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# The formation of disinfection by-products in water treated with chlorine dioxide

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## Abstract

In this study, chlorine dioxide ( $\text{ClO}_2$ ) was used as an alternative disinfection agent with humic acid as the organic precursor in a natural aquatic environment. The major topics in this investigation consisted of the disinfection efficiency of  $\text{ClO}_2$ , the formation of disinfection by-products (DBPs), and the operating conditions. The results indicated that the pH value (pH 5–9) did not affect the efficiency of disinfection while the concentration of organic precursors did. The primary DBPs formed were trihalomethanes (THMs) and haloacetic acids (HAAs). The distribution of the individual species was a function of the bromide content. The higher the  $\text{ClO}_2$  dosage, the lower the amount of DBPs produced. The amount of DBPs increased with reaction time, with chlorite ions as the primary inorganic by-product. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:*  $\text{ClO}_2$ ; Organic precursors; DBPs; Alternative disinfectant; THMs; HAAs

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## 1. Introduction

The extensive pollution of water resources during recent years has induced an elevation in the chlorination level in water treatment. The number of many DBPs, including trihalomethanes (THMs) [1,2], haloacetic acids (HAAs) [3–6], haloacetonitrile

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(HANs) [3,7,8], and haloketon (HKs) [3] has also increased as a result of the increased chlorination in the water treatment process. The occurrence of these DBPs in drinking water has been reported at 35 US water treatment facilities [9] and at 35 Utah water treatment facilities [10]. These DBPs are potential carcinogenic and teratogenic substances [8,11–15]. In view of the potential threat to human health caused by halogenated compounds present in drinking water, countries all over the world have placed special emphasis on this question and studies on decreasing the amount of halogenated compounds in drinking water are increasing day by day. This problem triggered the search for an alternative disinfectant [16–18] to prevent or reduce the formation of chlorinated DBPs [19,20]. As a powerful substitute or a supplemental disinfectant for chlorination,  $\text{ClO}_2$  [21,22] has caused people to follow studies on its use and effectiveness with interest.  $\text{ClO}_2$  is a strong disinfectant that is effective over a wide pH range [18], when distributed evenly throughout a water supply system [23].  $\text{ClO}_2$  can eliminate bad odor [18,24] and oxidize ferrous, manganous ions in underground water [18,25]. A smaller dosage and less reaction time is required for  $\text{ClO}_2$  to produce the same disinfection effect. A  $\text{ClO}_2$  manufacturing system is also easy to install, operate and maintain. Because of these characteristics, chlorine dioxide was investigated as one of the promising substitute disinfectants for chlorine.

Although  $\text{ClO}_2$  is widely used in the drinking water in Europe, the US and other countries all over the world, it has not been used in water treatment facilities in Taiwan as yet. Previous studies on  $\text{ClO}_2$  focused on the disinfection efficiency for harmful microorganism removal [22,26–28], bad odor control [18,24] and ferrous, manganous ions removal [18,25]. Few investigations have looked into DBPs formation. Most studies paid more attention to the trihalomethanes on disinfection by-products formation [21,29] compared with chlorine when  $\text{ClO}_2$  was used as an alternative disinfectant. In addition to disinfection efficiency, the objective of this study was to deeply investigate DBPs formation during water treatment and the influence of operating parameters using  $\text{ClO}_2$  as an alternative disinfectant to treat simulated raw water. In these experiments, humic acid was used to mimic natural aquatic organic matter.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. The preparation of $\text{ClO}_2$

Chlorine dioxide was produced from sodium chlorite activated by an HCl 10% solution [30]. The chlorine dioxide gas was driven off using air bubbling and absorbed into a distilled water-cooled ice bath. The obtained  $\text{ClO}_2$  solution was placed in brown bottles and kept in a refrigerator in darkness. The concentration was measured with the *N,N*-diethyl-*p*-phenylenediamine (DPD) methods just before application.

#### 2.1.2. Organic precursors

Humic acid (Aldrich Chem sodium salt) was used as the source of organic carbons in the artificial water samples to mimic the organic precursors found in aquatic environ-

ments. One gram of humic acid was dissolved in distilled water to produce a liter solution. The pH value was adjusted to 12.0 by adding 6N NaOH. It was then filtered using 0.45  $\mu\text{m}$  filter paper (MFS, Membrane Filters Cellulose Acetate) and stored in brown glass bottles. The concentration was measured for dissolved organic carbon (DOC) just before application to ensure the accuracy.

### 2.1.3. Microorganisms

Total coliform ( $1.5 \times 10^5$ – $3.2 \times 10^5$  MPN/ml) was used as the microorganism indicator. It was isolated from the Drought River, which is the primary pollution source of the domestic wastewater in Taichung, Taiwan, and was determined by the colony counting method on an Endo agar medium.

Endo agar medium: albumin pepton 10 g, beef extract 5 g, lactose 10 g, yeast extract 5 g, agar 20 g,  $\text{Na}_2\text{SO}_3$  5 g,  $\text{K}_2\text{HPO}_4$  3.5 g, 5% fuchsin ethanol solution 20 ml, distilled water 1000 ml, pH 7.2–7.4, sterilized at 0.75 kg/cm<sup>2</sup> for 20 min.

## 2.2. Procedure

In the disinfection efficiency study, various concentrations of  $\text{ClO}_2$ , pH value, humic acid concentration, and bromide ions were controlled and batch disinfection was performed on the various *T. coli* concentration in a 300-ml BOD bottle reactor with the stirring speed set at 100 rpm. The reaction time was set at 0–30 min (shown in Table 1).

Operational variables in the DBP formation study depended on several important factors, DBPs formed by the chlorine disinfection process, organic precursor concentration, quality of the organic [31–33], pH [34–36], chlorine dose [34,35], and the bromide ion concentration of the water [36–40]. In the DBP study, 5 ml of phosphate buffer solution and a proper amount of  $\text{ClO}_2$ , humic acid under pH and bromide ion control parameters, were added to each BOD bottle reactor (the ranges of concentration were described earlier). De-ionized water was added to fill the bottles, The bottles were then kept in a 20°C incubator. The bottles were sampled at different time intervals (0, 0.5, 1, 1.5, 2, 4, 8, 16, 24, 48, 96, 120, 168 h) over a total of 7 days. Three bottles were collected for analysis. The flow charts for these bottles are shown in Fig. 1. The samples were analyzed for  $\text{ClO}_2$  residual concentration immediately. A 10 ml portion from the 0.2  $\mu\text{m}$  filtrate was collected to analyze the inorganic DBPs ( $\text{Cl}^-$ ,  $\text{ClO}_2^-$ ,  $\text{Br}^-$  and  $\text{ClO}_3^-$ ) using Ion Chromatography (DIONEX, series 4500, column AS-12A, 4 mm

Table 1  
The parameters in disinfection efficiency experiments

Parameters in reaction	Controlled conditions	Unit
<i>T. coli</i>	$1.5 \times 10^5$ – $13.2 \times 10^5$	MPN/100 ml
$\text{ClO}_2$	0.1–5	mg/l
pH	5–9	
Humic acid	0.1–20	mg-DOC/l
$\text{Br}^-$	0.1–2	mg- $\text{Br}^-$ /l
Reaction time	0–30	min

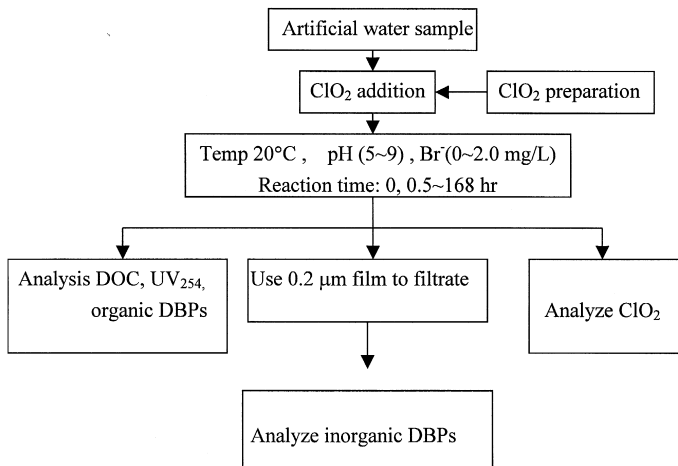


Fig. 1. Experimental procedure of DBPs.

(10–12), P/N 46034). To the remaining samples, 1 g of  $\text{Na}_2\text{S}_2\text{O}_3$  was added to terminate the reaction. One portion of this sample was used for DOC analysis using total organic carbon analyzer (O.I. Model 700). The THM sample was prepared in a 40-ml brown glass bottle (with Teflon ring and screw-on cap) with 100 mg  $\text{NH}_4\text{Cl}$  as the preservative. Water was added to the above solution to fill the bottle. Samples were capped with teflon-lined seals, returned to the laboratory in a cooler and stored in a cold room until analyzed. The analytical methods followed USEPA Standard Method 501.2. The pH was adjusted to pH 4.5 in the field and samples were extracted with normal pentane, containing dibromomethane and 1,2-dibromopropane as an internal standard. THMs were analyzed using a HP5890II plus gas chromatograph, equipped with an electron capture detector (GC-ECD), a one-column injector and a J & W DB-5 capillary column. The HAAs water samples were prepared by adding 150 ml  $\text{NH}_4\text{Cl}$  per 100 ml of the sample with the pH adjusted to below 0.5. Samples were extracted with methy-*tert*-butylether (MTBE) esterized by diazomethane and analyzed using GC-ECD based on USEPA Standard Method 502.2.

### 2.3. Quality control

All samples were collected in duplicate with control samples included for all-target analytes. All DBPs methods incorporated surrogate internal standards and quantification was based on response factors established by multi-level calibration with fortified samples analyzed under identical conditions. For the THMs, raw water samples (matrix spikes;  $n = 12$ ) were analyzed at a fortification level of  $5 \mu\text{g}/1$  (chloroform =  $25 \mu\text{g}/1$ ). The overall recovery was  $99.1\% \pm 3.6\%$ . The HAAs method precision was estimated at  $\pm 20\%$ . The mean recovery of HAAs was typically  $> 93\%$  as estimated from the recovery of the added MBBA internal standard. DBPs identified by GC-ECD were confirmed by GC-MS.

### 3. Results and discussion

#### 3.1. Disinfection efficiency of $\text{ClO}_2$

##### 3.1.1. Effect of $\text{ClO}_2$ concentration

For concentrations in the order of 1–5 mg/l of  $\text{ClO}_2$ , only 1–2 min was required to kill the germs. The residual colony ratio ( $N/N_0$ ) was reduced close to 0. However, with a  $\text{ClO}_2$  level lower than 0.1–0.5 mg/l, a substantial number of colonies remained after 30 min. As shown in Fig. 2, the higher the level of  $\text{ClO}_2$ , the lower the residual colony ratio. By plotting the  $k$  constant of Chick's law [ $\ln(N/N_0) = -kt$ ] into the  $\text{ClO}_2$  concentration, as shown in Fig. 3, the  $k$  value nearly reached its maximum above 1.0 mg/l of  $\text{ClO}_2$ , and the speed of reaction also reached a maximum level.

##### 3.1.2. Effect of pH value

To understand the effect of pH value on the disinfection efficiency, only 0.5 mg/l of  $\text{ClO}_2$  was used. In 30 min, the residual colony dropped to 15, 7, and 14 MPN/ml from an initial  $1.5 \times 10^5$  MPN/ml application at pH 5, 7, and 9 and the  $k$  values were 0.4214, 0.4208, and 0.4241 1/s respectively. This indicated that the pH value was not an important factor affecting the  $\text{ClO}_2$  disinfection procedure, as shown in Fig. 4. This result matched the results reported in the literature [41,42].

##### 3.1.3. Effect of organic matters

Regarding the organic precursors identified from natural aquatic river systems, humic acid (0–10 mg-DOC/l) was used for the disinfection test. It was found that the higher the concentration of humic acid, the larger the  $N/N_0$  ratio. The suggested reason was that when the concentration of organic precursor was raised, it would react with more functional groups. This decreased the possibility of  $\text{ClO}_2$  destroying *E. coli* and dropped the disinfection efficiency. As shown in Fig. 5, this result indicated that the organic precursor concentration was an important factor that influenced the efficacy of disinfection.

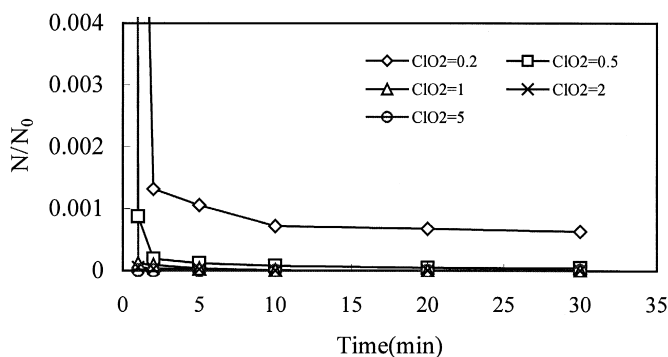


Fig. 2. Residual colony ratio at different  $\text{ClO}_2$  level ( $N_0 = 1.67 \times 10^5$  MPN/ml, DOC = 10.0 mg/l, pH = 7).

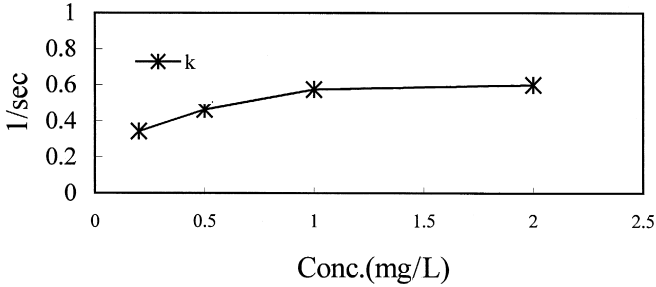
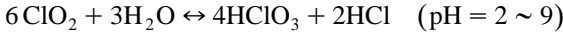
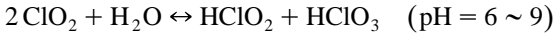


Fig. 3. The variation of *k* value at different ClO<sub>2</sub> level (pH = 7).

3.2. Disinfection by-products

In order to simulate higher organic levels, such as after rainstorms, DBP formation was studied under high levels of ClO<sub>2</sub> (15.0, 30.0 mg/l) instead of normal levels (0.1–5 mg/l) with different concentrations of organic precursors (5 mg-DOC/l, 10 mg-DOC/l) at neutral (pH = 7) and slightly alkaline (pH = 9) conditions. The primary organic DBPs formed were THMs and HAAs. These organic DBPs will be discussed in detail later and the distribution of individual species varied with the bromide ion content. In the portion of inorganic DBPs formation, shown in Fig. 6, chlorite (ClO<sub>2</sub><sup>-</sup>), chlorate (ClO<sub>3</sub><sup>-</sup>), chloride (Cl<sup>-</sup>) were the principal DBPs. This phenomenon could be explained by the following basic reaction equations when chlorine dioxide was in water:



From Fig. 6, we found that inorganic species increased with the dosage (mg-ClO<sub>2</sub> added/mg initial DOC).

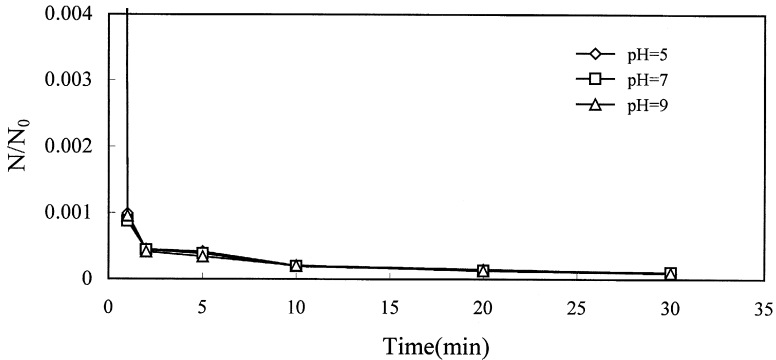


Fig. 4. Residual colony ratio at different pH value (*N*<sub>0</sub> = 1.67 \* 10<sup>5</sup> MPN/ml, ClO<sub>2</sub> = 0.5 mg/l).

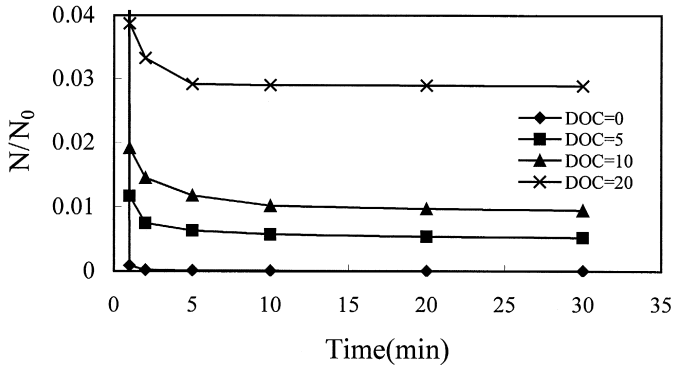


Fig. 5. Residual colony ratio at different humic acid level ( $N_0 = 1.67 \times 10^5$  MPN/ml,  $\text{ClO}_2 = 0.5$  mg/l, pH = 7).

### 3.2.1. Effect of pH value

From Table 2,  $\text{ClO}_2/\text{DOC}$  expressed the ratio of  $\text{ClO}_2$  consumption to DOC elimination and TTHMs/DOC (or THAAs/DOC) separately expressed the ratio of TTHMs (or THAAs) final production amount to DOC elimination amount. The test data from Table 2 indicates that there was no great difference under neutral or alkaline conditions in terms of  $\text{ClO}_2$  consumption, DOC elimination ratio, THMs and HAAs formation. It was supposed that the pH value would not affect the formation of DBPs by  $\text{ClO}_2$ , but a neutral condition did slightly favor DBP formation when compared with TTHMs/DOC or THAAs/DOC. In the individual species,  $\text{CH}_3\text{Cl}$  was the principal disinfection by-product among TTHMs, and it was profitable to produce the TCAA at pH = 7 and produce the DCAA at pH = 9.

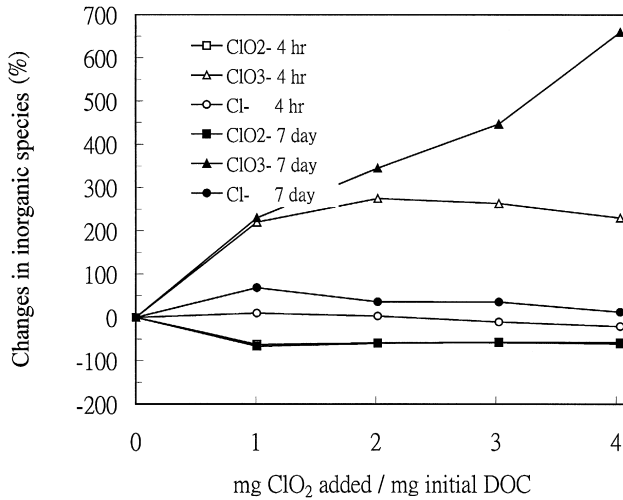


Fig. 6. Variation of inorganic DBPs (HA = 5 mg-DOC/l, pH = 7).

Table 2  
Effect of pH value (DOC = 10 mg/l, ClO<sub>2</sub> = 15 mg/l)

	pH = 7	pH = 9
ClO <sub>2</sub> /DOC <sup>a</sup>	1.89	2.5
TTHMs (μg/l)	2.8	2.6
TTHMs/DOC (μg/mg) <sup>b</sup>	0.62	0.74
THAAs (μg/l)	27.1	26.2
THAAs/DOC (μg/mg) <sup>c</sup>	6.02	7.5
Primary species	CH <sub>3</sub> Cl among TTHMs; TCAA (at pH 7) and DCAA (at pH 9) among THAAs	

<sup>a</sup>Ratio of ClO<sub>2</sub> consumption to DOC elimination amount.

<sup>b</sup>Ratio of TTHMs final production amount to DOC elimination amount.

<sup>c</sup>Ratio of THAAs final production amount to DOC elimination amount.

### 3.2.2. Effect of ClO<sub>2</sub> dosage

Comparisons between the two levels of ClO<sub>2</sub> (15 mg ClO<sub>2</sub>/l, 30 mg ClO<sub>2</sub>/l), in Fig. 7 show that the higher the dosage of ClO<sub>2</sub>, the higher the DOC elimination ratio. This result was similar to that in the literature by Lykins and Griese [21] and Drenat and Pouillot [41]. In the DBPs formation portion, the amount of TTHMs and THAAs formed faster in the first 24 h and the amounts were 81%–88% of the entire amount in 7 days reaction time. After the initial 24-h stage, the formation of DBPs was sluggish, as shown in Figs. 8 and 9. The greater the increased dosage of ClO<sub>2</sub>, the greater the decrease in the amount of DBPs (TTHMs, THAAs) as shown in Table 3. The possible cause is that an elevated ClO<sub>2</sub> level might increase the chances of interaction with active radicals

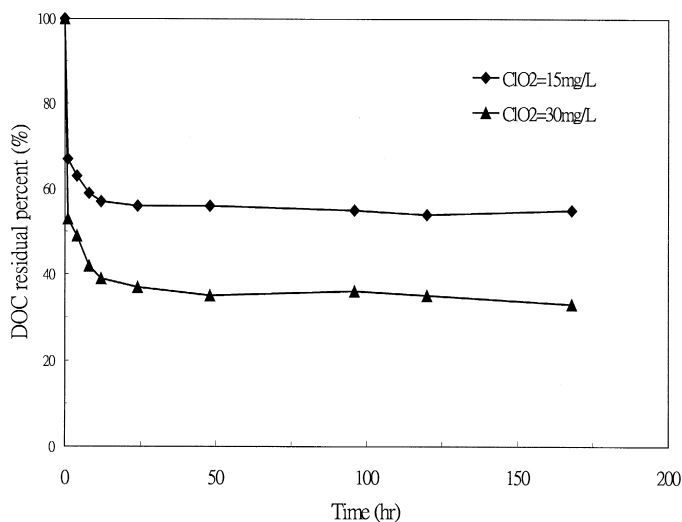


Fig. 7. Variation of DOC at different ClO<sub>2</sub> dosage (pH = 7, DOC = 10 mg/l).



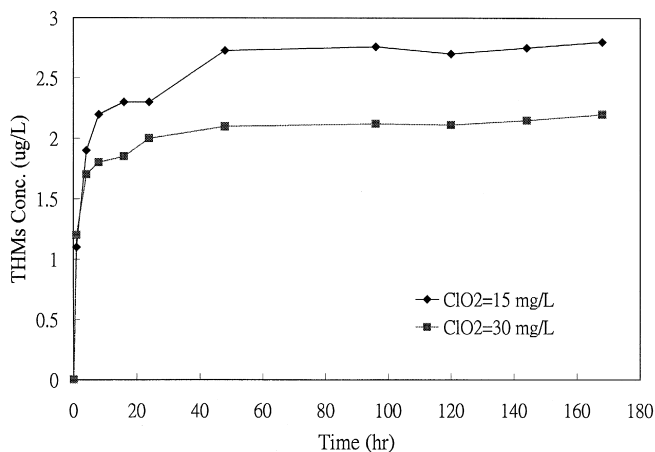


Fig. 8. Residual percent of TTHMs at different ClO<sub>2</sub> dosage (pH = 7, DOC = 10 mg/l).

(–OH, –OCH<sub>3</sub>) on humic acid and it inhibited the halo-organic disinfection by-products formation. The other possibility was that it was favored to proceed directly the oxidation reaction not chlorination reaction under the higher chlorine dioxide dosage condition.

### 3.2.3. Effect of concentration of organic precursors

In this portion, we chose two dosages (5.0 mg-DOC/l, 10 mg-DOC/l) to simulate the organic precursors in raw water under the ClO<sub>2</sub> = 15 mg/l, pH = 7 condition. In Table 4, there is a higher ratio of ClO<sub>2</sub>/DOC under higher organic precursor concentration and the results indicated that the amount of DOC removal increased with the increasing concentration of organic precursors. The reason was that when the organic

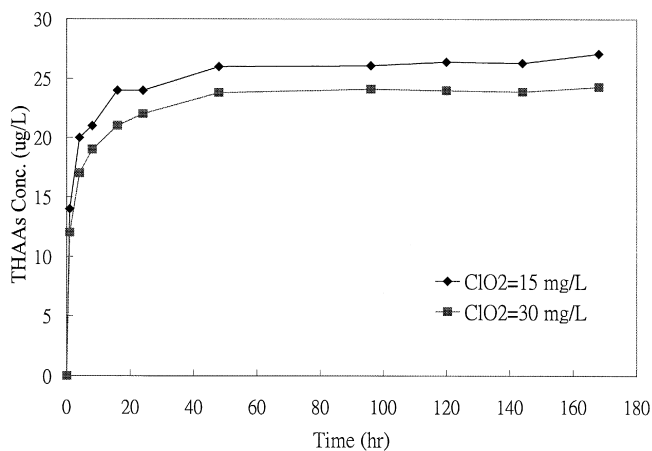


Fig. 9. Residual percent of THAAs at different ClO<sub>2</sub> dosage (pH = 7, DOC = 10 mg/l).

Table 3  
Effect of ClO<sub>2</sub> dosage (DOC = 10 mg/l, pH = 7)

	ClO <sub>2</sub> = 15 mg/l	ClO <sub>2</sub> = 30 mg/l
ClO <sub>2</sub> /DOC <sup>a</sup>	1.89	7.84
TTHMs (μg/l)	2.8	2.2
TTHMs/DOC (μg/mg) <sup>b</sup>	0.62	0.33
THAAs (μg/l)	27.1	24.2
THAAs/DOC (μg/mg) <sup>c</sup>	6.02	3.61
Primary species	CH <sub>3</sub> Cl among TTHMs; TCAA (low dosage) and DCAA (high dosage) among THAAs	

<sup>a</sup>Ratio of ClO<sub>2</sub> consumption to DOC elimination amount.

<sup>b</sup>Ratio of TTHMs final production amount to DOC elimination amount.

<sup>c</sup>Ratio of THAAs final production amount to DOC elimination amount.

precursor concentration was elevated, it could provide the opportunity for a reaction between the organic precursors and chlorine dioxide and raised the removal ratio of DOC under appropriate amounts of ClO<sub>2</sub>. The amount of disinfection by-products (TTHMs, THAAs) formation was similar to the Cl<sub>2</sub> disinfection process. Disinfection by-products increased with the organic precursor concentration in the water. However, the total amount of THMs and HAAs per unit amount of eliminated DOC (TTHMs/DOC and THAAs/DOC) became less with increasing concentrations of organic precursors.

#### 3.2.4. Effect of bromide ion

Following the procedures described earlier, bromide ions (0–2.0 mg Br<sup>-</sup>/l) were added to observe the effect on treatment. As expected, the DOC elimination ratio, TTHMs, THAAs, TTHMs/DOC, THAAs/DOC, ClO<sub>2</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> levels were not affected and Br<sup>-</sup> was the additional inorganic by-product formed (positively related to the amount added). However, the distribution of organic by-products changed with the bromide ion level: when it was less than 0.5 mg/l. The distribution among THMs was in the order of CHCl<sub>3</sub> > CHBrCl<sub>2</sub> > CHBr<sub>2</sub>Cl > CHBr<sub>3</sub>. Among the HAAs, both TCAA, DCAA and MCAA outnumbered MBAA and DBAA. When the bromide level was

Table 4  
Effect of the concentration of organic precursors (ClO<sub>2</sub> = 15 mg/l, pH = 7)

	DOC = 5.0 mg/l	DOC = 10 mg/l
ClO <sub>2</sub> /DOC <sup>a</sup>	4.7	1.89
TTHMs (μg/l)	2.4	2.8
TTHMs/DOC (μg/mg) <sup>b</sup>	1.13	0.62
THAAs (μg/l)	16.0	27.1
THAAs/DOC (μg/mg) <sup>c</sup>	7.53	6.02
Primary species	CH <sub>3</sub> Cl among TTHMs; TCAA (low dosage) and DCAA (high dosage) among THAAs	

<sup>a</sup>Ratio of ClO<sub>2</sub> consumption to DOC elimination amount.

<sup>b</sup>Ratio of TTHMs final production amount to DOC elimination amount.

<sup>c</sup>Ratio of THAAs final production amount to DOC elimination amount.

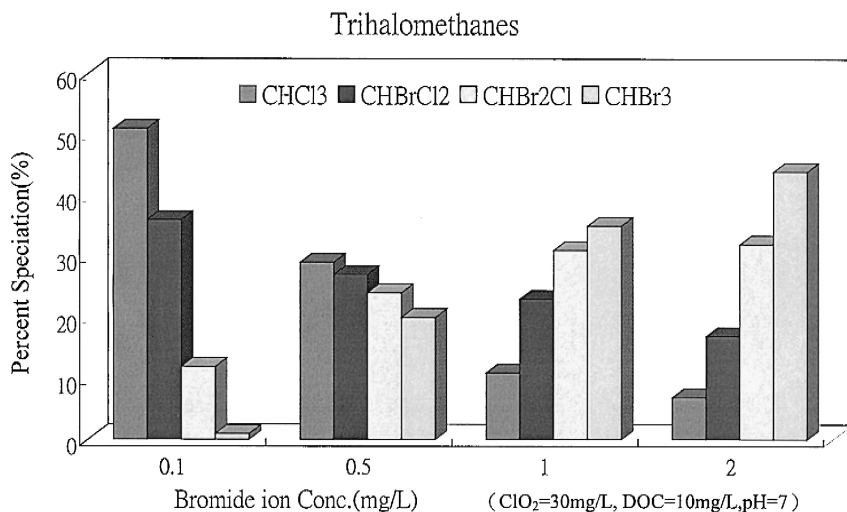


Fig. 10. Distribution of THMs at different bromide concentration.

above 1.0 mg/l, the order turned to  $\text{CHBr}_3 > \text{CHBr}_2\text{Cl} > \text{CHBrCl}_2 > \text{CHCl}_3$  and  $\text{DBAA} > \text{MBAA} > \text{TCAA}$ ,  $\text{DCAA}$  and  $\text{MCAA}$  (shown in Figs. 10 and 11). Because the redox potential of  $\text{ClO}_2$  and  $\text{Cl}_2$  was 1.91 (v) and 1.49 (v),  $\text{ClO}_2$  would be expected to be a stronger oxidant than  $\text{Cl}_2$ . Since  $\text{Cl}_2$  can oxidize bromide to form hydrobromous acid, which subsequently reacts with organic precursors to produce the bromine-substituted disinfection by-products [39,40] increased with bromide and chlorine dioxide concentration. Because these bromine-substituted DBPs were carcinogenic in mice and

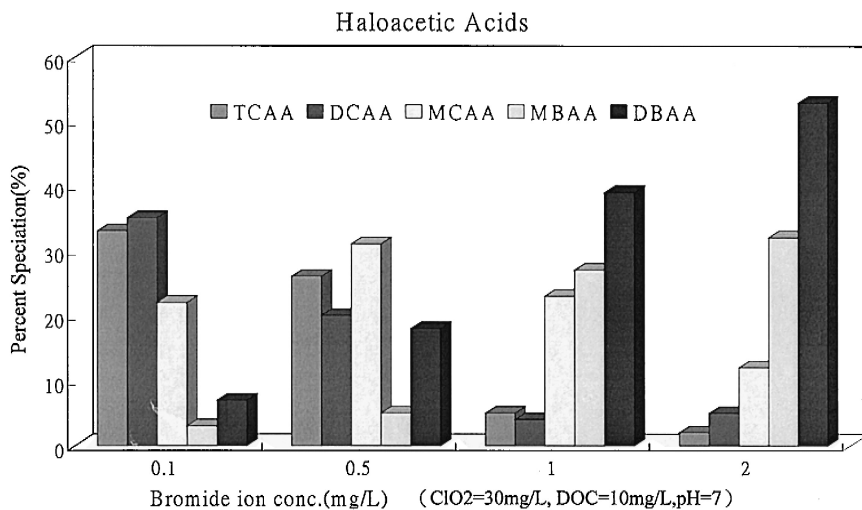


Fig. 11. Distribution of THAAs at different bromide concentration.

mutagenic in the Ames Salmonella assay, it is therefore necessary to investigate the formation of disinfection by-products in water containing bromide treated with chlorine dioxide.

#### 4. Conclusions

The disinfection efficiency of  $\text{ClO}_2$  was satisfactory. At only 1–5 mg/l, the residual colony ratio was close to zero in 1–2 min. The effect was not affected by pH value.

As to the DBPs, TTHMs and THAAs formed with  $\text{ClO}_2$  as an alternative disinfectant, but the levels were much lower than that occurring with the chlorination process. Furthermore, the experimental data results for these compounds were far lower than the legal limits of both the USEPA and Taiwan EPA. The chlorinated DBPs, like phenol and dichlorophenol, were not detected by High Performance Liquid Chromatography (HPLC, Waters 486 type, column: C18 (3.9\*150 nm)). This indicated that using  $\text{ClO}_2$  as an alternative disinfectant, phenol and dichlorophenol were not formed, or the levels were beyond the detection limit of HPLC.

Under the dosage used in this study, a higher  $\text{ClO}_2$  dosage lowers the amount of THMs and HAAs formed from humic acid. This provides a new direction for studies on DBP control in water purification processes. At higher levels of organic precursors,  $\text{ClO}_2$  did not improve the DOC elimination ratio. The result was similar to ozone oxidation, as  $\text{ClO}_2$  might only break down large molecules into small pieces without affecting the organic carbon content. Concerning the distribution of DBPs, the higher the concentration of bromide ions, the greater the number of bromide-containing TTHMs and THAAs formed. Bromide ions could be considered as an important reaction parameter.

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