

Comparison of commercial analytical techniques for measuring chlorine dioxide in urban desalinated drinking water

T. A. Ammar, K. Y. Abid, A. A. El-Bindary and A. Z. El-Sonbati

ABSTRACT

Most drinking water industries are closely examining options to maintain a certain level of disinfectant residual through the entire distribution system. Chlorine dioxide is one of the promising disinfectants that is usually used as a secondary disinfectant, whereas the selection of the proper monitoring analytical technique to ensure disinfection and regulatory compliance has been debated within the industry. This research endeavored to objectively compare the performance of commercially available analytical techniques used for chlorine dioxide measurements (namely, chronoamperometry, DPD (N,N-diethyl-p-phenylenediamine), Lissamine Green B (LGB WET) and amperometric titration), to determine the superior technique. The commonly available commercial analytical techniques were evaluated over a wide range of chlorine dioxide concentrations. In reference to pre-defined criteria, the superior analytical technique was determined. To discern the effectiveness of such superior technique, various factors, such as sample temperature, high ionic strength, and other interferences that might influence the performance were examined. Among the four techniques, chronoamperometry technique indicates a significant level of accuracy and precision. Furthermore, the various influencing factors studied did not diminish the technique's performance where it was fairly adequate in all matrices. This study is a step towards proper disinfection monitoring and it confidently assists engineers with chlorine dioxide disinfection system planning and management.

Key words | amperometric titration, chlorine dioxide monitoring, chlorite, chronoamperometry, DPD colorimetric, urban water

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INTRODUCTION

Disinfection is the last treatment stage of a drinking water treatment plant and is carried out to maintain a residual concentration of disinfectant in the water distribution system (Sorlini *et al.* 2014). The goal of the secondary disinfection is to maintain a disinfectant residual throughout the distribution system, so that a nominated residual is achieved even at the system extremities (WHO 2011). Chlorine dioxide is an oxidant that can be reduced in a variety of ways, depending on the system conditions and the nature of the reducing agent (Gates & Don 1998).

Chlorine dioxide (ClO₂) has attracted considerable attention as a chlorine (Cl₂) alternative for water disinfection and human consumption (Jin *et al.* 2013; Nie *et al.* 2014), as it could possess the same disinfection efficiency as chlorine does, with a smaller dosage and less reaction time (Liu *et al.* 2013).

Chlorine dioxide is a powerful disinfectant that has comparable biocidal efficacy, but less pH dependence (Chang *et al.* 2000; Karanfil *et al.* 2011; Yang *et al.* 2013a, b). Chlorine dioxide has become one of the promising disinfectants as it

does not produce THMs and total HAAs to a significant extent compared to chlorine (Jones *et al.* 2012a, b; Shah *et al.* 2012; Shaoxiu *et al.* 2013; Yang *et al.* 2013a, b).

Furthermore, chlorine dioxide is effective in controlling tastes and odors (Li *et al.* 2012; Zhang *et al.* 2012, 2013; Antonopoulou *et al.* 2014), as well as eliminating iron and manganese (Ginige *et al.* 2011; Wang *et al.* 2012; Cristo *et al.* 2013; Prasad & Danso-Amoako 2014). The immediate redox reactions with natural organic matter play the dominant role in the decay of chlorine dioxide into chlorite in drinking water (Wang *et al.* 2011; Li *et al.* 2013a, b). Although chlorine dioxide decay is quite complicated, a novel empirical mathematical model for chlorine dioxide decay prediction had been proposed (Ammar *et al.* 2014).

Nevertheless, the use of ClO_2 is not without drawbacks or risks. The potential hazard is attributed to its inorganic toxic by-products, namely chlorite (ClO_2^-) and chlorate (ClO_3^-), which have toxicological effects on both the environment and humans at high doses (Xue *et al.* 2013; Yi-Tze *et al.* 2014).

Several alternative analytical techniques for chlorine dioxide monitoring have long been available. However, many of these analytical techniques present their own peculiar sets of problems.

This paper endeavors to evaluate the most popular and widely used analytical techniques for chlorine dioxide measurements in drinking water systems.

Currently, there are four widely used analytical techniques for determining chlorine dioxide levels in drinking water systems. Those analytical techniques are as follows:

1. Amperometric titration.
2. DPD (N,N-diethyl-p-phenylenediamine) colorimetric analytical technique.
3. The Lissamine Green B (LGB WET) colorimetric analytical technique.
4. Chronoamperometry (ChlordioXense[®]).

These analytical techniques, along with the chemistry involved, are briefly described below.

Amperometric titration

To determine the levels of ClO_2 , chlorine, ClO_2^- and ClO_3^- that exist in any aqueous solution, amperometric titration is

the one of the preferable analytical techniques. Phenylarsine oxide (PAO) is the titrant used for such determination, and the sample pretreatment required to differentiate between the various chlorine species present can be accomplished by pH adjustment (Tang & Gordon 1989). This procedure in no way attempts to distinguish between free and combined chlorine.

The analytical technique can be affected by such commonplace interferences as the presence of manganese, copper, or nitrate because they interfere with the amperometric analytical technique for free available chlorine. Chloramines too, can potentially interfere with the success of ClO_2 measurements (Jensen & Johnson 1990; Dietrich *et al.* 1992).

The DPD colorimetric analytical technique

Although the DPD technique for measuring chlorine dioxide was not reported in the latest EPA methods and regulations, it is obviously one of the very famous and widely used techniques.

This colorimetric analytical technique uses chemical reagents added to the sample which react with chlorine dioxide to produce a color. The intensity of the color is directly proportional to the amount of chlorine dioxide present in the sample (Mark & William 2008). The analytical instrument used in this analytical technique measures the intensity of the color and converts this measurement into a concentration reading, typically parts per million (ppm). The most prevalent colorimetric analytical technique used in industry today is called the DPD colorimetric analytical technique. The DPD colorimetric analytical technique is based on the fact that the amount of colored reactive product produced during the process is in direct proportion to the level of oxidants in the water samples and due to the rapid and ready oxidation of DPD. Numerous adaptations of this analytical technique have been used to great success with many oxidant species (particularly Cl_2 , ClO_2 , etc.).

The LGB WET analytical technique

This test is based on the oxidation of LGB WET dye (triphenylmethane dye) by the presence of ClO_2 , which

results in reduced levels of color absorption. The decrease in the LGB WET is in direct proportion to the ClO_2 concentration.

Since LGB WET is a triphenylmethane dye and since the standard redox potential in LGB WET is about +1.0 V (Barry *et al.* 2007), this analytical technique proves exceptionally useful in determining chlorine species, particularly since most of them have a standard redox potential that equals or is greater than +1.0 V. The use of this reagent with an equal redox potential dramatically reduces the possibility that combined chlorine and chlorite (ClO_2^-) will interfere with the final measurement.

A comprehensive search of the literature identified four different dyes that had been investigated as a potential alternative method to determine chlorine dioxide in water – acid chrome violet K (ACVK), amaranth, Chlorophenol red (CPR) and LGB WET (Chiswell & O'Hallaran 1991; Masschelein 1996; Hoffmann *et al.* 1998; Emmert *et al.* 2000). All methods showed some interference associated with colored waters. LGB was selected for evaluation because it appeared to have the least number of potential interferences.

Chlorine dioxide rapidly oxidizes the LGB WET, reducing its absorption in the red region of the visible spectrum in proportion to the Chlorine dioxide concentration (Hoffmann *et al.* 1998).

Chronoamperometry (ChlordioXense®) technique

The ChlordioXense® uses a recently developed electrochemical analytical technique known as chronoamperometry. Chronoamperometry is an electrochemical analytical technique in which the potential of the working electrode is stepped (a fixed voltage is applied) and the resulting current from faradic processes occurring at the electrode (caused by the potential step and chlorine dioxide reduction) is monitored/recorded as a function of time (current – time dependence monitoring). The magnitude of the current is directly proportional to the concentration of chlorine dioxide in the test sample (Palintest 2011).

The analytical technique uses unique pre-calibrated disposable sensors (those sensors are designed for a single use). Once the sensor is inserted, the analysis is fully automatic and operator independent. The ChlordioXense precisely controls the sensor cycle and captures and collates

thousands of signal readings. The processor interprets these readings to identify ClO_2 and determines the exact concentration. The instrument display gives a direct reading of the test result in mg/L within less than 1 minute. The dose-response information is stored on the calibration chip through a 60 digit calibration code during manufacturing. This code is used to construct a calibration curve that exactly matches the sensor batch. A pre-programmed, plug in calibration chip is provided with each pack of sensors to automatically enter the calibration code into the instrument.

The objective of this work is to evaluate the widely used commercial analytical techniques for chlorine dioxide measurements to properly monitor disinfectant levels in desalinated drinking water, using the superior technique. The evaluation matrix includes the following factors:

- Accuracy and precision.
- Possible/Minimum detection limits.
- The time and skill required for implementation of the analytical technique (time consumption).
- Complications and ease of results display.

The superior analytical technique is obviously the one indicating the highest accuracy, precision, robustness, and sensitivity. Moreover, it should indicate lower detection limits and acceptable time consumption along with the ease of results' calculations and display.

The commonly used commercial analytical techniques will be evaluated at three different standard chlorine dioxide levels (0.15, 0.5, and 0.80 mg/L). These three standard concentrations have been selected to represent the most probable chlorine dioxide levels within the drinking water distribution system. The low chlorine dioxide level (0.15 mg/L) represents the chlorine dioxide level that is most likely to be found in the water distribution system (network), while moderate and high chlorine dioxide concentrations (0.5 and 0.80 mg/L) represent the initial dosage within the drinking water production facilities (desalination and reverse osmosis (RO) plants).

After the superior commercial analytical technique is identified through the evaluation of the pre-defined matrix criteria, various factors (sample temperature, high ionic strength, and interferences like chlorite and free chlorine) that might influence the performance of the superior analytical technique are examined.

MATERIALS AND METHODS

Reagent water

Pure and ultra-pure water were utilized. Both types of water were produced through Millipore[®] water purification systems.

Glassware preparations

Prior to the beginning of the study, all glassware was carefully prepared according to a multi-stage process, which began with its overnight soaking in a 1:1 nitric acid bath. The glassware was then rinsed five or six times in type II pure water, rinsed the same number of times in distilled water and then allowed to air dry. All pipettes, beakers, and volumetric flasks were prepared in a like manner.

Vial cleaning for reuse

Vials were reused. Prior to reuse, they were thoroughly cleaned with soap and water and rinsed several times with reagent water. Vials (without caps) were dried in an oven at 140 °C. Reusing vials may help avoid any potential for bias associated with chlorine dioxide demand of the glassware.

Reagents and chemicals for different analytical techniques

All chemicals were ACS grade unless otherwise noted.

Amperometric titration technique

The following reagents were purchased from HACH[®] Company: PAO titrant (0.00564 N), hydrochloric acid standard solution, 2.5 N, phosphate buffer pH 7, w/dropper potassium iodide.

DPD technique

The DPD free chlorine powder pillow and glycine reagents were purchased from HACH[®] Company.

LGB WET technique

Lissamine Green B, horseradish peroxidase (HRP) reagents were purchased from Sigma[®] Company.

Chronoamperometry technique

ChlordioXense[®] sensors were utilized.

Preparation of chlorine dioxide standard solution (American Public Health Association 2012)

A stock solution of chlorine dioxide was prepared according to the Standard Analytical technique (4,500 ClO₂ B – SM 2012) through a gas generating and absorbing system, using sodium chlorite and diluted sulfuric acid. The concentration of ClO₂ thus prepared varies between 250 and 600 mg/L, corresponding to approximately 500 to 1,200 mg free chlorine/L. The stock solution had been stored in a dark-colored bottle with glass or PTFE lined stopper in a refrigerator at 4 °C. The chlorine dioxide solution was standardized by titration with sodium thiosulfate in the presence of KI, acid, and starch indicator.

Performance at different sample temperature

After identifying the best commercially available analytical technique at 27 °C (as per the pre-determined criteria), the impact of temperature fluctuation on the performance of such analytical technique at various chlorine dioxide concentrations was evaluated.

Each of the three chlorine dioxide standard concentrations (0.15, 0.5, and 0.8 mg/L) were tested at three different temperatures (15, 20 and 35 °C). These temperature regimes were selected in order to ascertain the relationship between such analytical technique performance and the water's temperature, so that appropriate values for the winter and summer condition simulations are derived.

At temperatures higher than 35 °C, it was difficult to repeat testing because of the volatility of chlorine dioxide at elevated temperatures.

Detection of statistical outliers

Developing strategies to search for outliers and understanding their statistical impact are extremely important parts of a thorough analysis, particularly when statistical analytical techniques will be applied to the data. One simple, straightforward, and effective approach to outlier detection is to compute the inter-quartile range (IQR) and then use a multiple of it as a number that defines values considered outliers. The IQR analytical technique was used to identify the problematic outliers in the result set where outliers were calculated based on first quartile (Q_1), third quartile (Q_3), and inter-quartile range (IQR) values. Should any result lie below $Q_1 - (3 * IQR)$ or more than $Q_3 + (3 * IQR)$, such value should be considered a problematic outlier. Any problematic outlier will be filtered and eliminated and statistical analysis for such set of results should be recalculated again.

Raw water source (American Public Health Association 2012)

Given that the raw water should contain zero levels of chlorine dioxide but also should represent the same matrix normally found in the desalinated drinking water, an intermediate point within the desalination process was selected to fulfill both requirements. The point representing desalinated water after remineralization process just before the addition of any disinfectant was selected.

RESULTS AND DISCUSSION

Raw water source analysis

Analysis for raw water samples indicates typical desalinated water analysis. Given that raw water was collected before the disinfection process, no chlorine dioxide levels were detected.

Evaluation matrix for all analytical techniques

Accuracy and precision at 27 °C

The three chlorine dioxide standard concentrations (0.15, 0.5, and 0.8 mg/L) were used to test the accuracy and

precision for the four commercially available analytical techniques at 27 °C. For each analytical technique, the selected chlorine dioxide standard concentration was measured repeatedly 25 times. Descriptive analysis, IQR, Bias % and %CV were processed using Microsoft Excel®. To present the data in a way that precision and accuracy of the measurements could be determined properly, the probability normal distribution for each measurement had been calculated using the following equation:

$$p = \frac{1}{\sqrt{2\pi\sigma^2}} * \exp \frac{-(x - \mu)^2}{2\sigma^2} \quad (1)$$

where P = probability density, σ = standard deviation, X = ClO_2 measured concentration, and μ = mean.

The probability density values for the four different techniques were presented graphically where a straight vertical line was introduced at each chlorine dioxide standard concentration. The analytical technique will be considered as accurate as their response is closer to the straight vertical line at each chlorine dioxide standard concentration.

At low range (0.15 mg/L chlorine dioxide). The 25 repeated measurements for 0.15 mg/L chlorine dioxide standard concentrations, utilizing the four different techniques were performed and results were recorded. The probability density for the entire set of results were calculated using probability formula and then presented graphically in Figure 1(a) where a straight vertical line was introduced at 0.15 mg/L chlorine dioxide standard concentration.

Table 1 shows statistical descriptive analysis as well as detection for statistical outliers for the four different analytical techniques at 0.15 mg/L standard chlorine dioxide concentration. The entire set of results produced by the four different analytical techniques lie within the IQR limits indicating the absence of any problematic outliers.

Figure 2(a) shows average Bias % and %CV for the four analytical techniques at 0.15 mg/L chlorine dioxide standard concentration. Both amperometric titration and LGB WET analytical techniques show very high values for both Bias % and %CV ranging between 23.4% and 34.4% indicating low accuracy and low precision.

Although both chronoamperometry and DPD analytical techniques show considerably low values for %CV (4.5% and 5.2%, respectively) indicating good precision, the accuracy for

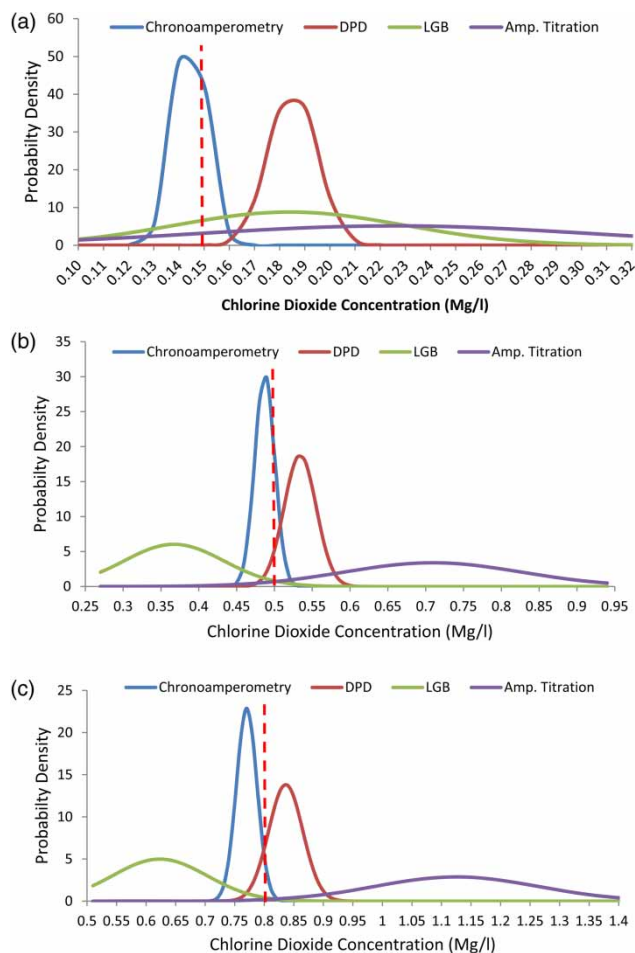


Figure 1 | Probability distribution at 27 °C for the four different analytical techniques at different chlorine dioxide standard concentrations: (a) 0.15 mg/L, (b) 0.5 mg/L, (c) 0.8 mg/L.

DPD technique was much lower than chronoamperometry given that % bias for both techniques were 18.8% and 4.6%, respectively.

As a summary, amperometric titration analytical technique produced results that were quite distant from the chlorine dioxide standard concentration (0.15 mg/L). While both LGB wet and DPD analytical techniques gave better results, the chronoamperometry analytical technique did considerably better and achieved superior accuracy and precision. Based on both accuracy and precision, the four analytical techniques were ranked as follows:

Chronoamperometry > DPD > LGB WET
> amperometric titration.

At medium range (0.5 mg/L chlorine dioxide). The 25 repeated measurements for 0.5 mg/L chlorine dioxide standard concentrations utilizing the four different techniques were performed and results were recorded. The probability density for the entire set of results was calculated using probability formula and then presented graphically in Figure 1(b) where a straight vertical line was introduced at 0.5 mg/L chlorine dioxide standard concentration.

Table 1 exhibits statistical descriptive analysis as well as detection for statistical outliers for the four different analytical techniques at 0.5 mg/L standard chlorine dioxide concentration. Given that none of the measured results lies outside the IQR limits, no problematic outliers were identified for the four analytical techniques at 0.5 mg/L ClO₂.

Average Bias % and %CV for the four analytical techniques at 0.5 mg/L chlorine dioxide standard concentration are graphically presented in Figure 2(b). Both amperometric titration and LGB WET analytical techniques show very high Bias % values (27.8% and 40.6%, respectively), indicating low precision while the high and quite similar %CV values (16.6% and 18%) indicate low accuracy for both techniques.

Although both chronoamperometry and DPD analytical techniques show considerably low values for %CV (2.7% and 4.0%, respectively) indicating good precision, the accuracy for DPD technique was lower but not that far from chronoamperometry given that Bias % for both techniques was 6.5% and 3.3%, respectively.

Based on both accuracy and precision, the four analytical techniques were ranked as follows:

Chronoamperometry > DPD > amperometric titration
> LGB WET.

At high range (0.80 mg/L chlorine dioxide). The 25 repeated measurements for 0.8 mg/L chlorine dioxide standard concentrations utilizing the four different techniques were performed and results were recorded. The probability density for the entire set of results were calculated using probability formula and then presented graphically in Figure 1(c), where a straight vertical line was introduced at 0.8 mg/L chlorine dioxide standard concentration.

Table 1 shows statistical descriptive analysis as well as detection for statistical outliers for the four different analytical techniques at 0.8 mg/L standard chlorine dioxide

Table 1 | Standard chlorine dioxide concentration measurements at 27 °C using the four different analytical techniques

ClO ₂ (mg/L)		Chronoamperometry	DPD	LGB WET	Amperometric titration
0.15	Descriptive statistical analysis				
	Smallest value	0.13	0.16	0.12	0.13
	Largest value	0.16	0.2	0.24	0.31
	Average	0.14	0.19	0.18	0.23
	Standard deviation	0.007	0.010	0.045	0.078
	Range	0.03	0.04	0.12	0.18
	Detection of statistical outliers				
	Q1	0.14	0.18	0.14	0.14
	Q3	0.15	0.19	0.23	0.29
	IQR (inter-quartile range)	0.01	0.01	0.09	0.15
	Lower limit 'Q1 - (3.0* IQR)'	0.11	0.15	-0.13	-0.31
Upper limit 'Q3 + (3.0* IQR)'	0.18	0.22	0.50	0.74	
0.5	Descriptive statistical analysis				
	Smallest value	0.47	0.49	0.27	0.6
	Largest value	0.51	0.57	0.48	0.92
	Average	0.49	0.53	0.37	0.71
	Standard deviation	0.013	0.021	0.066	0.118
	Range	0.04	0.08	0.21	0.32
	Detection of statistical outliers				
	Q1	0.48	0.52	0.31	0.61
	Q3	0.49	0.55	0.41	0.81
	IQR (inter-quartile range)	0.01	0.03	0.10	0.20
	Lower limit 'Q1 - (3.0* IQR)'	0.45	0.43	0.01	0.01
Upper limit 'Q3 + (3.0* IQR)'	0.52	0.64	0.71	1.41	
0.8	Descriptive statistical analysis				
	Smallest value	0.74	0.79	0.51	0.97
	Largest value	0.8	0.87	0.76	1.4
	Average	0.77	0.84	0.62	1.13
	Standard deviation	0.017	0.029	0.080	0.139
	Range	0.06	0.08	0.25	0.43
	Detection of statistical outliers				
	Q1	0.14	0.18	0.14	0.14
	Q3	0.15	0.19	0.23	0.29
	IQR (inter-quartile range)	0.01	0.01	0.09	0.15
	Lower limit 'Q1 - (3.0* IQR)'	0.11	0.15	-0.13	-0.31
Upper limit 'Q3 + (3.0* IQR)'	0.14	0.18	0.14	0.14	

concentration. The entire set of results produced by the four different analytical techniques lie within the IQR limits indicating the absence of any problematic outliers.

Figure 2(c) demonstrates average Bias % and %CV for the four analytical techniques at 0.8 mg/L chlorine dioxide standard concentration. Both amperometric titration and LGB WET analytical techniques show very high Bias % values (27.9% and 30.4%, respectively) indicating low precision while the high and quite similar %CV values (12.3% and 12.8%) indicate low accuracy for both techniques.

Although both chronoamperometry and DPD analytical techniques show considerably low values for %CV (3.9%

and 4.4%, respectively) indicating good precision, the accuracy for chronoamperometry technique was higher but not far from DPD technique given that Bias % for both techniques were 2.3% and 3.4%, respectively.

Based on both accuracy and precision, the four analytical techniques were ranked as follows:

Chronoamperometry > DPD > amperometric titration
> LGB Wet.

Accuracy and precision summary at 27 °C. As a summary, amperometric titration and LGB WET analytical techniques

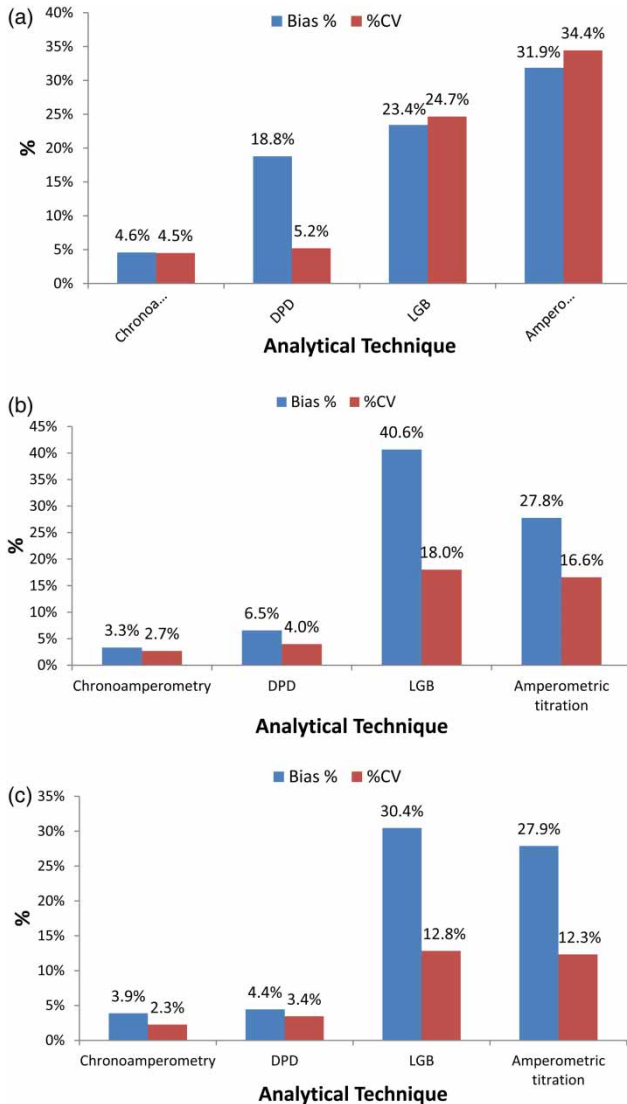


Figure 2 | Average Bias % and %CV at 27 °C for the four different analytical techniques at different chlorine dioxide standard concentrations: (a) 0.15 mg/L, (b) 0.5 mg/L, (c) 0.8 mg/L.

produced results that were quite distant from the chlorine dioxide standard concentrations (0.15, 0.5, and 0.8 mg/L). The chronoamperometry analytical technique did considerably better and achieved the superior accuracy and precision even compared to the DPD results.

Analytical technique detection limits (MDL)

Given that chronoamperometry analytical technique has the lowest detection levels (0.02 mg/L) among the rest of the

analytical techniques (0.05 mg/L for both DPD and LGB WET), chronoamperometry would have the advantage in such a comparison.

Time and skill required for implementation of the analytical technique (time consumption)

Utilizing a digital stop watch, the actual time to perform one sample (from start till results' availability) was determined. The test was repeated three times each and the average value was taken for each analytical technique. Table 2 shows the time spent to perform chlorine dioxide measurements.

Therefore, the four analytical techniques could be ranked based on their time consumption as follows:

LGB WET > amperometric titration > DPD
 ≥ chronoamperometry.

Both amperometric titration and LGB WET analytical techniques were more cumbersome and time-consuming to perform than either the DPD or chronoamperometry analytical techniques. Moreover, it is quite difficult to complete these techniques in the site/field. For this reason, they are less desirable even for routine use. Thus, the chronoamperometry analytical technique ultimately proved superior.

Evaluation matrix conclusion

Based on the predefined evaluation matrix, chronoamperometry is the best commercially available analytical technique to measure ClO₂ in finished drinking water.

Table 2 | Time spent to perform chlorine dioxide measurements for 1 and 25 samples utilizing different analytical techniques

	Analytical techniques			
	DPD	Chrono-amperometry	LGB WET	Amperometric titration
Analysis time				
1 sample	1 min	<1 min	25 min	20 min
25 samples	25 min	23–25 min	10.4 hours	8.3 hours

Study of the influence of various factors on the performance of the proved superior analytical technique

Given that chronoamperometry analytical technique performance was proven the best among the other four analytical techniques, the influence of various factors (sample temperature, high ionic strength, and interferences like chlorite and free chlorine) on the chronoamperometry analytical technique performance was studied.

Performance at various sample temperatures

Sample temperature is widely understood to affect some of the analytical techniques performances, which could adversely affect technique robustness and precision. To address this concern, the impact of sample temperature on the chronoamperometry analytical technique performance was tested at the three different chlorine dioxide standard concentrations (0.15, 0.5, and 0.8 mg/L). Each standard chlorine dioxide concentration was tested 15 times and the temperature regime included three different temperatures (15, 20, and 35 °C). Results for these three different temperatures were compiled with results previously achieved at 27 °C and were studied to evaluate the performance at a wide

range of temperature regimes. Table 3 shows some statistical indicators for the performed experiments.

At temperatures higher than 35 °C, it was difficult to repeat testing because of the volatility of chlorine dioxide at elevated temperatures.

The average chlorine dioxide reading for the different chlorine dioxide standard concentration is illustrated in Figure 3(a) while Figures 3(b) and 3(c) illustrate %CV and Bias % at each temperature, respectively.

At temperatures up to 27 °C, the results for all chlorine dioxide ranges reveal averages quite closer to the standard chlorine dioxide concentrations, with very narrow and quite small values for both %CV and Bias %, ranging from 2.0% to 4.6% and 1.1% to 4.6%, respectively. This indicates significant accuracy and precision. Therefore, the chronoamperometry analytical technique performance remained unaffected and nearly the same for temperatures closer to or below 27 °C.

Performance in high ionic strength samples

Tests were carried out to determine whether the chronoamperometry analytical technique performance is affected when conducting the test procedure in high ionic strength samples such as sea water.

Table 3 | Statistical indicators for different chlorine dioxide standard concentrations (0.15, 0.5, and 0.8 mg/L) at the four different temperatures (15, 20, 27, and 35 °C)

ClO ₂ (mg/L)	Statistical analysis	15 °C	20 °C	27 °C	35 °C
0.15 (low range)	Min.	0.15	0.14	0.13	0.11
	Max.	0.16	0.16	0.16	0.17
	Mean	0.156	0.148	0.148	0.133
	Standard deviation	0.00507	0.00560	0.00676	0.017915
	Range	0.01	0.02	0.03	0.06
	Bias %	4.0%	1.3%	1.3%	11.6%
0.5 (medium range)	Min.	0.47	0.48	0.47	0.39
	Max.	0.52	0.52	0.51	0.52
	Mean	0.489	0.505	0.487	0.439
	Standard deviation	0.01335	0.01552	0.01291	0.04138
	Range	0.05	0.04	0.04	0.13
	Bias %	2.1%	1.1%	2.7%	12.3%
0.8 (high range)	Min.	0.78	0.76	0.74	0.67
	Max.	0.83	0.82	0.8	0.84
	Mean	0.809	0.791	0.771	0.737
	Standard deviation	0.01642	0.02167	0.01807	0.06065
	Range	0.05	0.06	0.06	0.17
	Bias %	1.1%	1.1%	3.6%	7.8%

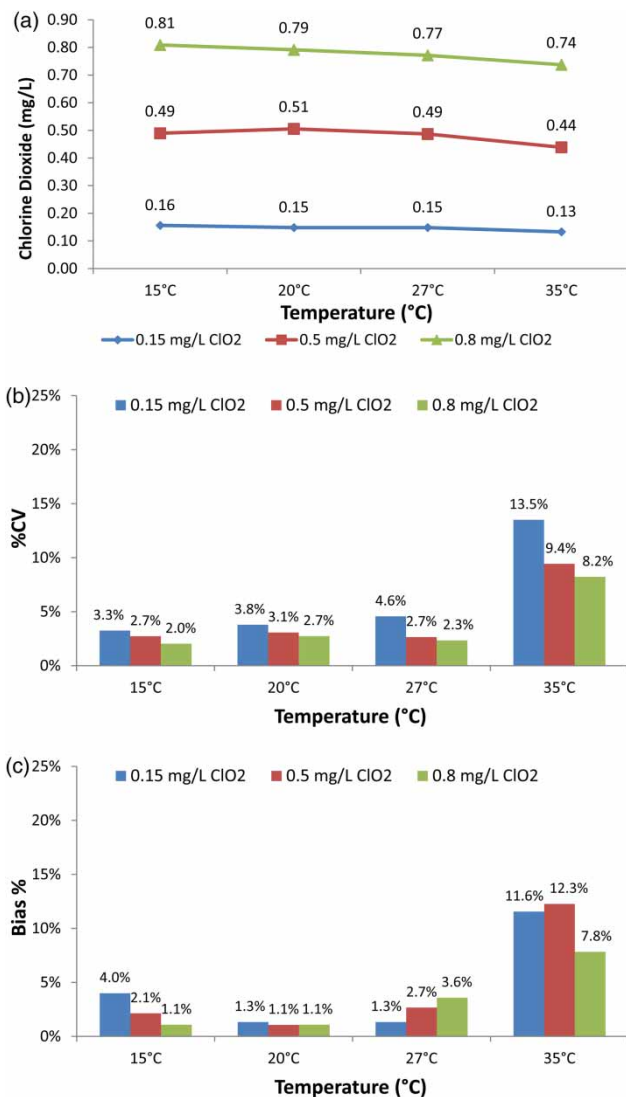


Figure 3 | Chronoamperometry analytical technique performance on different chlorine dioxide standard concentrations at various sample temperatures: (a) chlorine dioxide measurements, (b) %CV, (c) Bias %.

Along with the zero NaCl concentration sample, three different NaCl concentrations (10, 20, and 30 g/L) were tested. The different NaCl concentrations were achieved by diluting a real sea water sample. All the samples were tested at room temperature (27 °C).

Chlorine dioxide blank measurements at different NaCl concentrations. To confirm the analytical technique's performance at zero chlorine dioxide samples (blank) and 27 °C, the four different samples with different NaCl concentrations (ranging between zero and 30 g/L) and chlorine

dioxide levels were measured at least five times. Results shown in Table 4 indicate no difference in the blank reading at the different salt concentrations (ranging between zero and 30 g/L).

Performance at different ionic strength samples and different chlorine dioxide concentrations. The impact of sample ionic strength on the chronoamperometry analytical technique's performance at the three different chlorine dioxide standard concentrations (0.15, 0.5, and 0.8 mg/L) was tested. Each standard chlorine dioxide concentration was tested ten times. The ionic strength regime includes four different NaCl levels (0, 10, 20, and 30 g/L). Statistical significance testing (F-test and T-test) was calculated by Microsoft Excel[®] to evaluate significance difference among chlorine dioxide means (each value was compared in reference to the zero NaCl levels).

Table 5 exhibits statistical significance for all chlorine dioxide tested concentrations (0.15, 0.5, and 0.8 mg/L) at the four different NaCl levels (0, 10, 20, and 30 g/L). Furthermore, *P*-value for both F-test and T-test was included.

F-test (*P*-value) for all ionic strengths (in reference to zero level NaCl) and all chlorine dioxide standard concentrations (0.15, 0.5, and 0.8 mg/L) shows values higher than 0.05 indicating that variances are assumed to be equal. Given that *P*-value (for T-test with equal variance) was higher than 0.05, the difference in means for all concentrations (in reference to zero level NaCl) is not significant.

Given that all results (at all chlorine dioxide tested concentrations) were within a reasonable and a very good tolerance, high ionic strength samples (such as sea water with up to 30 g/L NaCl) had not diminished the chronoamperometry technique's performance. The chronoamperometry technique was fairly adequate in all matrices.

Table 4 | Chlorine dioxide raw water blank samples at different NaCl concentrations

Chlorine dioxide nominal concentration (mg/L)	NaCl (g/L)	Mean response (mg/L ClO ₂)
0	0	N.D.
0	10	N.D.
0	20	N.D.
0	30	N.D.

N.D., not detected.

Table 5 | Statistical significance for all chlorine dioxide tested concentrations (0.15, 0.5, and 0.8 mg/L) at the four different NaCl levels (0, 10, 20, and 30 g/L)

ClO ₂ (mg/L)	Statistical analysis	0 g/L NaCl	10 g/L NaCl	20 g/L NaCl	30 g/L NaCl
0.15 (low range)	Min.	0.14	0.15	0.14	0.13
	Max.	0.16	0.16	0.17	0.15
	Mean	0.147	0.142	0.154	0.140
	Standard deviation	0.0067	0.0092	0.0117	0.0082
	% CV	4.6%	6.5%	7.6%	5.8%
	F-test (<i>P</i> -value)	–	0.1858	0.0574	0.2898
	T-test (<i>P</i> -value)	–	0.1825	0.1194	0.0511
0.5 (medium range)	Min.	0.47	0.47	0.46	0.46
	Max.	0.51	0.52	0.5	0.5
	Mean	0.488	0.493	0.478	0.480
	Standard deviation	0.0132	0.0164	0.0123	0.0141
	% CV	2.7%	3.3%	2.6%	2.9%
	F-test (<i>P</i> -value)	–	0.2636	0.4207	0.4173
	T-test (<i>P</i> -value)	–	0.4613	0.0962	0.2069
0.8 (high range)	Min.	0.75	0.76	0.75	0.75
	Max.	0.79	0.81	0.77	0.79
	Mean	0.769	0.777	0.759	0.763
	Standard deviation	0.0152	0.0183	0.0088	0.0134
	% CV	2.0%	2.4%	1.2%	1.8%
	F-test (<i>P</i> -value)	–	0.2978	0.0571	0.3519
	T-test (<i>P</i> -value)	–	0.3020	0.3618	0.3618

Performance in presence of various chlorite concentrations

To identify and quantify the impact of chlorite concentrations (up to 1.0 mg/L) on chronoamperometry technique performance, three different chlorine dioxide standard concentrations (0.15, 0.5, and 0.8 mg/L) were tested where each standard chlorine dioxide concentration was tested ten times. The chlorite level regime includes four different concentrations: zero chlorite, 0.25, 0.5, and 1.0 mg/L. Statistical significance testing (F-test and T-test) was calculated by Microsoft Excel[®] to evaluate significance difference among chlorine dioxide means (each value was compared in reference to the zero chlorite level). All the samples were tested at room temperature (27 °C).

Table 6 shows statistical significance for all chlorine dioxide tested concentrations (0.15, 0.5, and 0.8 mg/L) at the four different chlorite levels (0, 0.25, 0.5, and 1.0 mg/L). Furthermore, *P*-value for both F-test and T-test was included.

F-test (*P*-value) for all ionic strengths (in reference to zero level NaCl) and all chlorine dioxide standard concentrations (0.15, 0.5, and 0.8 mg/L) shows values higher than

0.05 indicating that variances are assumed to be equal. Given that *P*-value (for T-test with equal variance) was higher than 0.05, the difference in means for all concentrations (in reference to zero level chlorite) is not significant.

Given that all results (at all chlorine dioxide tested concentrations) were within a reasonable and a very good tolerance, it was determined that the effect of chlorite on the chronoamperometry technique performance was negligible over the range of chlorite concentrations that are likely to be encountered in the drinking water samples.

Impact of free chlorine

To quantify the response of the chronoamperometry analytical technique to varying chlorine concentrations, different free chlorine concentrations ranging between 0.1 and 1.0 mg/L were added to water samples with low chlorine dioxide concentration (0.15 mg/L). Free chlorine concentrations (even quite small levels) show positive interference on the chronoamperometry analytical technique, however the addition of glycine drops prior to carrying out the chlorine dioxide measurements remove such effect.

Table 6 | Statistical significance for all chlorine dioxide tested concentrations (0.15, 0.5, and 0.8 mg/L) at the four different chlorite concentrations (0, 0.25, 0.5, and 1.0 mg/L)

ClO ₂ (mg/L)	Statistical analysis	0 mg/L chlorite	0.25 mg/L chlorite	0.5 mg/L chlorite	1.0 mg/L chlorite
0.15 (low range)	Min.	0.13	0.13	0.13	0.14
	Max.	0.16	0.16	0.16	0.18
	Mean	0.144	0.142	0.148	0.154
	Standard deviation	0.0084	0.0092	0.0123	0.0135
	% CV	5.9%	6.5%	8.3%	8.8%
	F-test (<i>P</i> -value)	–	0.4011	0.1384	0.0886
	T-test (<i>P</i> -value)	–	0.6182	0.4073	0.0624
0.5 (medium range)	Min.	0.45	0.45	0.45	0.44
	Max.	0.52	0.53	0.52	0.53
	Mean	0.483	0.473	0.468	0.465
	Standard deviation	0.0254	0.0291	0.0244	0.0317
	% CV	5.3%	6.1%	5.2%	6.8%
	F-test (<i>P</i> -value)	–	0.3471	0.4532	0.2598
	T-test (<i>P</i> -value)	–	0.4235	0.1949	0.1783
0.8 (high range)	Min.	0.76	0.74	0.74	0.74
	Max.	0.84	0.83	0.84	0.83
	Mean	0.788	0.771	0.791	0.766
	Standard deviation	0.0319	0.0321	0.0393	0.0299
	% CV	4.0%	4.2%	5.0%	3.9%
	F-test (<i>P</i> -value)	–	0.4918	0.2725	0.4246
	T-test (<i>P</i> -value)	–	0.2505	0.8534	0.1289

Implementation in desalinated drinking water distribution systems

Distribution system design and modeling

For network designers, the study deliverables can confidently assist chlorine dioxide disinfection planning/management in drinking water distribution systems. This enables system planners/managers to find efficiently the proper chlorine dioxide disinfection dosages that allow residual targets at system extremities to be met.

Booster disinfection stations

Disinfectant residuals are assumed to be sufficient to prevent growth of pathogenic bacteria, yet low enough to avoid taste and odor problems. Commonly, large quantities of disinfectants are released at the sources outlets for preserving minimum residual disinfectant concentrations throughout the network. Such an approach can cause taste and odor problems near the disinfectant injection locations, and, more importantly, hazardous, excessive, disinfectant by-product formations (DBPs) at the far network ends, of which some

may be carcinogenic. To cope with these deficiencies, booster chlorination stations were suggested to be placed at the distribution system itself and not just at the sources, motivating considerable research in recent years on placement, design, and operation of booster chlorination stations in water distribution systems.

The proper monitoring for chlorine dioxide residuals can aid in the decision variables for chlorine dioxide disinfection boosters in water distribution systems. Decision variables include but are not limited to boosters' design, placement, number of stations, and operation control and operation optimization.

Operation control for disinfection systems

Operational control and operation optimization strategies for chlorine dioxide disinfection systems can be easily adopted through the proper monitoring for residual chlorine dioxide. Thus, water treatment plant managers can easily plan/alter chlorine dioxide dosages vs. seasonal temperature profiles/changes. Those planned dosages may be fine-tuned by careful monitoring for chlorine dioxide residual at the far ends of the network. Optimum levels will take account of

the chlorine dioxide decay in the distribution system under normal and drain-down conditions.

CONCLUSIONS

In order to ensure delivery of high quality drinking water from treatment plants to customers, maintaining adequate levels of disinfectant is very important, therefore it is necessary to properly monitor the disinfection levels in drinking water.

Research has long been conducted and will continue to be performed on the topic of analytical techniques comparison. This research provides a unique insight into the comparison of a commercially available analytical technique for measuring chlorine dioxide in desalinated drinking water. The research work deliverables will aid not only in determining the correct concentration of a disinfectant in a solution, but also in disinfection planning/management including boosters.

The research work indicated the following:

- Based on the predefined criteria for selection of the best commercially available analytical techniques, none of the analytical techniques came close to ideal standards.
- Over a wide range of ClO_2 concentrations, the chronoamperometry and the DPD analytical techniques possess improvements over the most common analytical techniques, namely the amperometric titration and the LGB WET, which suffer from lack of precision, accuracy, skewed response, and relatively high detection limits.
- The chronoamperometry technique can be determined to possess several distinct advantages over the DPD technique; it is more sensitive, precise, and accurate. Lower detection limits and relatively small analysis time likewise signify that the chronoamperometry technique is more convenient.
- Based on the evaluation of predefined criteria, the four analytical techniques would be rated as follows:

Chronoamperometry > DPD > amperometric titration
> LGB WET.

Studying various factors that might influence the chronoamperometry technique's performance indicates the following:

- At decreased sample temperature (closer to or less than 27°C), no noticeable change was observed on the chronoamperometry technique performance. Although the performance was acceptable at 35°C , it is preferable to cool down the water samples to a temperature below or closer to 27°C to negate the possible negative contribution of chlorine dioxide volatility on the technique performance.
- High ionic strength samples (such as sea water with up to 30 g/L NaCl) did not diminish the technique's performance, where it was fairly adequate in all matrices.
- It was determined that the effect of chlorite on the technique performance was negligible over the range of chlorite concentrations that will likely be encountered in the drinking water samples.
- Even small concentrations, free of chlorine show positive interference on the chronoamperometry analytical technique, however the addition of glycine drops prior to carrying out the chlorine dioxide measurements removes such effect.

Given that the performance of the chronoamperometry analytical technique was proved superior to the other techniques while it shows robustness and quite stable performance against the different interference constituents, it is recommended for the monitoring of ClO_2 in desalinated drinking water. A deeper understanding of the other oxidative species influence on the accuracy of measurements would be recommended for future studies and research.

On the other hand, the study deliverables can confidently assist chlorine dioxide disinfection planning/management in drinking water distribution systems. Moreover, this study can aid in the decision variables (design, placement, number of stations, and operation control and operation optimization strategies) for primary and booster chlorine dioxide disinfection systems in water distribution systems.

REFERENCES

- American Public Health Association 2012 *Standard Methods for the Examination of Water and Wastewater*. 22nd edn. APHA AWWA-WEF, Washington, DC, USA.

- Ammar, T. A., Abid, K. Y., El-Bindary, A. A. & El-Sonbati, A. Z. 2014 Chlorine dioxide bulk decay prediction in desalinated drinking water. *Desalination* **352**, 45–51.
- Antonopoulou, M., Evgenidou, E., Lambropoulou, D. & Konstantinou, I. 2014 A review on advanced oxidation processes for the removal of taste and odor compounds from aqueous media. *Water Res.* **53**, 215–234.
- Barry, V. P., Teri, A. D., Patricia, S. F., David, J. M., Gilbert, G. & Zsolt, K. 2007 An improved colorimetric method for chlorine dioxide and chlorite ion in drinking water using lissamine green B and horseradish peroxidase. *Analyt. Chim. Acta* **596**, 37–45.
- Chang, C. Y., Hsieh, Y. H., Hsu, S. S., Hu, P. Y. & Wang, K. H. 2000 The formation of disinfection by-products in water treated with chlorine dioxide. *J. Hazard. Mater.* **79**, 89–102.
- Chiswell, B. & O'Hallaran, K. R. 1991 Use of Lissamine Green B as a spectrophotometric reagent for the determination of low residuals of chlorine dioxide. *Analyst* **116**, 657–661.
- Cristo, D. C., Esposito, G. & Leopardi, A. 2013 Modelling trihalomethanes formation in water supply systems. *Environ. Technol.* **34** (1), 61–70.
- Dietrich, A. M., Orr, M. P., Gallagher, D. L. & Hoehn, R. C. 1992 Tastes and odors associated with chlorine dioxide. *J. AWWA* **84** (6), 82–88.
- Emmert, G. L., Coutant, D. E., Sweetin, D. L., Gordon, G. & Bubnis, B. 2000 Studies of selectivity in the amaranth method for chlorine dioxide. *Talanta* **51**, 879–888.
- Gates, D. J. & Don, G. 1998 The Chlorine Dioxide Handbook, *Water Disinfection Series*. AWWA Publications, New York.
- Ginige, M. P., Wylie, J. & Plumb, J. 2011 Influence of biofilms on iron and manganese deposition in drinking water distribution systems. *Biofouling* **27**, 151–163.
- Hoffmann, R., Ye, Q. & Andrews, R. C. 1998 Comparison of spectrophotometric methods for measuring chlorine dioxide in drinking water. *Environ. Technol.* **19**, 761–773.
- Jensen, J. N. & Johnson, J. D. 1990 Interferences by monochloramine and organic chloramines in free available chlorine methods- amperometric titration. *Environ. Sci. Technol.* **24** (7), 981–985.
- Jin, M., Shan, J., Chen, Z., Guo, X., Shen, Z., Qiu, Z., Xue, B., Wang, Y., Zhu, D., Wang, X. & Li, J. 2013 Chlorine dioxide inactivation of enterovirus 71 in water and its impact on genomic targets. *Environ. Sci. Technol.* **47**, 4590–4597.
- Jones, D. B., Song, H. & Karanfil, T. 2012a The effects of selected peroxidation strategies on I-THM formation and speciation. *Water Res.* **46**, 5491–5498.
- Jones, D. B., Saglam, A., Song, H. & Karanfil, T. 2012b The impact of bromide/iodide concentration and ratio on iodinated trihalomethane formation and speciation. *Water Res.* **46**, 11–20.
- Karanfil, T., Hu, J., Jones, D. B., Addison, J. W. & Song, H. 2011 Formation of Halonitromethanes and Iodo-trihalomethanes in Drinking Water. Water Research Foundation, Denver, CO.
- Li, L., Gao, N. Y., Deng, Y., Yao, J. J. & Zhang, K. J. 2012 Characterization of intracellular and extracellular algae organic matters (AOM) of *Microcystis aeruginosa* and formation of AOM-associated disinfection byproducts and odor and taste compounds. *Water Res.* **46** (4), 1233–1240.
- Li, X., Jiang, D. & Zhang, Y. 2013a The self-decay characteristics of chlorine dioxide in water. *Adv. Mater. Res.* **610–613**, 296–299.
- Li, S., Zhao, D., Hu, S., Wang, Z., Li, D., Yuan, X. & Xie, B. 2013b Trichloromethane formation potential in killing algae with chlorine dioxide. *Procedia Environ. Sci.* **18**, 597–601.
- Liu, G., Lut, M. C., Verberk, J. O. & Van Dijk, J. C. 2013 A comparison of additional treatment processes to limit particle accumulation and microbial growth during drinking water distribution. *Water Res.* **47**, 2719–2728.
- Mark, K. M. & William, B. S. 2008 *Field Manual for Water Quality Monitoring: An Environmental Education Program for Schools*. 13th edn. Kendall Hunt Publishing, Dubuque County, Iowa, USA.
- Masschelein, W. J. 1996 Spectrophotometric determination of chlorine dioxide with Acid Chrome Violet K. *Anal. Chem.* **38** (13), 1839–1841.
- Nie, S., Liu, X., Wu, Z., Zhan, L., Yin, G., Yao, S., Song, H. & Wang, S. 2014 Kinetics study of oxidation of the lignin model compounds by chlorine dioxide. *Chem. Eng. J.* **241**, 410–417.
- Palintest 2011 *Chlordioxense Instrument Instructions Manual*. Palintest, Kentucky, USA.
- Prasad, T. D. & Danso-Amoako, E. 2014 Influence of chemical and biological parameters on iron and manganese accumulation in water distribution networks. *Procedia Eng.* **70**, 1353–1361.
- Shah, A. D., Krasner, S. W., Lee, C. F. T., Von Gunten, U. & Mitch, W. A. 2012 Trade-offs in disinfection byproduct formation associated with precursor preoxidation for control of n-nitrosodimethylamine formation. *Environ. Sci. Technol.* **46**, 4809–4818.
- Shaoxiu, L., Dejun, Z., Shujie, H., Zhihong, W., Dongmei, L., Xiuli, Y. & Baohong, X. 2013 Trichloromethane formation potential in killing algae with chlorine dioxide. *Procedia Environmental Sciences* **18**, 597–601.
- Sorlini, S., Gialdini, F., Biasibetti, M. & Collivignarelli, C. 2014 Influence of drinking water treatments on chlorine dioxide consumption and chlorite/chlorate formation. *Water Res.* **54**, 44–52.
- Tang, T. F. & Gordon, G. 1989 Quantitative determination of chloride, chlorite, and chlorate ions in mixtures by successive potentiometric titrations. *Anal. Chem.* **52**, 1430–1433.
- Wang, P., He, Y. L. & Huang, C. H. 2011 Reactions of tetracycline antibiotics with chlorine dioxide and free chlorine. *Water Res.* **45**, 1838–1846.
- Wang, W., Zhang, X., Wang, H., Wang, X., Zhou, L., Liu, R. & Liang, Y. 2012 Laboratory study on the adsorption of Mn^{2+} on suspended and deposited amorphous $Al(OH)_3$ in drinking water distribution systems. *Water Res.* **46** (13), 4063–4070.
- World Health Organization 2011 *Guidelines for Drinking-water Quality*. 4th edn, WHO, Geneva, Switzerland, pp. 61–69.
- Xue, B., Jin, M., Yang, D., Guo, X., Chen, Z., Shen, Z., Wang, X., Qiu, Z., Wang, J., Zhang, B. & Li, J. 2013 Effects of chlorine and chlorine dioxide on human rotavirus infectivity and genome stability. *Water Res.* **47**, 3329–3338.

- Yang, X., Wanhong, G., Xing, Z., Feng, C., Tingjin, Y. & Wei, L. 2013a Formation of disinfection by-products after pre-oxidation with chlorine dioxide or ferrate. *Water Res.* **47**, 5856–5864.
- Yang, X., Guo, W. H. & Lee, W. 2013b Formation of disinfection byproducts upon chlorine dioxide preoxidation followed by chlorination or chloramination of natural organic matter. *Chemosphere* **91**, 1477–1485.
- Yi-Tze, T., Jih-Hsing, C., Chen-Yu, C., Yung-Hsu, H. & Shan-Yi, S. 2014 Efficiency and mechanisms of chlorine dioxide generation by electrocatalytical process. *J. Taiwan Inst. Chem. Eng.* **45** (2), 404–410.
- Zhang, K. J., Gao, N. Y., Deng, Y., Zhang, T. O. & Li, C. 2012 Aqueous chlorination of algal odorants: Reaction kinetics and formation of disinfection by-products. *Sep. Purif. Technol.* **92**, 93–99.
- Zhang, K., Fuh, L. T., Zhang, T., Cong, L. & Naiyun, G. 2013 Characterization of typical taste and odor compounds formed by *Microcystis aeruginosa*. *J. Environ. Sci.* **25** (8), 1539–1548.

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