

## Disinfection Efficiency and Formation of Disinfection Byproducts in Jordanian Drinking Water Treated with Chlorine Dioxide

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### Abstract

In this study factors affecting disinfection efficiency and formation of disinfection byproducts (DBPs) in water treated with chlorine dioxide ( $\text{ClO}_2$ ) were investigated. The amount of trihalomethanes THM and haloacetic acids HAA and chlorite ion was determined in samples collected from three different sources in Jordan: Deir Alla surface water, Wadi Al Sir springs, and Yajooz spring. The amounts of THM and HAA in real treatment plants were determined. Focus on chlorite ion as a major DBP in  $\text{ClO}_2$  treatment was made to investigate the factor that affects its concentration. This study aims also to identify new DBPs associated with  $\text{ClO}_2$  disinfection. Results show that chlorite ion has its highest formation at higher  $\text{ClO}_2$  dose, TOC, pH and temperature. Analysis of real samples shows that using  $\text{ClO}_2$  for disinfection leads to formation of smaller amounts of THM and HAA compared to chlorine gas. Among the three investigated water sources in Jordan, Deir Alla water was found to have the highest formation of DBPs upon treatment with  $\text{ClO}_2$ . New DBPs were identified for the first time in water treated with  $\text{ClO}_2$  including some halogenated compounds, carboxylic acids and some aldehydes and ketones. Disinfection efficiency of  $\text{ClO}_2$  was found to increase by increasing  $\text{ClO}_2$ . Disinfection efficiency was found to be the lowest at temperature of  $30^\circ\text{C}$  and  $\text{pH}=7$ , deviation from these values result in an increase in the efficiency of disinfection.

**Keywords:** Chlorine dioxide; Disinfection byproducts; Haloacetic acid; Trihalomethanes; Disinfection efficiency.

### Introduction

Pure and good quality water is one of the main concerns in our world. After the use of chlorine in drinking water disinfection about one century ago, many of the epidemic diseases disappeared and millions of lives had been saved. However, the use of chlorine was like a dual face as the side effects of using chlorine started to show up. In 1974, Rook in Netherlands <sup>[1]</sup> and Bellar et al. in the United States <sup>[2]</sup> had found separately, that chloroform was produced, in chlorinated drinking water sources, and it was marked as disinfectant byproduct DBP. Later on, it was noticed that a group of trihalomethanes THM is produced also in the chlorinated drinking water. THM group contains four compounds, namely: chloroform  $\text{CHCl}_3$ , bromodichloromethane  $\text{CHBrCl}_2$ , dibromochloromethane  $\text{CHBr}_2\text{Cl}$  and bromoform  $\text{CHBr}_3$ . Many other DBP have been identified in the chlorinated drinking water. According to Clark et al. <sup>[3]</sup>, more than 500 DBP have been identified in the chlorinated water. In addition to THM, other major groups were also classified, such as haloacetic acids HAA, haloketones and

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haloaldehydes. HAA group contains six compounds: monochloroacetic acid MCAA, monobromoacetic acid MBAA, dichloroacetic acid DCAA, trichloroacetic acid TCAA, bromochloroacetic acid BCAA and dibromoacetic acid DBAA. Compounds of the groups of THM and HAA were found to be mutagenic and carcinogenic <sup>[4]</sup>, therefore they were regulated by the EPA not to exceed a limit of 100 µg/L for THM and 60 µg/L for HAA <sup>[5]</sup>.

These facts had triggered the search for alternative disinfectants that tend to produce fewer amounts of byproducts. Chlorine dioxide (ClO<sub>2</sub>) was proved to be a successful candidate in term of production of smaller amounts of THM and HAA, beside other advantages. ClO<sub>2</sub> provides better control of taste and odor problems and is also more effective than chlorine for inactivation of certain pathogens such as viruses, *cryptosporidium*, and *Giardia* <sup>[5]</sup>. Considering these interesting properties of ClO<sub>2</sub>, many water treatment facilities in the US and other countries had shifted toward employing it in their treatment plants. Despite the above mentioned advantages of ClO<sub>2</sub>, certain disadvantages have to be taken into consideration. The major one is the production of chlorite ion as a major DBP.

Chlorite ion (ClO<sub>2</sub><sup>-</sup>) is a result of disinfection with chlorine dioxide and is a unique concern to only this process. It is estimated that 70% of the chlorine dioxide is converted to chlorite and about 30% is converted to chlorate (ClO<sub>3</sub><sup>-</sup>) and chloride (Cl<sup>-</sup>). The EPA has set the maximum concentration of chlorite ion in the drinking water to 1.0 mg/L <sup>[5]</sup>. The Jordanian limit for chlorite ion is 0.8 mg/L <sup>[6]</sup>. Exposure to chlorite at levels above the MAC may cause nervous system effects in infants and young children along with fetuses in pregnant women. Also exposure to chlorite may cause anemia <sup>[7]</sup>.

Few studies had investigated the formation of DBP upon using ClO<sub>2</sub> like Chang et al. <sup>[8]</sup> who studied different factors that affect the formation of DBP. Nevertheless, that study tested only the formation of DBPs in artificial samples and they give little attention to factors such as pH and temperature. From another perspective, most studies had focused on the formation of THM and HAA as major DBPs and little attention had been given to other DBPs. Richardson et al. <sup>[9]</sup> showed that many compounds had been identified at ClO<sub>2</sub> pilot plant. In another research <sup>[10]</sup> the same group had identified new brominated and iodinated DBPs in high level bromide water treated with ClO<sub>2</sub>.

Results of author's work considering the factors affecting the formation of THM and HAA were published <sup>[11]</sup> and it show that formation of THM had increased by increasing ClO<sub>2</sub> dose, TOC content, bromide ion concentration, pH, temperature and at longer contact time. Higher HAA concentrations were formed at higher ClO<sub>2</sub> dose, total organic content TOC, bromide ion concentration, and temperature and contact time and at a lower pH.

In this paper, investigation of the effect of factors such as ClO<sub>2</sub> dose, TOC content, pH and temperature on the formation of chlorite ion after treatment with ClO<sub>2</sub>

will be discussed. The formation of DBP in drinking water collected from three different sources in Jordan treated with  $\text{ClO}_2$  was also investigated. Real samples from Zai water treatment plant, which is the only plant in Jordan that employs  $\text{ClO}_2$  in a pretreatment step, will be analyzed for DBP. Up to our knowledge this is the first study conducted in Jordan to account for the DBP form upon treatment of water with chlorine dioxide. All the previous studies in Jordan had studied the DBP in water treated with chlorine gas<sup>[12, 13]</sup>.

Part of this study will focus on the identification of new disinfection byproducts other than THM, HAA and chlorite ion that might be formed during the disinfection process with  $\text{ClO}_2$ . The findings of this study will draw the attention to new compounds that are formed as DBP and encourage the study of their health hazard and the need to be regulated in drinking water specification.

Determination of disinfection efficiency against certain bacterial forms under variable values of  $\text{ClO}_2$  dose, pH and temperature was made.

## **Experimental**

### *Materials and Methods*

All organic solvents were of GC grade (Scharlau). Solid chemicals were of the highest purity available (mostly > 99%). GC standards for THM and HAA were purchased from Supleco. Commercial Humic acid was purchased from Merck/Germany.

### *Preparation of Chlorine Dioxide*

$\text{ClO}_2$  was prepared according to Standard Methods for the Analysis of Water and Wastewater of the American Public Health Association, method number 4500 B<sup>[14]</sup> by acidifying a solution of sodium chlorite with 20% solution of sulfuric acid. The concentration of the generated  $\text{ClO}_2$  was determined using colorimetric Diethyl phenylenediamine DPD method of number 4500 D<sup>[14]</sup> and it was checked before every usage.

### *Methodology of the Study*

#### *Study of Chlorite ion Formation*

To study Chlorite ion formation, different jar tests were performed to account for each factor. Humic acid was used as the source of organic matter in the jar tests to mimic the organic precursors in the real aquatic environment. One liter volumetric flask is used to place the proper amount of humic acid, phosphate buffer and the pH was adjusted by addition of sodium hydroxide or phosphoric acid. Finally the specified  $\text{ClO}_2$  dose was added and the volume was completed to 1.0L using distilled water. The content of this flask was mixed well and placed at constant temperature water bath. After 24 hour, the solution was analyzed for chlorite ion.

Chlorite ion analysis was done according to iodometric standard method number (4500- $\text{ClO}_2$  E)<sup>[14]</sup>. The concentration of chlorite ion was rechecked using colorimetric DPD standard method number 4500 D<sup>[14]</sup>

### *Study of Formation of DBP in Real Samples*

Samples were collected from three different sources in Jordan. They were characterized for their TOC, pH and bromide ion content. The specified dose of  $\text{ClO}_2$  was added and samples were placed at constant temperature water bath. After 24 hour, the reaction of  $\text{ClO}_2$  was quenched by addition of sodium thiosulfate and the solution was analyzed for THM, HAA and other organic DBP. (Chlorite ion concentration was determined before the addition of sodium thiosulfate)

A 30.0 mL of each solution was used for the analysis of HAAs. Extraction and analysis follow the standard method number 6251 B <sup>[14]</sup>. The extraction of haloacids was done using methyl tertiary butyl ether MTBE followed by derivatization using freshly prepared diazomethane to obtain methyl ester derivatives.

For analysis of THMs, 25.0 mL of the sample was extracted by using hexane according to the standard method number 6232 <sup>[14]</sup>.

### *Chromatographic Conditions*

THM and HAA analyses were carried out using Varian CP-3800 gas chromatograph, with a  $^{63}\text{Ni}$  electron capture detector ECD. For THM, DB-624 capillary column with 60 m x 0.25 mm, 1.4  $\mu\text{m}$  film thickness was used. Split ratio was 1:10, make up gas flow: 25 mL/min (Ar/ $\text{CH}_4$ ). Carrier gas: 2mL/ min (He 99.999% purity). Detector temperature: 300°C. Injector temperature: 200°C. Column temperature program: 60°C (4 min), 60- 150 °C (15°C /min). For HAA analysis, DB-5 capillary column with 30 m x 0.32 mm, 1.4  $\mu\text{m}$  film thickness was used. Split ratio was 1:100, make up gas flow: 25 mL/min (Ar/ $\text{CH}_4$ ). Carrier gas: 2mL/min (He 99.999% purity). Detector temperature: 300°C. Injector temperature: 210°C. Column temperature program: 40°C (10 min), 40-65°C (2.5 °C/min), 65°C- 85°C(10°C/min), then 85-205°C(20°C/min) and hold for 7 min.

GC/MS Agilent 6890 Series II, HP-5 capillary column (30m x 0.32 mm and 0.2  $\mu\text{m}$  film thickness) was used. The extract (hexane and MTBE extracts) was introduced via splitless injector. Injector temperature: 250°C. Oven temperature program: 35°C held for 4 min, 9°C/min to 285 °C. Detector (MSD) temperature was 280°C.

### *Characterization of Real Samples*

Total organic content TOC was determined using TOC analyzer according to standard method number (TOC 5310) <sup>[14]</sup>.

Bromide ion concentration was measured by phenol red spectrophotometric method according to standard method number (4500 Br<sup>-</sup> B) <sup>[14]</sup>.

### *Study of Disinfection Efficiency*

Disinfection efficiency of  $\text{ClO}_2$  was studied using water samples obtained from Deir Alla surface water. Water samples were collected in previously sterilized bottles. Investigation of this water was done immediately after collection. The source water was initially characterized for its TOC, pH and its total coliform content.

In order to study the effect of different factors mentioned previously on disinfection efficiency, the following procedure was followed: to a one liter of water a specified ClO<sub>2</sub> dose was added and mixed well. The solution was emptied in six 125 ml sterilized bottles each labeled for certain time period. The bottles were placed in a constant temperature water bath. After a distinct period of time the total coliform was determined followed by determination of *E.coli* after two days. The experimental variables that were used to perform this study are summarized in table 1.

Bacterial analysis was made using the two following methods:

- a- Membrane filtration method (Heterotrophic total count method) according to standard method number (9222) <sup>[14]</sup>.
- b- Multiple –Tube Fermentation method according to standard method number (9221 B and 9221 F) <sup>[14]</sup>.

**Table 1:** Description of experiments performed to study factors affecting disinfection efficiency of chlorine dioxide.

Exp. No.	Variable parameters	Fixed parameters	Measured variable
1	1- ClO <sub>2</sub> dose (0.1, 0.2, 0.5, 1.00, 2.00, 5.00 mg/L) 2- Time interval (0, 10, 20, 30, 60 minutes)	1- pH= 8.19 2- TOC= 3.24 mg/L 3- Temperature= 20°C	1- number of bacterial colonies 2- MPN for total coliform 3- MPN for <i>E. Coli</i>
2	1- pH (5, 7, 9) 2- Time interval (0, 10, 20, 30, 60 minutes)	1- ClO <sub>2</sub> dose (0.2 mg/l) 2- Temperature= 25 °C 3- TOC= 3.1 mg/L	1- MPN for total coliform 2- MPN for <i>E. Coli</i>
3	1- Temperature( 20, 30, 45 °C) 2- Time interval (0, 10, 20, 30, 60 minutes)	1- ClO <sub>2</sub> dose(0.2 mg/L) 2- TOC=2.55 mg/L 3- pH=8.25	1- MPN for total coliform 2- MPN for <i>E. Coli</i>

## Results and Discussion

### *Chlorite Ion Formation*

Table 2 shows the result of analysis of chlorite ion resulted from treating water with chlorine dioxide at different conditions of ClO<sub>2</sub> dose, TOC, pH and temperature.

Chlorine dioxide attacks the electron-rich centers of humic acid (represented as TOC). One electron is transferred and chlorine dioxide is reduced to chlorite ion as in equation 1:



Therefore, most of ClO<sub>2</sub> is converted to chlorite ion and it is considered as the major DBP. Table 2 shows that chlorite ion concentration comprises about 45-78% of the transformation of the initial chlorine dioxide dose. This value agrees with the reported values of the EPA of 50-70% <sup>[5]</sup>.

The variation of chlorite ion concentration could be attributed to the effect of different factors. It was noticed that higher ClO<sub>2</sub> dose cause higher formation of chlorite ion. However, the percentage of conversion of ClO<sub>2</sub> to chlorite ion is higher at lower ClO<sub>2</sub> dose.

Also it was found that higher TOC values cause formation of more chlorite ion. Because higher TOC values mean that there are more active sites for ClO<sub>2</sub> to react with, therefore, higher conversion to chlorite ion is taking place.

The concentration of chlorite ion and the percent of conversion of ClO<sub>2</sub> were found to increase at higher pH values. These phenomena could be explained by considering the fact that at lower pH values, chlorite ion will react with the present organic matter and chloride ion will be formed as a final product as in equation 2. Therefore, lower chlorite ion concentrations were observed in the solution.



An increase in the chlorite formation was observed at higher temperatures. This could be attributed to faster reaction kinetics at higher temperature that will cause more ClO<sub>2</sub> conversion during the specified time period.

**Table 2:** Concentrations of chlorite ion at different conditions after 24 hour

Sample Number	Initial ClO <sub>2</sub> dose	TOC (mg/L)	pH	Temperature °C	Chlorite ion concentration
1	5.00	5.00	7.00	30.0	3.88
2	10.00	5.00	7.00	30.0	6.91
3	10.00	2.00	7.00	30.0	4.47
4	10.00	5.00	5.00	30.0	5.73
5	10.00	5.00	9.00	30.0	7.76
6	10.00	5.00	7.00	40.0	7.25

*Analysis of DBP in Water from Different Sources*

Deir Alla source receives its water from Yarmuk River, Al-Mukhayba artesian wells, Tabarya Lake and Wadi El Arab dam. Water from these sources gather in King Abdullah Canal located at Deir Alla. At Deir Alla station, water receives pretreatment by chlorine dioxide and then water is pumped to Zai station to continue the treatment processes which ended by the addition of chlorine gas to maintain an adequate disinfectant residual throughout the distribution system. Chlorine is added instead of ClO<sub>2</sub> because the amount of ClO<sub>2</sub> that could be applied is limited due to the continuous formation of chlorite ion, which should not exceed the Jordanian maximum contaminant level. (see figure 1 for illustration of the sampling sites)

Raw water samples were collected from three different sources in Jordan. Then each sample was treated with 5.00 mg/L ClO<sub>2</sub>, placed at 30.0°C water bath for 24 hours and analyzed for DBPs. The characteristics of each water source are presented in table 3.

After treatment with chlorine dioxide, the results of analysis was obtained, summation of the concentration of the four THM is represented as TTHM and the summation of the six HAA is represented as THAA as in table 3. Deir Alla water was found to form the highest concentrations of all DPB as shown in table 3, followed by Wadi Al Sir water and Yajooz water which forms the least amounts of DBP.

This could be attributed to the high TOC values and high bromide ion concentration of Deir Alla water compared to the other two sources.

Table 3 shows also that Deir Alla water has formed the highest concentration of chlorite ion and it has the highest percent of conversion of chlorine dioxide to chlorite ion, which was 46.4%. This could be attributed to the higher TOC value and higher pH of Deir Alla water. This result agrees with the finding of this research in the previous section.

**Table 3:** Characterization of water sources and concentration of the formed DBP

Water source	pH	Br <sup>-</sup> (mg/L)	TOC (mg/L)	TTHM (µg/L)	THHA (µg/L)	Chlorite ion (mg/L)
Dier Alla	8.2	1.50	2.6	0.96	34.5	2.3
Wadi Al Sir spring	7.1	0.74	0.8	0.49	11.5	1.8
Yajooz spring	7.6	0.50	0.7	0.18	7.3	1.7

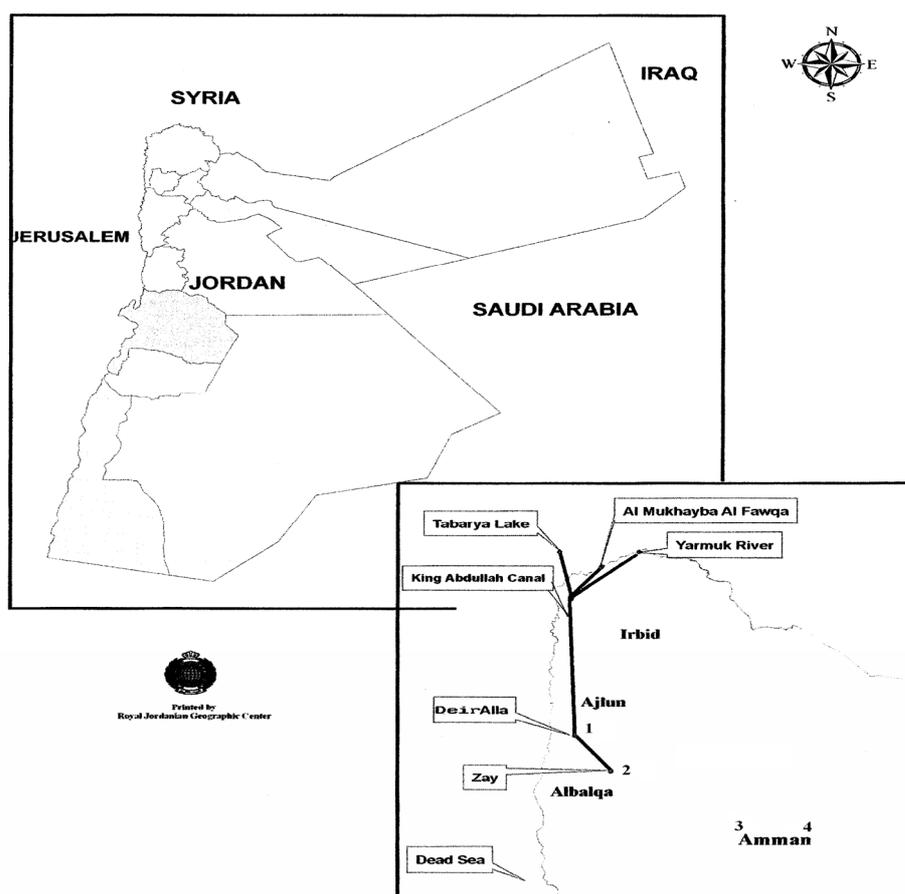
Analytical results of THM and HAA in the effluent of the real treatment plants are presented in table 4.

Although higher concentrations of TTHM were formed after the addition of chlorine, these concentrations are still below the regulated amount of THM according to drinking water specification in Jordan which is 150 µg/L<sup>[6]</sup>. On the other hand, it can be noticed the relatively large gap between concentration of THAA in water before entering Zai plant (i.e. treated only by ClO<sub>2</sub>) and after that due to addition of chlorine. In fact the high amount of THAA formed after the addition of Cl<sub>2</sub> exceeds the EPA regulated limit of 60 µg/L<sup>[5]</sup>.

The amounts of THAA formed in Wadi Al Sir water are relatively lower, despite its treatment with chlorine as was the case in Zai water. This might be attributed to the lower TOC and bromide ion content in Wadi Al Sir water as well as lower dose of chlorine since UV treatment was also applied for disinfection.

**Table 4:** Concentrations of TTHM and THAA in the samples from different locations

Samples	TTHM ( $\mu\text{g/L}$ )	THAA ( $\mu\text{g/L}$ )
Deir Alla + $\text{ClO}_2$	1.2	13.7
Zai + $\text{Cl}_2$	35.9	157.8
Wadi Al Sir + $\text{Cl}_2$ and UV treatment	7.5	20.7



**Figure 1:** Location of Deir Alla station and Zai treatment plant in Jordan. The numbers refer to the sampling site: 1- Deir Alla water. 2- Zai water treatment plant. 3- Wadi al Sir springs. 4- Yajooz spring. (This map is prepared by Royal Geographic Center in Jordan)

The reported values of THM and HAA formed upon treatment with chlorine gas are substantially higher than what was formed using only chlorine dioxide. For example Nikolaou et al. <sup>[15]</sup> had reported TTHM concentration of 65  $\mu\text{g/L}$  and THAA of 142  $\mu\text{g/L}$  formed upon treatment of water from Tsiknias River (that has TOC value of 1.12 mg/L) with 4 mg/L chlorine.

### Formation of Other Disinfection Byproducts

Table 5 lists examples of the disinfection byproducts that were identified using GC/MS after treatment of Deir Alla water with 5.00 mg/L ClO<sub>2</sub>. The criteria that were used for listing an identified compound as a DBP was its presence in the treated sample in quantities at least 2 or 3 times greater than those in an untreated blank water samples, as judged by comparing chromatographic peak areas.

Library of the NIST data base was used for the identification of several compounds. However, many DBPs were not present in the NIST data base. In some of those cases the mass spectra were extensively interpreted to provide a tentative chemical identification. In other cases the obtained mass spectra were compared with those of some expected compounds that are published in the literature.

**Table 5:** Some of the identified DBPs

Number	Halogenated compounds
1	2,3-dibromo butenedioic acid
2	3,3-dibromo 2-propenoic acid
3	2,3,3-tribromo 2-propenoic acid
4	2,2-dibromo propane
5	2,6 bis (1,1 dimethyl) 4- bromophenol
6	2- iodo-4- methyl 6-nitrophenol
7	2-chlorobenzoic acid
8	2,5-dichloro bezoic acid
9	2,3,6-trichloro benzoic acid
10	2,4-dibromo 1-methoxy benzene
11	1,3,5- tribromo 2-methoxy benzene
12	2,4-dibromo-5-methyl imidazole
13	2-bromo 2-nitropropane
14	2,3-dibromo thieno[3,2-c] pyridine
	1-chloro-2-nitrobenzene
	3-bromo 2,6-di-tert butyl benzoquinone
	<b>Non Halogenated Carboxylic acids</b>
16	Ethanedioic acid (Oxalic acid)
17	Succinic acid
18	4-oxo-petanoic acid
19	hexanoic acid
20	benzoic acid
21	3,5-bis(1,1 dimethyl) 4-hydroxy benzoic acid
22	1,4-benzene dicarboxylic acid
23	1,2,4-benzene tricarboxylic acid
24	1,2,4,5 benzene tetra carboxylic acid
25	4-oxo-4-toulyl butyric acid
26	2,5-dicarboxylic acid thiophene
	<b>Aldehydes and Ketones</b>
27	Benzoquinone
28	4-hydroxy 2-pentanone
29	4-hydroxy 4-methyl 2-pentanone
30	benzaldehyde
31	4-hydroxy benzaldehyde
31	3-phenyl 2-propenal
33	benzophenone
34	1,2,3- dioxathiolane-2-oxide
35	S-methyl methane thiosulphinate

### *Halogenated DBP*

Few halogenated acids were identified such as 3, 3-dibromopropenoic acid, tribromopropenoic acids and 2, 3-dibromobutedioic acid. These compounds were identified before as disinfection byproduct in water treated with  $\text{ClO}_2$  [10]. Observation of more brominated acid rather than chlorinated ones is probably attributed to the high level of bromide ion in the source water. One halopropane was identified which is 2, 2-dibromopropane and this is the first time that this particular halo propane compound has been identified.

The polyphenolic content of the Jordanian humic materials makes up a large fraction of organic materials present in natural water sources [16] and [17]. This enhanced the prediction of finding many aromatic and phenolic byproducts in treated water with chlorine dioxide and as expected, two of them were formed. Among the identified aromatic compounds was 2, 6 bis (1, 1 dimethyl) 4- bromophenol.

An iodinated nitrophenole (2- iodo-4- methyl 6-nitrophenol), was also identified. Iodinated byproduct could be expected to be formed since Deir Alla water source is expected to have certain iodide levels, since the presence of iodide in Sea of Galilee (Tabarya Lake) had been reported [10]. This sea is one of the main sources of King Abdullah Canal which in turn supplies Deir Alla station with water.

Some chlorinated benzoic acid derivatives were also identified in the reaction mixture such as 2-chlorobenzoic acid, 2, 5-dichlorobenzoic acid and 2, 3, 6-trichlorobenzoic acid. Occurrence of these compounds could be attributed to the reaction of chlorine dioxide with benzyl alcohol as reported in the literature [18].

Other halogenated aromatic compounds were identified, such as 2, 4-dibromo 1-methoxy benzene and 1, 3, 5- tribromo-2-methoxy benzene. Other brominated methoxy benzenes were identified elsewhere as DBP [10]. However, this is the first time to identify these two particular compounds as  $\text{ClO}_2$  disinfection byproduct. Other identified brominated byproducts was 3-bromo 2, 6-di-tert butyl benzoquinone. Chlorinated benzoquinones were formed upon reaction of chlorine dioxide and phenol [19]. Consequently, this bromo benzoquinone could be formed by similar reaction due to the high level of bromide ion in water.

An interesting brominated compound was formed and we suppose that it is the first time to be identified as DBP, it is 2, 4-dibromo-5-methyl imidazol. This compound could be formed as a result of bromination of imidazol. Imidazol moiety could have some natural source since it is present in the essential amino acid histadien [20]. Elemental analysis of humic acid of Jordan shows the presence of 1-4% of nitrogen in the formula [16]. This justifies the finding of this compound and other nitrogen containing DBPs.

### *Carboxylic Acids*

Many carboxylic acids were identified in the water samples treated with ClO<sub>2</sub>. However, most of these carboxylic acids were identified also in raw water samples. Some of them were found in relatively high concentrations in the treated water. In fact, carboxylic acids have been reported as reaction product of humic acid and ClO<sub>2</sub> in many references [21] and this describes their formation in the treated water.

Many references had reported maleic acid and oxalic acid as the main reaction products of the reaction between ClO<sub>2</sub> and phenol such as [22] and [21]. However, only oxalic acid has been identified in this study. On the other hand, evidence on the formation of maleic acid could be realized from the formation of 2, 3-dibromobutenedioic acid that was mentioned earlier. This suggests that maleic acid undergoes bromination reaction as it forms.

### *Aldehydes, Ketones and other compounds*

Few aldehydes and ketones were formed upon treatment with ClO<sub>2</sub>. The most important one was benzoquinone, which are among the most commonly reported products of ClO<sub>2</sub> reaction with phenols [19], [21]. Other keto compounds were identified such as: 4-hydroxy 2-pentanone and benzophenone. Derivatization with o-(2, 3, 4, 5, 6-penta fluorobenzyl)-hydroxylamine hydrochloride (PFBHA) was used to identify low molecular weight aldehydes and ketones such as formaldehyde, acetaldehyde, glyoxal, and methyl glyoxal. However, these compounds were observed at approximately the same concentrations in both treated and the untreated samples, so they could not be judged as disinfection byproducts.

Some other compounds were identified in the treated water such as 1,2,3-dioxathiolane-2-oxide, and S-methyl methane thiosulphinate. These two compounds are believed to be a result of the reaction between chlorine dioxide and the sulfides present in water [23] and [24].

### *Disinfection Efficiency of Chlorine Dioxide*

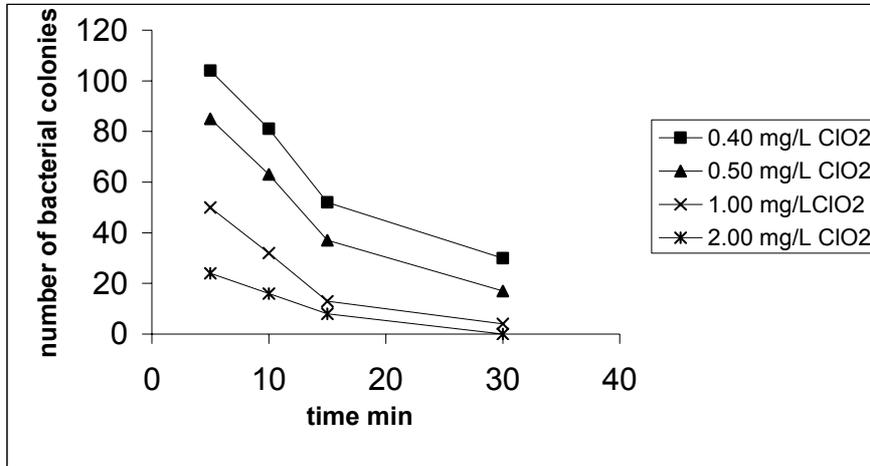
#### *Effect of Chlorine Dioxide Dose*

Heterotrophic plate count was used to calculate the number of bacterial colonies per 0.10 ml of Deir Alla water treated with different doses of ClO<sub>2</sub>. Results show that bacterial killing had been increased with increasing the dose of ClO<sub>2</sub> as shown in Figure 2. This is because at higher ClO<sub>2</sub> dose the amount of ClO<sub>2</sub> remaining in the matrix after TOC consumption will be higher. Therefore, this will increase the chance for killing bacteria.

Total coliform and *E.coli* were detected using multiple tube fermentation method. These bacterial forms are used frequently as indicators for verifying microbiological water quality.

When applying different ClO<sub>2</sub> doses to water and employing multiple fermentation tube method, it was found that with ClO<sub>2</sub> doses higher than 0.20 mg/L, immediate complete kill of the total coliform and consequently for *E.coli* was attained.

A dose 0.2 mg/L of ClO<sub>2</sub> was found to be able to attain 100% kill of the bacteria after 60 minutes of the addition of ClO<sub>2</sub>. Therefore, we decided to employ this particular dose (0.20 mg/L) to study the effect of pH and temperature on disinfection efficiency using multiple fermentation tube method.

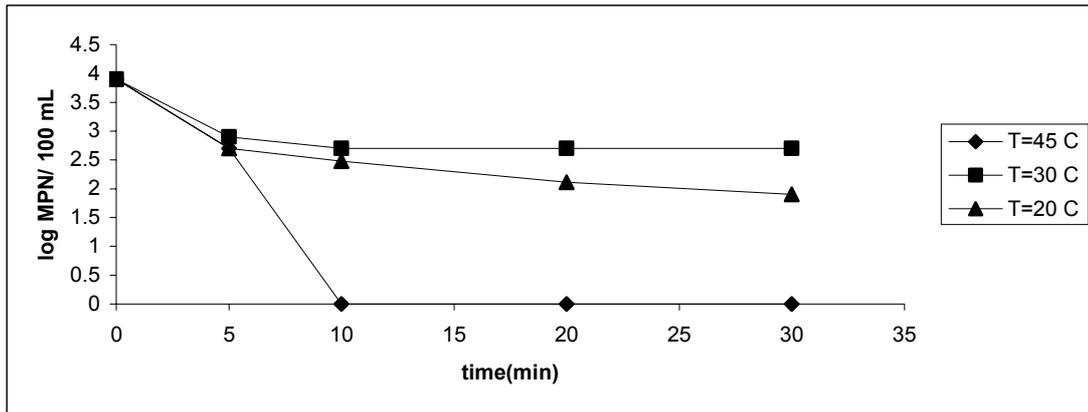


**Figure 2:** Showing killing effect of different ClO<sub>2</sub> doses on bacterial colonies, TOC=3.24, pH= 8.26, T= 20.0°C in Dier Alla water

#### *Effect of Temperature on Disinfection Efficiency*

Figure 3 show that at T= 30°C complete kill has not been achieved after 30 minutes of the treatment, which means that ClO<sub>2</sub> has its lowest efficiency at this temperature. While at T= 45°C all total coliform and *E.coli* had disappeared only after 10 minutes of application of ClO<sub>2</sub>. On the other hand, at T= 20 °C the amount of total coliform and *E.coli* was slightly lower than at 30°C.

This finding suggests that coliform resistance to chlorine dioxide disinfection is the highest at temperature around 30°C. At lower or at higher temperature the efficiency of killing the bacteria was improved. This agrees with the fact that this type of bacteria has its optimum growth at T=37°C, which implies that it has the highest resistance to killing at this optimum temperature, therefore deviation from this temperature either higher or lower cause this resistance to decrease.



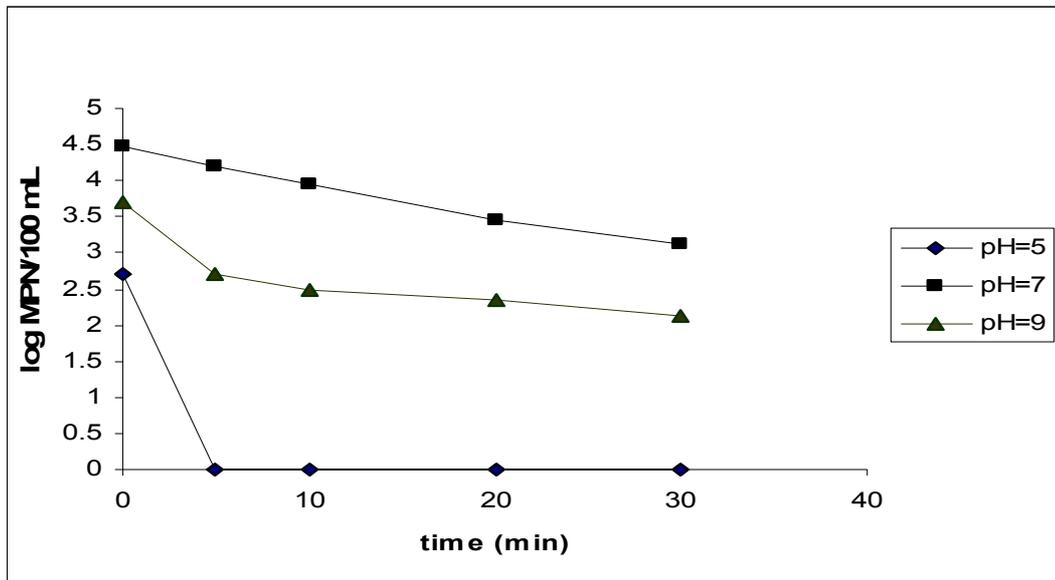
**Figure 3:** Showing the Effect of different temperature on total coliform in Deir Alla water treated with 0.2 mg/l  $\text{ClO}_2$ , TOC= 2.55, pH= 8.25.

#### *Effect of pH on Disinfection Efficiency*

The effect of pH on disinfection efficiency could be realized from the data presented in figure 4. It can be noticed that complete killing of total coliform was attained at pH=5 only after 5 minutes of addition of  $\text{ClO}_2$ . The lowest disinfection efficiency was at pH=7. The disinfection efficiency is slightly higher at pH=9 than at neutral pH.

These results do not match with what was found in the literature <sup>[8]</sup>, since this reference reported no accountable changes in disinfection efficiency when the pH was changed from 5 to 9. They attributed their observation to the established knowledge of remaining  $\text{ClO}_2$  as true dissolved gas in solution so it does not react with water and therefore, this lead to a prediction of retaining its biocidal effectiveness over a wide pH range. However, the observations in this study agree with the fact that the coliform bacteria has its optimum growth at pH =7, therefore, it has the highest growth at this particular pH and hence, the highest resistance to disinfection. Higher or lower pH values will lead to a lower bacterial resistance and higher disinfection efficiency of chlorine dioxide.

Considering all the results obtained on the factors that affect disinfection efficiency and formation of disinfection byproducts and considering as well the water condition at Deir Alla source water we can conclude that dose of 0.50 to 1.5 mg/L of chlorine dioxide is able to attain complete disinfection within 30 minutes. This dose will assure that the levels of THM, HAA and chlorite ion will not exceed the regulated MCL.



**Figure 4:** Showing the effect of different pH's on total coliform in Deir Alla water treated with 0.2 mg/l  $\text{ClO}_2$ , TOC= 3.10

### Conclusions

Chlorite ion is considered as the major inorganic disinfection byproduct of  $\text{ClO}_2$  treatment. Concentration of chlorite ion increases with increasing doses of  $\text{ClO}_2$ , TOC, pH and temperature.

Treatment of water obtained from different sources in Jordan lead to formation of THMs and HAA. Nevertheless, the formed amounts were always lower than the maximum allowable limits. The concentrations of HAA formed upon treatment of Deir Alla water by different  $\text{ClO}_2$  doses were always lower than the EPA regulated MCL.

Investigations on the formation of other disinfection byproducts using GC/MSD led to identifying many DBPs including some halogenated compounds. Most of the identified compounds were not regulated among the hazardous materials in the environment. However, some of the identified compounds are considered as harmful and toxic materials.

Treatment of water obtained from different sources in Jordan lead to the formation of THMs and HAA. Nevertheless, the formed amounts were always lower than the maximum allowable limits. The concentrations of HAA formed upon treatment of Deir Alla water by different  $\text{ClO}_2$  doses were always lower than the EPA regulated MCL.

Disinfection efficiency of chlorine dioxide was found to be affected by several factors. Increasing  $\text{ClO}_2$  dose was found to increase the efficiency of killing the bacteria. It was found that doses higher than 2.00 mg/L of  $\text{ClO}_2$  were able to attain 100% bacterial kill within 30 minutes. It was found that total coliform and *E.coli* have the highest resistance to  $\text{ClO}_2$  disinfection at  $T=30^\circ\text{C}$  and  $\text{pH}=7$ . While the killing increases at higher and lower temperature and pH values.

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