aqueous systems, as this has a major impact on ozonation by-product formation. In aqueous solution, ozone reacts with chemicals in two ways:

- by direct reaction of molecular ozone; or
- by indirect reaction of radical species, formed from the decomposition of ozone.

The relative importance of these mechanisms depends on the nature of the aqueous solution. Certain ions and organic molecules act as radical inhibitors and help stabilise molecular ozone in solution. In these cases, the direct reaction will be more important. Other species will act as radical initiators which will favour ozone decomposition and radical formation. Chemicals can also act as radical promoters to enhance radical chain reactions, which generate further radicals and increase ozone decomposition. Therefore, there will be enhanced ozone decay and indirect oxidation will predominate.

Some complex molecules, such as humic acids, can act as radical initiators, promoters and inhibitors, depending on the site at which the radical attack occurs. The specific mechanism involved in many reactions is therefore often very difficult to establish.

Table 2.1 summarises the effect of various parameters on the reactions of ozone.

**Table 2.1 Effect of chemical species on ozone decomposition**

Initiator	Promoter	Inhibitor
OH <sup>-</sup> H <sub>2</sub> O <sub>2</sub> Fe <sup>2+</sup> Humics	R-OH chlorination groups Formate Humics	RCOO <sup>-</sup> Alkyl chains Carbonate/Bicarbonate Humics

Taken from Langlais *et al.*, 1991

Oxidation by molecular ozone is a relatively slow reaction, and tends to be very specific. It typically reacts with organic compounds via attack on unsaturated aliphatic and aromatic bonds and tends to result in specific addition reaction products, such as carbonyl and acid compounds.

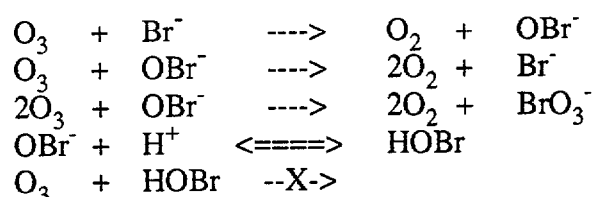
Radical oxidation is much less specific and relatively rapid. Radical attack forms radical inorganic and organic species, which in turn can act as radical promoters in a variety of chain reactions. This can result in a wide range of radical-derived reaction products. This is a highly oxidising system and is encouraged during the use of Advanced Oxidation Processes (AOPs) for destroying pollutants (e.g. pesticides) during water treatment.

If it is possible to identify which process favours bromate production, it may be possible to alter the chemistry of the solution in order to limit oxidation by that particular mechanism.

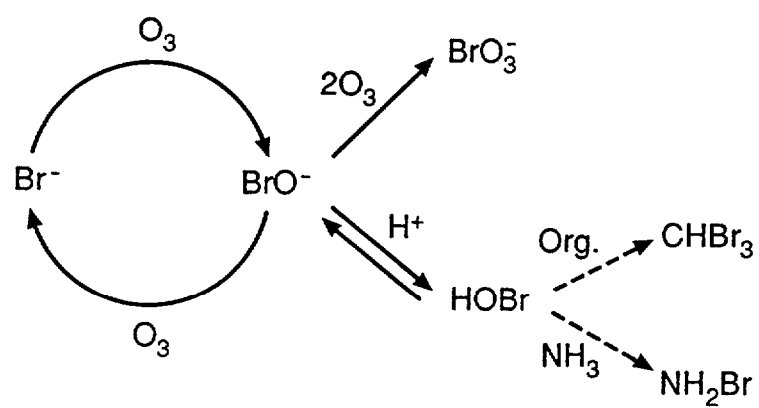
Early studies on the production of bromate from ozonation, were mainly concerned with marine cooling water systems (Crecelius 1979, Richardson *et al.*, 1981). It was found that ozone could oxidise bromide to 'reactive bromine', which is then oxidised to bromate.

Richardson *et al.* (1981) investigated the yield of bromate from ozonated sea-water under light and dark conditions. During ozonation no differences were observed between the bromate levels produced. However, when ozonation was stopped, there was a small increase in bromate concentration in the samples exposed to sunlight. This increase was of a similar level to the bromate formed by the photolysis of chlorinated sea-water samples (Section 2.2.1). It was postulated that bromate was formed via a radical mechanism, with the radicals being produced by the catalytic decomposition of ozone by bromide. Further radicals were then generated in the light systems allowing additional bromate formation.

Haag and Hoigné (1983) investigated the reaction between ozone and bromide in detail. The following equations were used to describe the overall reaction scheme although the equations do not show the intermediate species (e.g. bromite) that are thought to be involved in the reactions.



There are two important points to note from the study. Hypobromite is oxidised not only to bromate, but also to a species that regenerates bromide; in effect bromide acts as a catalyst for ozone decomposition. Ozone does not oxidise hypobromous acid to bromate, but does oxidise the hypobromite ion. Figure 2.2 (Haag and Hoigné 1983) summarises the findings.



**Figure 2.2** Reactions of ozone with bromide and 'bromine' in aqueous media (Haag and Hoigné, 1983)

Sayato *et al.* (1990) found that the formation of active 'reactive bromine' from the ozonation of bromide proceeded by a radical mechanism and was hindered in the presence of radical scavengers (e.g. bicarbonate).

In summary:

- Ozone can oxidise bromide to bromate much more readily than chlorine.
- Several tens of  $\mu\text{g l}^{-1}$  bromate can be produced from the ozonation of waters containing bromide.
- The hypobromite ion is more readily oxidised to bromate than hypobromous acid.
- The decomposition of ozone to oxidising radical species is thought to increase bromate formation.
- Bromide can catalyse ozone decomposition to radical species.

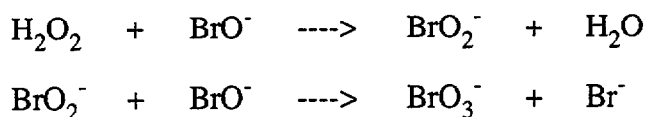
### 2.2.3 Chlorine dioxide

It is reported that chlorine dioxide will not oxidise bromide to 'reactive bromine' (White 1986b). Therefore it is unlikely that bromate will be formed from the use of chlorine dioxide under normal conditions (e.g. without the action of UV light).

### 2.2.4 Other oxidants

Advanced oxidation processes (e.g.  $\text{H}_2\text{O}_2/\text{UV}$ ) are likely to result in the oxidation of bromide to bromate, since the processes involve generating highly oxidising non-specific radical species. As has been demonstrated for both chlorine and ozone, radical generation during disinfection can lead to bromate formation (Richardson *et al.*, 1981). Sayato *et al.* (1990) demonstrated that the action of radical species during disinfection is the main pathway for the formation of 'reactive bromine' which is the precursor for bromate.

Amy and Siddiqui (1991) observed a 25% increase in bromate formation in a Peroxone ( $\text{H}_2\text{O}_2 + \text{O}_3$ ) system compared with ozone on its own. This was attributed to the generation of radicals and by the direct reaction of hydrogen peroxide with hypobromite ions.



## 2.3 Summary

There have been a number of studies demonstrating that bromate can be formed at significant levels from the ozonation of water containing bromide. Limited research has

been carried out into bromate formation from other disinfectants. This has shown that bromide can be oxidised to bromate by chlorine. However, there have been no reports of studies into this under realistic drinking water conditions and it remains to be proven that bromate formation will occur under such conditions.



### 3. CONTROLLING BROMATE FORMATION

There has been some research into the factors that affect bromate formation during ozonation. These are discussed below, particularly in relation to possible methods of controlling bromate formation. The lack of information on bromate formation from chlorination precludes any discussion of controlling bromate production from the use of chlorine at this stage.

#### 3.1 Factors affecting bromate formation

##### 3.1.1 Bromide

An obvious starting point is to look at the effect of bromide on bromate formation. As perhaps expected, increasing bromide concentration leads to an increase in bromate formation during drinking water treatment (Amy and Siddiqui 1991). Some authors state that there is a bromide concentration threshold, below which bromate will not form (Amy and Siddiqui 1991, Krasner *et al.*, 1991, Krasner *et al.*, 1993). Although this threshold appears to vary for different source waters (e.g. dependent on pH, DOC), it is generally of the order 0.18 - 0.3 mg l<sup>-1</sup> bromide. However the concept of a threshold value may not be a realistic approach given that variations in other parameters may be of equal or greater importance in determining the extent of bromate formation.

It is probably not practical to remove bromide before ozonation (e.g. by ion exchange) but if the threshold values prove to be generally correct, they may be used to pin-point source waters where bromate formation is more likely.

In summary:

- Bromate formation increases with increasing bromide concentration.
- The possibility of a bromide concentration threshold for bromate formation is currently under investigation in studies in the US.

##### 3.1.2 Ozone

Another obvious area to examine is the effect of ozone (disinfectant) dose on bromate formation. Krasner *et al.* (1993) found that if there was no residual ozone present, then no bromate was formed. This suggests that bromine species do not favourably compete with other substances in water that have a disinfectant demand (e.g. ammonia, organic matter). Hydrogen sulphide was also found to exert a considerable ozone demand at one treatment facility that had a ground water supply and therefore reduced bromate formation.

Amy and Siddiqui (1991) found that after ozonating to remove the initial demand of a water, continued ozonation produced a steady increase in bromate until all the bromide had been converted to bromate. Miltner *et al.* (1992) found that bromate was not detected until an ozone to TOC ratio of 1 was reached during treatment. The studies also indicated

that at higher ozone doses (i.e. increasing bromate formation), there was a reduction in brominated organic by-products.

In summary:

- Ozonation to a residual is required to form bromate (i.e. an ozone dose in excess of the demand from TOC etc).
- Continued ozonation can result in complete oxidation of all the bromide in solution to bromate.

### 3.1.3 pH

Bromine speciation is an important consideration in bromate formation. Most authors agree that the formation of bromate from hypobromous acid is very limited and that the main route is via the hypobromite ion. Therefore pH is an obvious control method since this will drive the 'bromine' equilibrium towards hypobromous acid, which is less amenable to further oxidation to bromate. However, hypobromous acid reacts more readily with organic compounds than hypobromite ion. Therefore, a reduction in bromate concentration may be achieved at the expense of a corresponding increase in brominated organic by-products (e.g. bromoform).

Increasing pH from 6 to 8.5 led to an increase in bromate formation on ozonation (Amy and Siddiqui 1991). This was attributed to a greater ratio of hypobromite to hypobromous acid at higher pH, and also a shift from molecular to radical oxidation. Over the same pH range, brominated organic by-product formation decreased with increasing pH.

A significant reduction in bromate formation was also observed by reducing pH from 7.9 to 7 (Krasner *et al.*, 1993). Further reduction to pH 6 did not produce any further reduction in bromate. However, during peroxone disinfection, a further reduction in bromate was achieved by lowering the pH to 6. This effect may be due to a reduction in ozone dose since the applied ozone doses decreased with decreasing pH. This was because in the USA the disinfectant dose is controlled by the requirement to meet the C x T criteria. This requirement states that in order to achieve satisfactory disinfection, a certain residual concentration of disinfectant (C) must be maintained for a given contact time (T). Since ozone is more stable at lower pH values, less applied ozone dose is required to maintain a residual concentration over a period of time (C x T value).

In summary:

- Bromate formation appears to be greater at higher pH.
- This may be due to an increased ratio of hypobromite to hypobromous acid and faster ozone decomposition to radical species.
- A reduction in pH will limit bromate formation, but may result in an increase in levels of brominated organic compounds.

### 3.1.4 Temperature

An increase in bromate formation was observed by Amy and Siddiqui (1991) with increasing temperature (20 to 30 °C) for both ozonation temperature and for incubation temperature, although it was not as dramatic in the latter case. This was thought to be due to an increase in the dissociation constant for hypobromous acid with increasing temperature, resulting in the formation of more hypobromite ions. Faster reaction kinetics at higher temperature were also thought to contribute to this effect. Brominated organic by-products also increased at elevated temperatures.

However, increasing temperature (13 to 23 °C) reduced bromate (and brominated organics) concentrations on the ozonation of pre-ammoniated water in a study by Krasner *et al.* (1991). This was attributed to accelerated ozone decay at higher temperatures.

This apparent contradiction in findings is difficult to explain. It may be that source water type can have a major influence on the effect of temperature. If the water has a high ozone demand, bromate concentration may decrease on increasing temperature due to greater ozone decay. Temperature will also affect the speciation of 'reactive bromine' which also depends on general water parameters (e.g. pH). Increasing temperature will increase the concentration of hypobromite ions which would be expected to favour bromate formation. Therefore no general conclusion can be made other than changing temperature will affect bromate formation. Although temperature control may not be a viable option during water treatment, seasonal fluctuations in temperature may well have an impact on bromate levels in drinking water.

In summary:

- Increasing temperature can increase or reduce bromate formation depending on other water parameters, although this effect is difficult to predict.
- Increasing temperature will increase the ratio of  $\text{OBr}^-/\text{HOBr}$  at a given pH and may therefore increase bromate formation.
- Increasing temperature can increase the reaction rate of ozone with water constituents, such as organic matter and ammonia, and therefore may reduce the ozone available to oxidise bromide to bromate.

### 3.1.5 Alkalinity

Sayato *et al.* (1990) found that increasing bicarbonate concentration reduced 'reactive bromine' formation. At pH 8, increasing alkalinity caused an increase in bromate formation, whereas at pH 7, increasing alkalinity reduced bromate formation (Krasner *et al.*, 1993). It is recognised that carbonate and bicarbonate act as scavengers of radical species (Langlais *et al.*, 1991). Therefore it would be expected that increasing alkalinity would decrease bromate by quenching radicals, which are thought to be involved in bromate formation. Clearly the effects of alkalinity are not well understood and more work is required in this area.

In summary:

- It is not clear what effect alkalinity has on bromate formation.

### 3.1.6 Ammonia

Haag and Hoigné (1983) found that ammonia could react with 'reactive bromine' to form monobromamine, which would then slowly react to form nitrate and bromide.

Ammonia, at a concentration of  $50 \mu\text{g l}^{-1}$ , was found to cause a lag in bromate formation in a computer simulation of ozonation treatment (von Gunten and Hoigné 1992). Only after most of the ammonia has been depleted does bromate formation occur. The reaction with ammonia was the dominant sink for 'reactive bromine' in the system.

Bromate concentration was reduced by 30% by adding ammonia either before or immediately after ozonation ( $[\text{NH}_3]/[\text{O}_3] = 0.25 \text{ w/w}$ ) in a study by Amy and Siddiqui (1991). The concentration of bromoform was also reduced in the same study. Most of the waters studied were in the pH range 8 - 8.5.

Ozonation of high bromide concentration ( $2 \text{ mg l}^{-1}$ ) water in the presence of ammonia ( $0.5 \text{ mg l}^{-1}$ ) produced less bromate (and bromoform) than ozonation alone during pilot plant tests (Gramith *et al.*, 1991). The pH range of the waters in this study was 7.8 - 8.6.

Ammonia addition did not reduce bromate formation in studies by Krasner *et al.* (1991). This was confirmed by Krasner *et al.* (1993) who concluded that the addition of ammonia to form bromamines did not appear to be a control option at  $\text{pH} \leq 8$ .

Ammonia may also exert an effect on ozone availability. Haag *et al.* (1984) found that bromide could catalyse ammonia oxidation by ozone to form nitrate. Therefore ammonia could be a source of ozone demand, despite having a slow direct reaction rate (Hoigné *et al.*, 1985) and hence would reduce the amount of ozone available to oxidise 'reactive bromine'.

It does appear that pH could be important in determining the effectiveness of ammonia addition as a method of controlling bromate formation. At  $\text{pH} > 8$ , the addition of ammonia does appear to reduce bromate formation. This is perhaps not surprising given the high pH dependence of both 'reactive bromine' and ammonia speciation. With the formation of nitrate as a by-product, the use of ammonia addition may not be viable as a control option.

In summary:

- The addition of ammonia to reduce bromate (and bromoform) formation appears to be effective only at  $\text{pH} > 8$ .
- Ammonia can be oxidised to nitrate by ozone and therefore may not be viable as a control option.

### 3.1.7 Organic matter

The concentration of Total and Dissolved Organic Carbon (TOC, DOC) will vary dramatically in different raw waters. This will have an effect on ozone demand and consequently an effect on bromate formation (Section 3.1.2).

In summary:

- Ozone demand from TOC needs to be satisfied before bromate formation occurs.

### 3.1.8 Hydrogen peroxide

As discussed earlier, hydrogen peroxide is used in conjunction with ozone (PEROXONE) or UV light in advanced oxidation processes (AOPs). The combination of oxidants produces radicals which are very reactive and unspecific oxidising species. Radical species have been shown to play a prominent part in bromate formation from chlorination and ozonation (Section 2).

Therefore it would be expected that the use of PEROXONE would increase bromate formation. A 25% increase in bromate formation was observed when hydrogen peroxide was added to an ozonation reactor (Amy and Siddiqui 1991). A 55% reduction in brominated organic by-products was observed for the same system.

Gramith *et al.* (1991) found that PEROXONE dramatically increased bromate formation. On average a 50% increase in bromate was observed using a ratio of 0.2 hydrogen peroxide to ozone.

However Krasner *et al.* (1991) found conflicting results. In a bench scale test, hydrogen peroxide addition was found to decrease bromate formation. In pilot plant studies, it was found to increase bromate formation.

The stage of hydrogen peroxide addition in the treatment process was found to be critical (Krasner *et al.* 1993). The use of PEROXONE early in the process resulted in elevated bromate levels. This may be partly due to the increased ozone dose required to meet CxT criteria after hydrogen peroxide was added early in the system. Delaying addition until after the CxT criteria were met may reduce this effect.

In summary:

- In theory the addition of hydrogen peroxide during ozonation should result in increased bromate formation.
- The use of PEROXONE can increase or decrease bromate formation.
- The ratio of  $O_3/H_2O_2$  and the stage of addition seem to be critical factors in bromate formation.

### 3.1.9 Reactor dynamics

The effect of reactor dynamics was studied by Krasner *et al.* (1993). The ozone dose to TOC ratio (w/w) that produced bromate was studied in a variety of systems.

**Table 3.1 Effect of reactor dynamics on bromate production**

Reactor	Ozone: TOC (w/w)	Bromate ( $\mu\text{g l}^{-1}$ )
Semibatch	1	0
CSTR	1	31
Countercurrent	0.5	23

Note: CSTR = continuously stirred tank reactor

In summary:

- The hydrodynamics of the ozonation reactor can influence bromate formation.

### 3.1.10 Removal of bromate

Currently, there is no reported method of removing bromate during drinking water treatment.

## 3.2 Summary

A number of methods of controlling bromate formation during ozonation have been examined. However, there have been several ambiguous findings. This is mainly because of the diversity of source waters and treatment conditions used. For example, ammonia appears to limit bromate formation in one study, but not in another. This may be due to a single parameter such as pH or be due to a combination of factors (e.g. temperature, reactor dynamics). Work needs to be carried out into the effect of one parameter on other parameters (e.g. the effect of temperature on the effectiveness of ammonia in reducing bromate formation). Methods where minimising bromate formation centre on reducing the hypobromite concentration compared with the hypobromous acid (e.g. pH) are likely to cause an increase in brominated organic by-products.

Table 3.2 summarises the apparent findings of current research into limiting bromate formation.

**Table 3.2      Effect of various factors on bromate formation**

Factor	Effect	Comments
Increase in:		
Bromide	+	
Ozone dose	+	Assumes O <sub>3</sub> in excess of demand
pH	+	
Temperature	*	Dependent on source water
Alkalinity	*	Depends on pH
Ammonia	-(*)	No effect observed ≤ pH 8
TOC	-	Decreases available O <sub>3</sub> to react with bromide
H <sub>2</sub> O <sub>2</sub>	+(*)	Dependent on pH, PEROXONE ratio, stage
Reactor Dynamics	+	Countercurrent > CSTR > semibatch

**Key**

+ = increase in bromate formation

- = decrease in bromate formation

\* = ambiguous results

## 4. BROMATE AND BROMIDE SURVEY

### 4.1 Introduction

A limited survey of bromate and bromide concentrations in raw and treated waters was undertaken. Samples were taken from treatment works (chlorination and ozonation), pilot-plants (ozonation) and distribution systems. The possible production of bromate from chlorination was investigated by the analysis of samples taken from a number of plants using different methods of chlorination (chlorine gas, hypochlorite or on-site electrolytically-generated chlorine).

### 4.2 Bromate formation from chlorination

#### 4.2.1 Chlorine gas

The potential formation of bromate from reaction with chlorine was discussed in detail in Section 2.2.1. Table 4.1 shows the results from the bromate and bromide analysis of samples taken from treatment works utilising chlorine gas. No bromate was detected in any of the samples analysed. It would appear that under typical drinking water treatment conditions, bromide present will be readily oxidised to hypobromous acid (reflected in the decrease in bromide concentrations on chlorination), but further oxidation to form bromate does not occur.

**Table 4.1 Bromate and bromide concentrations in samples taken from treatment works using chlorine gas**

Site	Sample	Bromide ( $\mu\text{g l}^{-1}$ )	Bromate ( $\mu\text{g l}^{-1}$ )
A	Raw (lowland river)	91	<2
	Clarified	37	<2
	Superchlorinated <sup>a</sup>	<20	<2
	Filtered	54	<2
	Final	31	<2
	Distribution	45	<2
B	Raw	120	<2
	Clarified	117	<2
	Filtered	121	<2
	Final	26	<2
C	Final	<20	<2

Note: <sup>a</sup>Chlorine residual  $0.4 \text{ mg l}^{-1}$



#### 4.2.2 Hypochlorite

Data recently published on the concentration of bromate in hypochlorite solutions indicate that bromate is present as a contaminant of hypochlorite (Bolyard *et al.*, 1992). The levels found varied and no indication was given whether the bromate arose from the manufacture or storage of the hypochlorite solution. It has been suggested that in extreme cases, bromate concentrations in final waters could exceed  $10 \mu\text{g l}^{-1}$  for a chlorine dose of  $5 \text{ mg l}^{-1}$  (Mole 1992). Bromate was detected in one of the chlorinated samples taken from a treatment works using hypochlorite (Table 4.2), which would support this view, although further data would be required to confirm this.

**Table 4.2 Bromide and bromate concentrations in samples taken from treatment works using hypochlorite**

Site	Sample	Bromide ( $\mu\text{g l}^{-1}$ )	Bromate ( $\mu\text{g l}^{-1}$ )
A	Raw	<20	<2
	Final	<20	<2
B	Final	<20	8

Notes: Chlorine dose at both sites varies ( $1\text{-}5 \text{ mg l}^{-1}$ ) depending on raw water quality

#### 4.2.3 On-site electrolytically-generated chlorine

The brine used in the generation of chlorine will contain bromide, which can undergo electrolysis to form bromate. It has been estimated that for a typical chlorine dose of  $5 \text{ mg l}^{-1}$ , the bromate concentration in the final water could reach  $15 \mu\text{g l}^{-1}$  (Mole 1992). No bromate, however, was detected in any of the samples taken from plants using electrolytically-generated chlorine (Table 4.3). The chlorine doses used were not available in all cases, but it is possible that they were not high enough to result in a detectable level of bromate being present in the final waters. Two samples of hypochlorite solution produced by electrolytic chlorine generation were analysed and found to contain  $9.5$  and  $13.5 \text{ mg l}^{-1}$  of bromate respectively. It is clear, therefore, that bromate is produced by electrolytic chlorine generation - the concentration of bromate in the final water will depend on the chlorine dose used, as well as the bromide concentration in the original brine.

**Table 4.3 Bromide and bromate concentrations in samples taken from treatment works using on-site electrolytically-generated chlorine**

Site	Sample	Bromide ( $\mu\text{g l}^{-1}$ )	Bromate ( $\mu\text{g l}^{-1}$ )
A	Raw (lowland river) <sup>a</sup>	96	<2
	Raw (gravel pit) <sup>a</sup>	142	<2
	Superchlorinated <sup>b</sup>	23	<2
	Final	48	<2
	Distribution	66	<2
B	Raw (upland reservoir)	<20	<2
	Filtered	<20	<2
	Final <sup>c</sup>	<20	<2
	Distribution 1	<20	<2
	Distribution 2	<20	<2
C	Raw (upland reservoir)	36	<2
	Post flotation	26	<2
	Final <sup>d</sup>	<20	<2
	Distribution 1	<20	<2
	Distribution 2	<20	<2
D	Final <sup>e</sup>	<20	<2

Notes: <sup>a</sup>Two sources of raw water mixed prior to chlorination

<sup>b</sup>Chlorine dose of  $2 \text{ mg l}^{-1}$

<sup>c</sup>Chlorinated to residual of  $0.6 \text{ mg l}^{-1}$

<sup>d</sup>Chlorinated to residual of  $0.3 \text{ mg l}^{-1}$

<sup>e</sup>Chlorinated to residual of  $0.4\text{-}0.6 \text{ mg l}^{-1}$

### 4.3 Bromate formation from ozonation

Samples were taken from three ozonation pilot-plants and one treatment works which employs ozone for disinfection. Bromate was detected in ozonated samples from two of the sites sampled (Table 4.4). At site A no bromate was detected after pre-ozonation, but  $10 \mu\text{g l}^{-1}$  was formed after the intermediate stage of ozonation. The level of bromate was maintained throughout the rest of the treatment process - final chlorination did not result in further bromate production. The raw waters from sites B and C contained very low levels of bromide and it is, therefore, perhaps not surprising that no bromate was detected at either of these sites. Relatively high concentrations of bromate were detected in samples taken from site D. Again, no bromate was detected after pre-ozonation, but after

intermediate ozonation  $17 \mu\text{g l}^{-1}$  was produced. GAC filtration did not appear to remove any of the bromate.

**Table 4.4 Bromide and bromate concentrations in samples taken from ozonation plants**

Site	Sample	Bromide ( $\mu\text{g l}^{-1}$ )	Bromate ( $\mu\text{g l}^{-1}$ )
A	Raw (lowland river)	122	<2
	Settled	126	<2
	Pre-ozone	125	<2
	Intermediate ozone	120	10
	Treated (final $\text{Cl}_2$ )	32	10
B	Raw (upland reservoir)	<20	<2
	1st Stage ozone	<20	<2
	2nd Stage ozone	<20	<2
C	Raw (upland lake)	<20	<2
	Post ozone	<20	<2
	Final	<20	<2
	Distribution	<20	<2
D	Raw (lowland river)	131	<2
	Pre-ozone	148	<2
	Sand filtered	140	<2
	Inter ozone	112	17
	GAC 1	131	21
	GAC 2	131	21
	BAC	160	21

Notes:

Site A - Pre-ozone dose  $0.24 \text{ mg l}^{-1}$ ; no residual. Intermediate ozone dose  $3.74 \text{ mg l}^{-1}$ ; residual  $0.68 \text{ mg l}^{-1}$

Site B - 1st stage ozone  $1\text{-}2 \text{ mg l}^{-1}$ ; trace residual. 2nd stage ozone  $0.8 \text{ mg l}^{-1}$ ; residual  $0.2 \text{ mg l}^{-1}$

Site C - Ozone dose  $2 \text{ mg l}^{-1}$

Site D - Pre-ozone dose  $1 \text{ mg l}^{-1}$ ; no residual. Intermediate ozone dose  $2.5 \text{ mg l}^{-1}$ ; residual  $0.5 \text{ mg l}^{-1}$

## 4.4 Summary

The limited data obtained from the survey of bromate levels in treated waters indicated that bromate could be formed under typical ozonation conditions, leading to concentrations of  $10\text{-}20 \mu\text{g l}^{-1}$  in the treated waters. At sites where the raw water contained very little bromide, no bromate was detected after ozonation. The results

obtained from treatment plants using chlorine suggest that bromate formation is unlikely to occur from the use of chlorine as a disinfectant. One sample from a plant using hypochlorite, however, contained measurable concentrations of bromate. It is suspected that the bromate in this sample arose from an impurity in the hypochlorite solution, although further sampling would be required to confirm this. This hypothesis is supported by published data on the occurrence of bromate in hypochlorite solution. No bromate was detected in samples taken from treatment plants using on-site electrolytically-generated chlorine. Bromate was detected in samples of hypochlorite generated by this process, and it, therefore, remains a possible source of bromate in chlorinated drinking water.

## 5. CONCLUSIONS AND RECOMMENDATIONS

The main findings from the literature review may be summarised as follows:

1. Bromate can readily be formed from the ozonation of waters containing bromide under typical water treatment conditions. A low ( $<5 \mu\text{g l}^{-1}$ ) limit for bromate in drinking water could impose restrictions on the use of ozone in drinking water treatment.
2. There is some evidence that, under certain conditions, chlorine can oxidise bromide to bromate. However, there have been no reports of bromate formation from chlorination under realistic drinking water treatment conditions. Hypochlorite (either supplied commercially as a solution or generated on-site) is likely to contain bromate as a contaminant and this could give rise to low  $\mu\text{g l}^{-1}$  levels of bromate in chlorinated drinking waters.
3. By altering the physico-chemical conditions of certain treatment processes (e.g. ozone dose, pH) it would appear possible to limit bromate formation. However, limiting bromate formation could cause an increase in levels of undesirable brominated organic by-products.

The results from the survey of bromide and bromate levels in UK raw and treated waters revealed the following:

1. Bromate is formed under typical ozonation conditions at concentrations of 10 - 20  $\mu\text{g l}^{-1}$  in the treated waters. The corresponding raw waters contained  $>100 \mu\text{g l}^{-1}$  bromide. At sites where the raw water contained very low concentrations of bromide, no bromate was detected after ozonation.
2. Bromate was only detected in one chlorinated final water - taken from a treatment works using hypochlorite for disinfection. Bromate was also detected in samples of hypochlorite produced by on-site electrolytic generation, although no bromate was detected in final waters chlorinated using hypochlorite generated in this way. The use of hypochlorite would seem to be the most likely source of bromate in chlorinated drinking waters.

From the above it is apparent that there are a number of areas which merit further investigation:

1. A more comprehensive study is needed investigating the factors controlling ozone and bromine chemistry, how they inter-relate and how they could be used to minimise bromate formation.
2. The concentrations of bromate in hypochlorite solutions (both as delivered by manufacturers and generated on-site) should be determined. In addition the effect of storage on bromate levels in hypochlorite should be evaluated. Further analysis of chlorinated waters treated with hypochlorite should be undertaken to determine whether detectable levels of bromate are likely to be present in the final waters.

3. In view of the ease with which ozone can oxidise bromide to bromate during drinking water treatment, regular monitoring of bromate levels in ozonated waters should be considered.

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