

## Orthogonal Experiments for Controlling the Formation of DBPs During Preozonation of Bromide-Containing Raw Water\*

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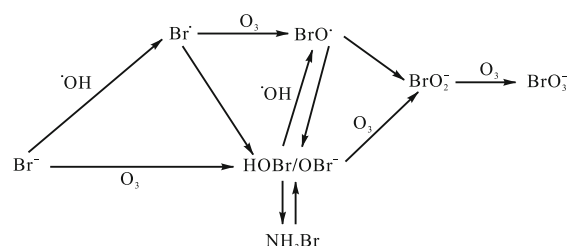
**Abstract:** Orthogonal method was adopted to optimize the preozonation process and to minimize the bromate formation. Factors such as contact time, pH and ammonia concentration were investigated by orthogonal experiments to understand the interaction of various operation conditions on the formation of bromate and other disinfection by-products (DBPs). Results showed that pH had the most significant influence on the minimization of bromate formation. The factors influencing the formation of bromate were in order of pH > contact time > ammonia concentration. For the formation of trihalomethanes (THMs) and haloacetic acids (HAAs), however, contact time significantly influenced their formation potential. In the practical preozonation process of waterworks, it is appropriate to set preozonation contact time to be 20 min. In order to minimize the formation of bromate, pH value of the raw water should be adjusted to 6.0, and a certain concentration of ammonia could be added into the water to strengthen the minimization effect when the concentration of bromide in the raw water is higher than that in the experimental water.

**Keywords:** orthogonal experiment; preozonation; bromate; THMs; HAAs

Ozone has been widely used since 1980s instead of chlorine as a preoxidant due to its high oxidation potential<sup>[1]</sup>. In potable water treatment, preozonation has been applied throughout the world due to its important role in sterilization, bleaching, algae removal and flocculation<sup>[2,3]</sup> as well as reducing the formation potential of many halogenated disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs)<sup>[4,5]</sup>.

The most notable limitation of preozonation, however, is the formation of bromate as a major by-product in water with high bromide content. It is well known that the preozonation of bromide-containing water can oxidize the bromide ion ( $\text{Br}^-$ ) to bromate ( $\text{BrO}_3^-$ ) with normal water quality treatment parameter<sup>[6]</sup>. It has been found that bromate is a genotoxic carcinogen which produces the toxic response through the damage resulting from the increased levels of lipid peroxides (LPO) or from oxygen radicals generated from LPO and induces DNA damage<sup>[7]</sup>. Based on these findings, bromate was declared a potential human carcinogen which recently led to stringent drinking-water standards. The United States

Environmental Protection Agency (USEPA), European Union (EU) and Standards for Drinking Water Quality of China (GB 5749—2006) have set a maximum contaminant level (MCL) of 10  $\mu\text{g/L}$  for this contaminant in drinking water<sup>[8-10]</sup>. In addition, the USEPA recommends a maximum contaminant level goal (MCLG) of zero for bromate. A simplified mechanism for bromate formation by ozone and OH radicals ( $\cdot\text{OH}$ ) is shown in Fig. 1.



**Fig. 1** Reaction scheme for bromate formation during the ozonation of bromide-containing water (Adapted from von Gunten<sup>[7]</sup>)

The level of bromate formed during preozonation usually depends on the amount of bromide found in the

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source water, the dosage of ozone and the pH value of the water. Although previous studies have found that pH reduction and ammonia addition can successfully decrease the formation of  $\text{BrO}_3^-$  [11-14], they have their own defects. For example, although acidification could decrease the formation of  $\text{BrO}_3^-$ , it also deteriorated the oxidation ability of ozone [15]. When the ammonia-based methods were used, residual ammonia after preozonation may be problematic for utilities using free chlorine for secondary disinfection by exerting a chlorine demand as high as 10:1 by weight during breakpoint chlorination [16]. With bromide present in water, the preozonation of natural organic matter (NOM) results in the formation of brominated DBPs which are suggested to be more toxic [17]. It has been reported that ozonation prior to chlorination can reduce DBP formation potential (DBFP) [18, 19]. Huang and Zhang [20] reported a decrease of THM formation potential (THMFP) after ozonation. But changes in pH or ammonia concentration in raw water may also cause more formation of THMs or HAAs. Hence, it is crucial to study the formation of bromate and other DBPs under various operating conditions during preozonation.

The raw water from the Luan River, a typical source water in North China, was treated by preozonation followed by coagulation-clarification, filtration and a final disinfection with UV irradiation and chlorination in a drinking water plant located in Tianjin. Previous study found that, under present treatment parameter ( $\text{O}_3$  dosage 1.5 mg/L, contact time 10 min), when  $\text{Br}^-$  concentration reached 145  $\mu\text{g/L}$ , 10.5  $\mu\text{g/L}$  bromate formed, which was beyond the MCL set by GB 5749—2006 [21]. It is of great importance to optimize operating parameters to control bromate formation.

The orthogonal experiment is a practical method based on the probability theory and mathematical statistics, which can be used to arrange the multi-factor and multi-level test scientifically and reasonably [22]. Its essence is using a ready-made standardized orthogonal table to carry out multi-factor test design, and the statistical results were analyzed. The outstanding feature is that satisfactory results can be obtained from less experiments by properly selecting representative experiment points [23].

In this study, factors such as contact time, pH and ammonia concentration were investigated by orthogonal experiments to optimize the preozonation process and minimize or eliminate the bromate formation. The aim of this study is to learn the interaction of various operation conditions on the formation of bromate and other DBPs.

The results will identify the optimal treatment conditions of the raw water for the removal of regular DBPs by preozonation process while preventing the formation of bromate.

## 1 Materials and methods

### 1.1 Source water

The source water in this work, which was collected from the influent of a water treatment plant from the Luan River in Tianjin, China, in November 2012, was the typical source water in North China. The characteristics of the general raw water are summarized in Tab. 1. All the water samples were firstly filtered with a 0.45  $\mu\text{m}$  membrane filter to eliminate any suspended solids present in it and then the initial pH and ammonia concentration were adjusted with 1 mol/L  $\text{H}_2\text{SO}_4$  or NaOH solution and 1 mg/mL  $\text{NH}_4\text{Cl}$  solution before the experiments.

Tab. 1 Raw water characteristics

Parameter	Mean value ( $n = 3$ )
pH	7.50
$\text{UV}_{254}/(\text{cm}^{-1})$	0.022
Dissolved organic carbon (DOC) / ( $\text{mg}\cdot\text{L}^{-1}$ )	3.68
Bromide / ( $\mu\text{g}\cdot\text{L}^{-1}$ )	143.520
Bromate / ( $\mu\text{g}\cdot\text{L}^{-1}$ )	BDL
THMFP / ( $\mu\text{g}\cdot\text{L}^{-1}$ )	91.398
HAAFP / ( $\mu\text{g}\cdot\text{L}^{-1}$ )	124.196

Note:  $n$  is detection time; BDL is the below detection limit of 1.000  $\mu\text{g/L}$ ; HAAFP is HAA formation potential.

### 1.2 Orthogonal design

The orthogonal method was used to determine the effects of major operating variables on the formation of bromate and other DBPs to find the combination of variables resulting in minimum concentrations of bromate and other DBPs.

Results calculated from the single factor tests and previous study [24] indicated that contact time, pH and ammonia concentration always have great influence on the formation of bromate and other regular DBPs. In order to discuss the influence levels of these factors, 3-factor and 3-level orthogonal experiments were designed. Three important operating parameters: contact time, pH and ammonia concentration, were chosen as the independent variables and designated as A, B, and C, respectively. As presented in Tab. 2, the experimental design involves three levels for each factor coded 1, 2 and 3, respectively.

**Tab. 2 Design of 3-factor and 3-level orthogonal experiment**

Levels	Factor		
	Contact time (A)/ min	pH (B)	Ammonia concentration (C)/ (mg·L <sup>-1</sup> )
1	5	6	0.3
2	10	7.5	0.5
3	20	9	1.0

### 1.3 Preozonation procedure

Milli-Q water maintained at room temperature was continuously bubbled with gaseous ozone generated from dried oxygen with an ozone generator (3S-A, Tonglin Technology, China). The aqueous ozone concentration was detected continuously until it reached a steady state. The steady ozone concentration in water was controlled through adjusting the electric current of the ozone generator. In this study, an aqueous ozone concentration of 3.0 mg/L was used. About 200 mL of raw water was quickly mixed with 200 mL of the ozone-bearing water in a glass reactor. Thus, the initial ozone concentration in the actual reaction was approximately 1.5 mg/L, which was the same as the concentration of ozone used in the waterworks. Then, the reactor was sealed and magnetically stirred at room temperature. After each required contact time, the residual ozone concentrations were measured immediately to ensure that there was ozone residual and then the unreacted ozone was stripped off with nitrogen gas for 10 min to quench the reaction before other analyses. The raw water without preozonation was diluted with the same amount of Milli-Q water to have the same concentration as the preozonated samples. The concentration of every index of raw water was referred to the concentration in such diluted raw water.

### 1.4 Analytical methods

Indigo method by Bader and Hoigne was used to measure the concentration of ozone in water<sup>[25]</sup>. Free chlorine and combined chlorine residuals were measured by DPD/FAS titration<sup>[26]</sup>. UV<sub>254</sub> was analyzed by a spectrophotometer (DR/4000U, Hach, USA). DOC was de-

termined as nonpurgeable organic carbon (NPOC) by total organic carbon (TOC) analyzer (Multi N/C 3100, analytik Jena, Germany). Bromide and bromate in aqueous samples were detected by ion chromatography (ICS1500 equipped with AS23 analytical column, ASRS300-4mm suppressor and conductivity detector, Dionex, USA).

The THMFP and HAAFP were determined by gas chromatography with electron capture detection (GC/ECD) according to USEPA method 551.1 and 552.2 with minor modifications<sup>[27]</sup>. All the samples were adjusted to pH = 7 ± 0.2 by the addition of 0.1 mol/L H<sub>2</sub>SO<sub>4</sub> or NaOH. Then a NaClO solution was added with a mass ratio of 5 : 1 (Cl/DOC) to ensure excessive free chlorine residue of 3—5 mg/L. The neutralized solutions were buffered by a phosphate solution prior to the incubation at (25 ± 2) °C. After the chlorination period of 72 h, all the samples were quenched by adding enough NH<sub>4</sub>Cl. Four THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) were extracted with 3 mL methyl tert-butyl ether (MTBE, HPLC grade, Sigma-aldrich Chemicals, Canada). THMFP was the sum of mass concentrations of the four THM species. Five HAAs (monochloro-, dichloro-, trichloro-, monobromo- and dibromoacetic acid) were analyzed by liquid-liquid extraction with methyl tert-butyl ether followed by derivatization with acidic methanol. HAAFP was the sum of mass concentrations of the five HAAFP species.

## 2 Results and discussion

### 2.1 Effects of treatment parameters on the formation of DBPs

The experiments were carried out according to the conditions listed in Tab. 2. UV<sub>254</sub>, DOC, bromate concentration, THMFP and HAAFP of each sample were tested. All the measurements were carried out on three parallel sample sets. The results are listed in Tab. 3.

**Tab. 3 Orthogonal experimental results**

Entry	A	B	C	Removal ratio of UV <sub>254</sub> / %	Removal ratio of DOC / %	Bromate / (μg·L <sup>-1</sup> )	THMFP / (μg·L <sup>-1</sup> )	HAAFP / (μg·L <sup>-1</sup> )
1	1	1	1	45.45	11.96	BDL	237.160 ± 1.136	139.492 ± 3.470
2	1	2	2	31.82	13.04	1.829 ± 0.032	268.357 ± 2.259	174.401 ± 2.201
3	1	3	3	59.09	9.78	2.809 ± 0.017	183.963 ± 5.453	162.505 ± 2.449
4	2	1	2	45.45	15.49	BDL	115.383 ± 2.046	109.938 ± 3.655
5	2	2	3	63.64	13.59	2.225 ± 0.005	127.974 ± 0.716	65.087 ± 3.326
6	2	3	1	59.09	10.60	4.510 ± 0.069	112.294 ± 1.490	89.688 ± 4.148
7	3	1	3	27.27	14.13	1.345 ± 0.026	72.993 ± 3.114	61.383 ± 2.179
8	3	2	1	54.55	17.93	6.403 ± 0.010	67.897 ± 3.615	67.199 ± 0.935
9	3	3	2	59.09	12.23	6.601 ± 0.013	81.980 ± 1.861	87.309 ± 1.561

As seen in Tab. 3, preozonation has a great contribution to the removal of  $UV_{254}$ . The removal ratio under different treatment conditions ranges from 27.27% to 63.64% with an average of 49.49%. However, DOC of the effluent under each treatment parameter does not decrease too much, the average removal ratio of which is only 13.19%. The results indicate that ozone can oxidize the organic matter, in particular the compounds having double bonds or aromatic structures that determine the value of  $UV_{254}$ . The observed impact of preozonation on DOC concentration was less because of the partial oxidation of NOM to other intermediate<sup>[28]</sup>. Ozone reacts with aromatic fraction of NOM, resulting in a significant decrease in  $UV_{254}$  during preozonation<sup>[29]</sup>. Preozonation converts DOC from hydrophobic to hydrophilic organic carbon without significant removal of DOC<sup>[30]</sup>.

10.5  $\mu\text{g/L}$  bromate formed in preozonated water under regular condition ( $O_3$  dosage 1.5  $\text{mg/L}$ , reaction time 10 min)<sup>[21]</sup>. In this experiment, the most bromate concentration was only 6.6  $\mu\text{g/L}$ , which was even below the detection limit in the effluents of Entry 1 and 4. This indicates that the combination of changes in each treatment parameter can minimize or eliminate the bromate formation effectively.

When bromide is present in source water, it may be oxidized by ozone to form hypobromite ion ( $OBr^-$ ) and then further oxidized to form bromate ( $BrO_3^-$ ). In water,  $OBr^-$  exists in equilibrium with HOBr as an acid/base conjugate pair in which the speciation depends on the pH. The reaction of  $O_3$  with HOBr is negligible ( $k \leq 0.013 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ ), while with  $OBr^-$  ( $k = 330 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ ) is the main reaction forming bromate<sup>[31]</sup>. However, HOBr may react with NOM to form brominated organic compounds. Fig. 2 shows the distributions of THMFP and HAAFP of each water sample.

The brominated THMFPs, especially  $CHBr_3$  formation potential, were dominant in all the water samples in this study, and the chloroform formation potential accounted for only a small amount of THMFP, as can be seen in Fig. 2(a). The result was opposite to water with a low bromide concentration, in which chloroform was the main THM<sup>[32]</sup>. In Fig. 2(b), dichloroacetic acid (DCAA) formation potential was the predominant HAAFP in all the water samples. However, dibromoacetic acid (DBAA) formation potential also accounted for a considerable part, which was higher than trichloroacetic acid (TCAA) formation potential in several water samples. The results showed that bromate formation was prevented

under different treatment parameters. At the same time, HOBr may accumulate in the preozonated water and react with NOM to form more brominated DBPs which may be more harmful. This means that when treatment parameters are changed to minimize bromate formation, the formation of regular DBPs such as THMs and HAAs must be considered comprehensively.

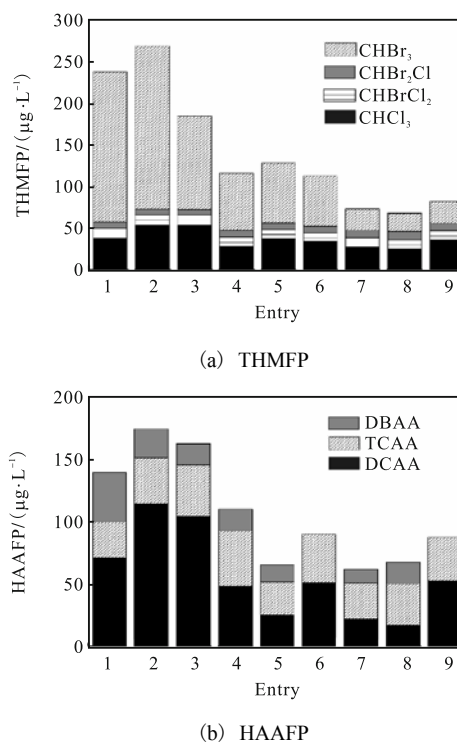


Fig. 2 Distributions of THMFPs and HAAFPs

## 2.2 Optimal combination of treatment parameters

According to the theory of orthogonal design, the optimal project does not necessarily exist in the test project in orthogonal table, and it is determined by calculating analysis. Since the removal ratio of  $UV_{254}$  and DOC under different treatment conditions did not change too much, visual analysis was carried out only on the formation of DBPs by Minitab 15. 1. The results are shown in Tab. 4.

In Tab. 4,  $K_i$  ( $i = 1, 2, 3$ ) represents the sum of corresponding experimental items of level  $i$  in  $j$  column, reflecting the influence on the formation of DBPs when  $j$  is at  $i$  level; and  $k_i$  ( $i = 1, 2, 3$ ) is the average of corresponding experimental items of level  $i$  in  $j$  column. The variance of each factor ( $R$ ) denotes the range among  $k_i$ , reflecting the importance of the corresponding experimental items: the higher the  $R$  value, the more important the corresponding factor.

By calculating the mean indicator  $k_i$  and the variance of mean indicator  $R$  of treatment parameters for different

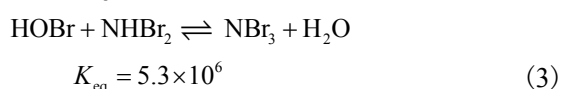
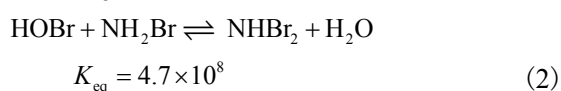
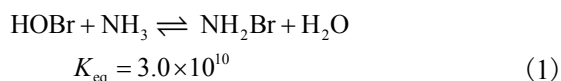
levels, the following studies can be carried out: (1) Identifying the optimal level of each treatment parameter and obtaining the optimal combination project; (2) Ordering the parameters in accordance with their significance. The greater the variance is, the more important the parameter will be.

**Tab. 4 Visual analysis of DBPs formation**

Parameter	Range (Bromate)/( $\mu\text{g} \cdot \text{L}^{-1}$ )			Range (THMFP)/( $\mu\text{g} \cdot \text{L}^{-1}$ )			Range (HAAFP)/( $\mu\text{g} \cdot \text{L}^{-1}$ )		
	A	B	C	A	B	C	A	B	C
$K_1$	4.638	1.345	10.913	689.48	425.54	417.35	476.40	310.81	296.38
$K_2$	6.735	10.457	8.430	355.65	464.23	465.72	264.71	306.69	371.65
$K_3$	14.349	13.920	6.379	222.87	378.24	384.93	215.89	339.50	288.98
$k_1$	1.5460	0.4483	3.6377	229.83	141.85	139.12	158.80	103.60	98.79
$k_2$	2.2450	3.4857	2.8100	118.55	154.74	155.24	88.24	102.23	123.88
$k_3$	4.7830	4.6400	2.1263	74.29	126.08	128.31	71.96	113.17	96.33
$R$	3.2370	4.1917	1.5133	155.54	28.66	26.93	86.84	10.94	27.55
Factor order	B>A>C			A>B>C			A>C>B		
Optimal level	A <sub>1</sub>	B <sub>1</sub>	C <sub>3</sub>	A <sub>3</sub>	B <sub>3</sub>	C <sub>3</sub>	A <sub>3</sub>	B <sub>2</sub>	C <sub>3</sub>

As seen from  $R$  in Tab. 4, it could be deduced that the influence of the factors on the formation of bromate is in the order of pH > contact time > ammonia concentration. For the purpose of the minimization of bromate formation, the optimal treatment conditions, namely  $k_i$  of each parameter was the lowest, were that the contact time was 5 min, pH value was 6 and ammonia concentration was 1.0 mg/L.

pH reduction influences bromate formation by shifting the HOBr/OBr<sup>-</sup> equilibrium to HOBr and altering the oxidant exposures (ozone and ·OH radicals). The shift of the equilibrium toward HOBr slows down its oxidation by ozone molecule since only OBr<sup>-</sup> can be oxidized by O<sub>3</sub><sup>[13]</sup>. pH reduction is an effective way to control bromate formation, since the hydroxyl radical (·OH) is more reactive with bromide than the ozone molecule at low pH, and the concentration of ·OH in the reactor would be less at high pH<sup>[33]</sup>. It has been reported that the formation amount of BrO<sub>3</sub><sup>-</sup> decreased by 50%—63% when pH value decreased one unit.<sup>[12]</sup> Ammonia can inhibit the formation of bromate in preozonated drinking water by reacting with free bromine (HOBr/OBr<sup>-</sup>), an intermediate in bromate formation, to form bromamines. The reaction can be described as<sup>[34]</sup>



Bromamines do not participate in bromate formation, but they will decay due to autonomous decomposition

and the reaction with ozone and hydroxyl radicals<sup>[34]</sup>. Preozonated water containing ammonia should therefore yield lower bromate concentrations than ammonia-free water. Previous research reported that bromate formation increased with the extension of the reaction time<sup>[24]</sup>, but the rate of bromate formation gradually slowed after five-minute contact<sup>[35]</sup>. The results indicate that bromate is generated mainly in the initial stage of the preozonation which is a critical period for bromate control.

Taking THMFP and HAAFP into consideration, however, contact time is the main factor affecting the formation amount of THM and HAA. Compared with contact time, pH and ammonia concentration have less effects on the formation of THM and HAA. In order to control the formation of THMs, the optimal conditions were that the contact time was 20 min, pH value was 9 and ammonia concentration was 1.0 mg/L. In order to control the formation of HAAs, the optimal conditions were that the contact time was 20 min, pH value was 7.5 and ammonia concentration was 1.0 mg/L.

The role of ozone for the removal of THMs and HAAs mainly manifests in two aspects. One is to oxidize the precursors of DBPs. The other is to react with NOM and decompose organic matter to form precursors of new DBPs. Changes in the concentration of DBPs are related to the balance between these two effects. Ozone decomposes organic matter to aldehydes which are precursors of brominated THMs and HAAs. The accumulation of these intermediates in water results in the increase of the THMFP and HAAFP concentrations. With the extension of contact time, aldehydes will be decomposed by ozone, and consequently the concentrations of THMFP and HAAFP in water will be reduced<sup>[36, 37]</sup>.

### 2.3 Influence degree analysis of treatment parameters

In order to investigate the influence degree of the treatment parameters on the formation of DBPs, variance analysis was performed with Minitab 15. 1 to study the

orthogonal experimental results listed in Tab. 3, as shown in Tab. 5. If the *P* value is very low (lower than 0. 05 in this study), the individual terms in the model have a significant effect on the response.

Tab. 5 Variance analysis of DBPs formation

DBPs	Sources of variance	Degree of freedom	Sum of squares	Mean square	<i>F</i>	<i>P</i>	Significance
Bromate	A	2	17.408 2	8.704 1	41.36	0.024	significant
	B	2	28.127 9	14.0640	66.83	0.015	significant
	C	2	3.436 6	1.718 3	8.17	0.109	
	Error	2	0.420 9	0.210 4			
	Total	8	49.393 6				
THMFP	A	2	38 533. 1	19 266.5	24. 97	0.039	significant
	B	2	1 236. 5	618.3	0.80	0.555	
	C	2	1 102.0	551.0	0.71	0.583	
	Error	2	1 543.0	771.5			
	Total	8	42 414.6				
HAAFP	A	2	12 784.2	6 392.1	31.88	0.030	significant
	B	2	213.0	106.5	0.53	0.653	
	C	2	1 395.0	697.5	3.48	0.223	
	Error	2	401.0	200.5			
	Total	8	14 793.2				

The checking level was set at 0. 05 in this study, and it can be concluded from Tab. 5 that pH has the most significant influence on the minimization of bromate formation, followed by the contact time and ammonia concentration. This is not surprising because pH affects both the concentration of hydroxyl radicals and the speed of ammonia reacting with bromine. An important feature of pH reduction is the increased ozone stability. As a consequence, for a certain ozone exposure, the ·OH radical exposure decreases with decreasing pH<sup>[38]</sup>. On the other hand, ammonia reacts with bromine most rapidly at pH = 9, which is the mid-point of the pKa values of the ammonium ion (pKa = 9.3) and HOBr (pKa = 8.8). When pH values range from 6 to 8, calculations suggest that it may take up to several seconds for ammonia to react with bromine<sup>[39]</sup>. As the reaction between ammonia and free bromine slows down, more free bromine will be allowed to proceed to form bromate. Thus, pH has the most significant influence on bromate formation among the three factors.

For the formation of THMs and HAAs, however, contact time has a significant influence on the control of formation of both THMs and HAAs. The influences of pH and ammonia concentration are not so significant. The results are the same as the analysis in Section 2.2.

Contact time, pH and ammonia concentration have different effects on the formation of bromate, THMFP

and HAAFP. In practical preozonation process of waterworks, the selection of treatment parameters must be taken into account comprehensively. In order to oxidize NOM and inactivate microorganisms more effectively, it is appropriate to make preozonation contact time 20 min. For the minimization of bromate formation, pH of the raw water could be adjusted to 6.0. Previous study showed that the effective ammonia dose for BrO<sub>3</sub><sup>-</sup> reduction was limited to 200 µg/L and further increase in ammonia addition did not enhance the BrO<sub>3</sub><sup>-</sup> minimization<sup>[14]</sup>. The results in this study also indicated that the influence of ammonia concentration is not so significant for both the minimization of bromate and the formation of THMs and HAAs. Taking the cost of water treatment plant into consideration, a certain concentration of ammonia could be added into the water when the concentration of bromide in the raw water is even higher to strengthen the minimization effect. As seen in Tab. 3, when contact time was 20 min, pH value of the raw water was 6.0 and ammonia added into the raw water was 1 mg/L, only 1.345 µg/L bromate formed, which was far below the MCL set by GB 5749—2006. When the raw water quality is acidic, the rate of ozone decomposition is slower, and therefore the concentration of ozone in the water is higher. It is favorable to remove precursors of THMs and HAAs due to the larger *ct* value<sup>[40]</sup>. Thus, both the removal of formation potential of DBPs and the mini-

mization of bromate generation can be strengthened. Chemical and biological safety of drinking water can also be guaranteed under such treatment conditions.

### 3 Conclusions

pH had the most significant influence on the minimization of bromate formation. The influence of factors on the formation of bromate is in order of pH > contact time > ammonia concentration. For the purpose of the minimization of bromate formation, the optimal treatment conditions were that the contact time was 5 min, pH value was 6 and ammonia concentration was 1.0 mg/L.

For the formation of THMs and HAAs, contact time had a significant influence. The influences of pH and ammonia concentration were not so significant.

For the purpose of controlling the formation of THMs, the optimal conditions were that the contact time was 20 min, pH value was 9 and ammonia concentration was 1.0 mg/L. In order to control the formation of HAAs, the optimal conditions were that the contact time was 20 min, pH value was 7.5 and ammonia concentration was 1.0 mg/L.

In practical preozonation process of waterworks, the selection of treatment parameters must be taken into account comprehensively. In order to oxidize NOM and inactivate microorganisms more effectively, it is appropriate to make preozonation contact time 20 min. For the minimization of bromate formation, pH of the raw water could be adjusted to 6.0. A certain concentration of ammonia could be added into the water when the concentration of bromide in the raw water is even higher to strengthen the minimization effect. Thus, both the removal of formation potential of DBPs and the minimization of bromate generation can be strengthened. Chemical and biological safety of drinking water can also be guaranteed under such treatment conditions.

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