Chlorine Dioxide as a Potable Water Disinfectant: Application, Residuals, and By-products Monitoring

by

Justin Michel Rak-Banville

A Thesis submitted to the Faculty of Graduate Studies of

The University of Manitoba

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Of

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Abstract

The objectives of this work where to study the effectiveness of the standard DPD (N, N-diethyl-p-phenylenediamine) method's for the detection of chlorine dioxide. This included evaluating calibration using potassium permanganate and alternative free chlorine masking agents, diethanolamine and triethanolamine. Additional objectives included the development of suitable spectrophotometric methods alternative to DPD from which a new detection platform could be established. Candidates such as N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD), alizarin red S (ARS), and copper(II) sulfate were selected.

Results suggest that calibration of DPD using a potassium permanganate surrogate is susceptible to temporal changes, whereas use of diethanolamine and triethanolamine as a free available chlorine mask proved to interfere with DPD chlorine dioxide testing. Use of Alizarin red S provided a detection mechanism for chlorine dioxide (0-4 ppm) in the presence of low concentrations of chlorite ion (0.2 and 0.5 ppm). Detection of chlorite concentrations using copper(II) sulfate were established for chlorite concentrations ranging from to 6 ppm to 10 ppm which is much higher than regulated residual concentrations in drinking water. Lastly, the combination of TMPD and cerium(IV) provided for residual chlorine dioxide analysis in concentrations less than 1 ppm.

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Thank you.

Dedication

I would like to dedicate this work to the researchers of chlorine dioxide, and those dedicated to improving the quality of drinking water through a multidisciplinary team approach; to those whom have come and gone and to those who will hopefully build on this work.

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List of Abbreviations

ACVK	Acid Chrome Violet K
ADWG	Australian Drinking Water Guidelines
ARS	Alizarin Red S
AWWA	American Water Works Association
BSRIA	Building Services Research and Information Association
CDHP	California Department of Public Health
CCD	Charged Coupled Device
CPR	Chlorophenol Red
CDW	Committee on Drinking Water
CT	Contact Time
DBP	Disinfection By-product
DEA	Diethanolamine
DIN	Deutsches Institut für Normung (German Institute for Standardization)
DOC	Dissolved Organic Carbon
DPD	N,N-Diethyl-p-phenylenediamine
DMSO	Dimethylsulfoxide
DDBR	Disinfectants/Disinfection By-products Rule
DWA	Drinking Water Act
DWD	Drinking Water Directive

DWP	Drinking Water Program
EPA	Environmental Protection Agency
EDA	Ethylenediamine
EU	European Union
FAC	Free Available Chlorine
FACE	Free Available Chlorine Equivalent
GAC	Granular Activated Carbon
GCDWQ	Guidelines for Canadian Drinking Water Quality
HRP	Horseradish Peroxidase
IC	Ion Chromatography
LGB	Lissamine Green B
LGB-HRP	Lissamine Green B - Horseradish Peroxidase
MAC	Maximum Acceptable Concentrations
MAV	Maximum Acceptable Value
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MRDL	Maximum Residual Disinfectant Level
MRDLG	Maximum Residual Disinfectant Level Goal
NHMRC	National Health and Medical Research Council
NOAEL	No Observable Adverse Effect Level
NOM	Natural Organic Matter

NZDS	New Zealand Drinking Water Standard
ORP	Oxidation Reduction Potential
PAO	Phenylarsine Oxide
PCR	Postcolumn Reagents
NTS	Sodium Thiosulfate
SPE	Solid Phase Extraction
TDI	Tolerable Daily Intake
TEA	Triethanolamine
THM	Trihalomethanes
tTHM	Total Trihalomethanes
TMPD	N,N,N',N'-Tetramethyl-p-phenylenediamine
UK	United Kingdom
US	United States
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
UV-VIS	Ultraviolet-Visible
WHO	World Health Organization

Part 1: Research Objectives

Chapter 1: Problem Statement

Chlorine (Cl_2) is arguably the most common potable water disinfectant used throughout North America. Although it is important to supply safe, potable water, analytical and toxicological research has shown the emergence (since the mid 1970's) of disinfection by-products, namely trihalomethanes (THMs) which have been shown to cause adverse reproductive or developmental effects among laboratory animal testing (World Health Organization (WHO), 2008, Clark and Boutin, 2001, American Water Works Association., 1990). Consequently, Regulators are now actively curbing THM concentrations in treatment plants. Driven by a low regulated THM content in finished waters, the replacement of chlorination, in favour of adopting chlorine dioxide, is becoming an increasingly admired scenario.

The large scale use and acceptance of chlorine dioxide has routinely presented a certain magnitude of dissonance among scientists, engineers, and regulators. This discord is presented as the difficulty in achieving a targeted dosage level, without over producing by-products (chlorite and chlorate) beyond regulated concentrations. Particularly, the hypothetical dosage level which is targeted at meeting oxidant demand and achieving potable water disinfection may potentially exceed current guidelines set for maximum dosages. The exceedance of guideline dosages can potentially lead to the subsequent formation of increased chlorite and chlorate concentrations beyond regulated by-product concentrations.

Numerous chlorine dioxide detection systems have been proposed throughout the last two to three decades, with some being more effective than others. Of those proposed, a few have matured to become standardized, while others are simply the result of research studies (Pepich, et al., 2007, Hodgden and Ingols, 2002, Pinkernell, et al., 2000, Hui, et al., 1997, Xin and Jinyu, 1995, Fletcher and Hemmings, 1985, Knechtel, et al., 1978). These growing research interests may be considered the result of concern regarding the adverse health effects of THMs in finished waters. In particular, as THM formation has been shown to be linked to the use of free chlorine, chlorine dioxide does not produce THMs (Johnson and Jensen, 1986) and has become an attractive alternative.

A leading disadvantage to the use of chlorine dioxide has been the lack of available established standardized monitoring and analysis methods to which regulators, operators, and researchers may refer. This situation is further complicated when chlorine dioxide is added to systems which cannot maintain a residual concentration, therefore necessitating an additional disinfectant such as the addition of free available chlorine (FAC) throughout the treatment process or within the distribution system. It is the combination of disinfectants which can proliferate the multitude of oxychlorine species present in these waters leading to analysis interferences. These include chlorine dioxide, chlorite, chlorate, FAC, and combined chlorine which either exist as a residual concentration or by-products arising from the use of a mixed chlorine dioxide and free chlorine treatment process. Therefore, any detection system (specifically the chromophoric reagent) designed for a particular oxychlorine species must be, at minimum, sensitive to typical residual concentrations (sub 1 ppm range), but also provide

the necessary selectivity among common interferences and reproducibility required of such a method which regulates water for human consumption.

An ideal method would provide operators with an inexpensive daily routine (including quality control calibration) of which is straightforward, non-labour intensive and reproducible; these demands largely limit such development to spectrophotometry. While there are a multitude of generator designs which exploit different synthesis reactions, both regulators and operators must be aware of generator purity and potential by-products introduced which may affect the adoption of a particular analysis method. Though such criteria suggest the benefits of on-line chlorine dioxide and chlorite selective electrodes, for the most part, North American regulators have yet to adopt such methods.

Efforts to eliminate current drawbacks to the use of chlorine dioxide include improvements to current field detection methods and regulations which not only approve, but also encourage such developmental use. As such, the use of standardized EPA approved methods for residual analysis, on-line real-time amperometric sensor based monitoring systems, and discontinuance of the reliance on DPD are all initial, but crucial steps, to developing chlorine dioxide as not only a THM-solution, but also a small economic treatment center disinfectant.

Consequently, the reliance upon spectrophotometry for both the selectivity and sensitivity required to determine low levels of chlorine dioxide in the presence of chlorite, FAC, chlorate, and other species requires extensive research and testing. This manuscript presents three spectrophotometric reagents which exhibit potential for further

advancement and prospective development of a spectrophotometric method alternative to DPD for detection of chlorine dioxide and its by-products.

The principal focus of this research was to study the effectiveness of the standard DPD method for the detection of chlorine dioxide in potable waters, including an evaluation of the spectrophotometric calibration using potassium permanganate. The fundamental theory supporting DPD for chlorine dioxide involves the incorporation of the FAC masking agent known as glycine, which when reacted, forms a non-oxidizable product. Through the elimination of FAC (via the formation of non-oxidizable product, ie. "masking"), the potential for reaction between FAC and chlorine dioxide is negated, and in turn, provides DPD to be the sole reactant for chlorine dioxide. This masking is the basic theory which effectively gives rise to the DPD detection method for chlorine dioxide. Though this fundamental supposition is debated in literature, and typically there exist other oxidative candidates in water sources (ranging from metal ions to other oxy-chlorine species, or even potentially oxidative pharmaceuticals), studies investigating alternative masking agents which exhibit potential for a wider spectrum of masking are warranted. This research included evaluating the use of an alternative masking agent consisting of a mixture of both diethanolamine and triethanolamine which was hypothesized to completely mask FAC, and potentially other oxidative species excluding chlorine dioxide.

Finally, the development of potential alternative spectrophotometric reagents was explored to provide a foundation for further research. Promising candidates, such as alizarin red, copper(II) sulfate, and N,N,N',N'-tetramethyl-p-phenylenediamine were investigated for their potential to measure chlorine dioxide and chlorite for typical

drinking water treatment residual concentrations (sub 1ppm). To carry out these objectives, current available data and literature pertaining to the current use of chlorine dioxide as a drinking water disinfectant, its popularity among North America, and analytical residual measurement methods available for Regulators to rely upon were compiled.

Part 2: Literature Review

Chapter 2: Potable Water Disinfection

2.1 A Brief Review of Chlorination

Safe potable water for consumption is indubitably a critical necessity of all living organisms. On a cellular level, water acts as a plasma to support cellular functions, yet on a systemic or social level, water sources are required for a plethora of civic and industrial purposes. Throughout the history of human existence, civilizations have consistently been rooted and established in close proximity to large bodies of water. Between evidence of unrefined charcoal filtering systems in India as early as 2000 BC (Bagwell, et al., 2001) and the complex architecture of the Roman Aqueducts which date back to 197 BC (Fagerberg, et al., 2006) it is easily recognizable that even these earlier populations were capable of identifying the importance of water. Further recognizable is the increasing demand for large quantities of this natural resource for consumption, as well as other use which have further spurred the exploration of new or alternate water sources that coincide with population growth. It is apparent that not only ancient civilizations, but also contemporary cultures have long understood the merit of accessing

large quantities of water to support the needs of their societies. Despite this, the emphasis throughout the greater part of human history has been placed more on securing large quantities of water rather than monitoring or treating the quality of these sources to prevent the spread of water borne diseases. Historically, one of the earliest disinfection methods recognized for its continued value came from Hippocrates' work and admonition that water should be boiled prior to consumption or use in order to achieve potable waters (Bagwell, et al., 2001).

History has provided documentation detailing organoleptic problems associated with the quality of drinking water sources, specifically turbidity, taste and smell. The realization that basic techniques such as reliance on the use of olfactory and gustatory reflexes to judge water quality are inadequate is a fundamental maturation step for the development of the drinking water disinfection and education processes. The established relationship held between drinking water, water born diseases and consequent death have forced societies to develop our knowledge base for disinfection and further advance technologies for the treatment and prevention of drinking water contamination.

Among these technologies, the application of chlorine (Cl_2) has arguably been the most widely used disinfectant in Canada and the United States (US) for nearly the past 90 years. The disinfection of drinking water has been credited with increasing life expectancy throughout the past century by as much as 50 percent (Simonovic, 2002). The first documented chlorination occurred in 1850, by John Snow in his attempt to disinfect the Broad Street Pump water supply in London (England) following an outbreak of cholera. By 1897, Sims Woodhead synthesized a dilute sodium hypochlorite (NaOCl) solution as a temporary countermeasure to sterilize the potable water distribution mains

in Kent (England) in response to a typhoid outbreak (Irwin, et al., 2006). The success of Woodhead's counter measure was evident, as the response was a remarkable decrease in the number of deaths associated with typhoid, leading to wider adoption throughout Great Britain by the turn of the century. Shortly after, the first large-scale chlorination protocol was developed and carried out by the Jersey City Water Works (New Jersey, U.S.) in 1908 (Irwin, et al., 2006). As more water distribution systems slowly adopted the procedure of chlorination, a subsequent decrease was observed in the death toll primarily due to the cholera, typhoid, dysentery and hepatitis A associated with water born diseases (American Water Works Association., 2006). This decline made possible the disappearing transition of a mortality "penalty" associated with living in congested urban areas. The resultant reduction in lives lost from 25 to 1 in 100,000 people proved significant (Armstrong, et al., 1999). Thus, consistent with Hippocrates' theory that the quality of water is linked with public health, current research suggests that clean water was responsible for nearly half of the total mortality reduction in major cities, three-quarters of the infant mortality reduction, and nearly two-thirds of the child mortality reduction (Cutler and Miller, 2004). Furthermore, Culter estimates that the social rate of return on the disinfection of drinking water was greater than 23 to 1 with a cost per life-year saved by clean water of about $500 in 2003 dollars. This dramatic reduction in mortality is regarded as one of the most important advances for public health and safety of the 21st century.

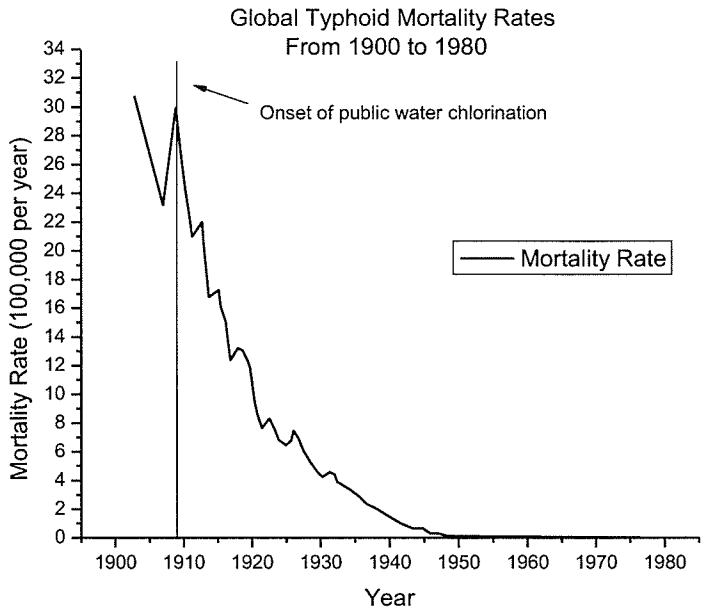


Figure 1: Global typhoid mortality rates exemplifying the effects of large scale chlorination, figure adapted from American Water Works Association, 2006.

One of the greatest advantages gained from the use of chlorine is the ability to effectively achieve a broad-spectrum germicidal potency, while simultaneously allowing for residual disinfection throughout drinking water distribution systems. Furthermore, chlorine also permits the control of various taste and odour problems via the chlorination of problem substrates such as algae, decaying organic matters, manganese, iron, sulphur, nitrogen and ammonia containing compounds.

2.1.1 Chemistry of Chlorination

The mechanism of chlorination begins via the hydrolysis of either liquid or solid sodium hypochlorite in solution (NaOCl), or gas chlorine (Cl_2) upon contact with water, producing a pH dependent equilibrium mixture of chlorine ion (Cl^-), hypochlorous acid (HOCl) and hydrochloric acid (HCl). Chlorine gas undergoes the following hydrolysis, equation (1).

$$Cl_{2_{(g)}} + H_2O \rightleftarrows HOCl_{(aq)} + HCl \quad (1)$$

Equation (1) is then followed by the partial dissociation of the weak acid, hypochlorous acid, to the hypochlorite anion, presented in equation (2).

$$HOCl_{(aq)} + \longrightarrow H^+ + OCl^- \quad (2)$$

The combination of equations (1) and (2) is the prevailing reaction for a low pH range, which results in the formation of chloramines from the presence of nitrogen containing organic matter, in part due to the acidity of hypochlorous acid. As most drinking water sources fit for consumption range higher than a pH of 4, the result is the displacement of the equilibrium to the right, forming more hypochlorite, subsequently minimizing any available hypochlorous acid. This is expected as the pH approaches the pKa ($pKa_{HOCl} = 7.5$). As evident in both the above equations (1) and (2), the amount to which the hypochlorous anion will dissociate is strongly associated with the system's pH. These equations can describe two common treatment scenarios; the set describe the hydrolysis of chlorine gas forming hypochlorous acid, whereas the later describes the addition of liquid sodium hypochlorite. The hydrolyzation of chlorine gas relies upon the equilibrium constant as follows (equation (3)).

$$K_H = \frac{[HOCl][H^+][Cl^-]}{[Cl_2]} = 4.5 \times 10^{-4} \text{ (mol/L atm) at } 25^{\circ}C \quad (3)$$

As equation (3) suggests, a large equilibrium constant provides for the notion that large quantities of chlorine gas may dissolve in water. Equation (2) further defines the displacement of hypochlorous acid (HClO), to the hypochlorite ion (describing the addition of sodium hypochlorite) as follows.

$$K_{ocl^-} = \frac{[H^+][OCl^-]}{[HOCl]} = 3x10^{-8} \text{ M at } 25^\circ C \quad (4)$$

Thus any equilibrium concentrations established will reflect differing concentrations of the products due to the pH, and are presented in Figure 2.

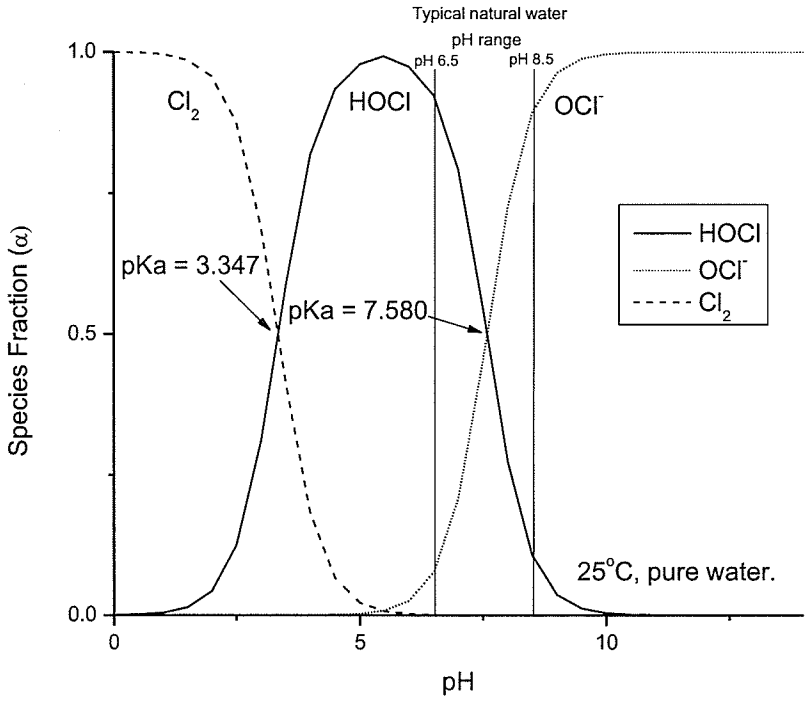


Figure 2: Distribution of Cl_2, HOCl, and OCl^- as a function of pH in pure water.

Though the effect of temperature on the equilibrium constant for equation (4) may appear subtle, the trend becomes more evident when several constants are compared at once, as computed and illustrated in Table 1.

Table 1: Select temperatures and their computed effect on the equilibrium constant of the hypochlorite ion. Values calculated based on ionization constants.

Temperature (°C)	K_{OCl^-} ($x10^{-08}$)	pKa_{OCl^-}
0	1.36	7.868
5	1.56	7.806
10	1.79	7.746
15	2.05	7.689
20	2.33	7.633
25	2.63	7.580
30	2.97	7.528
35	3.33	7.477
40	3.73	7.429
45	4.15	7.382
50	4.61	7.336

The distribution between hypochlorous acid and the hypochlorite ion gives rise to the notion of free available chlorine (FAC), a term commonly used throughout drinking water disinfection plants.

Upon the addition of hypochlorous acid to water (referred to as chlorine), initial reactions proceed first with both organic materials and various metal ions - those with an oxidative capacity - which subtract from the initially applied dose. Such chlorine is often not available for disinfection. The chlorine remaining following disinfection is referred to as the total chlorine residual. This total chlorine residual may then be further subdivided into the following categories: combined chlorine and free available chlorine. The combined chlorine accounts for the chlorine which has further reacted with additional substrates, such as ammonium ions, nitrites, nitrates, etc for a given period of contact time (CT). The remaining chlorine, known as the FAC, is the amount of hypochlorous acid and hypochlorite ion available to further inactivate the proliferation of disease causing bacteria and organisms. The FAC parameter is a standard monitoring

measurement of potable waters. As such, taking into account the relative distribution of both hypochlorous acid and hypochlorite ion at different water pH's is important as the disinfection capacity of hypochlorous acid is greater than that of the hypochlorite ion. White notes that hypochlorous acid is considered to have more biocidal activity than the hypochlorite ion, as it can easily penetrate microbial cell walls due to the lack of a charge. When compared the hypochlorite ion's negative charge interfering with cell wall diffusion, hypochlorous acid is generally thought to provide significantly more disinfection potential (White, 1986). The consequential distribution of hypochlorous acid at varying temperatures must be accounted for when designing a treatment process targeted at a specific FAC value. The theoretical hypochlorous acid distribution may be calculated at a given temperature, as shown in Table 1 and equation (6) under ideal circumstances involving pure water and no chlorine demand.

$$Ratio\ of\ HOCl = \left[\frac{[HOCl]}{[HOCl]+[OCl^-]}\right] = \left[\frac{1}{1+\left[OCl^-/HOCl\right]}\right] \tag{5}$$

Substituting equation (4) into equation (5), the ratio of hypochlorite ion to hypochlorous acid at a given temperature and pH is elaborated in equation (6).

$$Ratio\ of\ HOCl = \frac{1}{1+K_{OCl^-}/[H^+]} = \frac{1}{1+K_{OCl^-}\bullet 10^{pH}} \tag{6}$$

As a further impediment in the goal of achieving a specific FAC, side reactions with ammonia are a common occurrence, and are even more of a concern for the small groundwater treatment plants throughout Manitoba experiencing elevated levels of ammonia. As hypochlorous acid is an oxidizing agent, it will react with ammonia present

in the water, effectively increasing the combined chlorine and reducing the targeted FAC value. The increase in combined chlorine can be explained through the successive formation of monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and nitrogen trichloride (NCl_3). Their formation, specifically their rate constants and temperature dependencies, are expressed in the following equation set (Ozekin, et al., 1995, Valentine, et al., 1988). The formation of nitrogen trichloride, equation (9), is known to predominantly occur at a pH less than 4.4 and relatively slowly; rate constants have been reported for this reaction at specific temperatures although no formation of a rate constant-temperature dependent equation was found, in contrast to equations (7) and (8) (Asano, 2007).

$$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O \quad k_{NH_2Cl} = 2.37x10^{12} e^{(-1510/T)} \quad (M^{-1}h^{-1}) \qquad (7)$$

$$NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O \quad k_{NHCl_2} = 1.08x10^{9} e^{(-2010/T)} \quad (M^{-1}h^{-1}) \qquad (8)$$

$$NH_2Cl + HOCl \longrightarrow NCl_3 + H_2O \quad (pH < 4.4) \qquad (9)$$

As hypochlorous acid is both temperature and pH dependent, equations (7), (8), and (9) will not only be dependent on pH and temperature, but also contact time and the ratio of chlorine dosed to the ammonia present, which is normally presented in terms of nitrogen. Both monochloramine and dichloramine are the predominant species formed from the reactions of ammonia with chlorine, and will subsequently form as a function of the chlorine to ammonia ratio at any given pH. It is reported that the amount of nitrogen trichloride present under a chlorine-to-ammonia molar ratio of two or less is negligible (Sawyer, et al., 2002). A pH between approximately 7 and 9 is optimum for the formation of monochloramine, while a pH of 8.3 is frequently considered the most effective. In contrast, a lower pH (in the pH range of 4 to 6) favors dichloramine

formation and trichloramine (pH <4) formation and therefore are not expected given the pH levels of typical drinking water (White, 1992, Rice and Gomeztaylor, 1986).

2.1.2 Breakpoint Chlorination

Chlorination chemistry requires a thorough understanding of the potential cumulative effects of the chemical makeup that represents the source water in order to properly produce breakpoint chlorination within a distribution system. Maintaining breakpoint within a system can be difficult due to the multitude of potential reactions which affect both the chlorine demand and the FAC. Breakpoint chlorination is defined as the point at which a specific amount of chlorine has been added to the water to completely react with oxidizable substances, such that if more chlorine is added, it will be a direct contribution to the free chlorine parameter. Achieving breakpoint chlorination provides a basis for effective disinfection. As such, the amount of chlorine that must be added to attain a desired level of residual free chlorine within a distribution system is referred to as the chlorine dose. Chlorine demand is the difference between the chlorine dose and the residual at the breakpoint.

The process of arriving at breakpoint is illustrated in Figure 3. As chlorine is added, immediately oxidizable substances, DOC, various metals such as iron, manganese, copper, and other organoleptic compounds react first with chlorine and reduce it to chloride (Cl^-). This reduction is illustrated in Figure 3 as point (A). Once this immediate demand has been completely reduced, the chlorine continues to react with any available ammonia present (according to equations (7), (8), (9)), this is depicted in the region between points (A) and (B). At point (B) the theoretical mole ratio of chlorine to

ammonia is considered to be 1:1. Though the distribution between the formation of mono- and di- chloramines is based on their rates of formation, this formation is also dependent upon temperature and pH. The breakpoint (C) is marked by the destruction of chloramines and characterized by a noticeable dip in the chlorine residual. Beyond this dip, the free chlorine rises again with a slope similar to the zero chlorine demand line and directly contributes to the residual chlorine content.

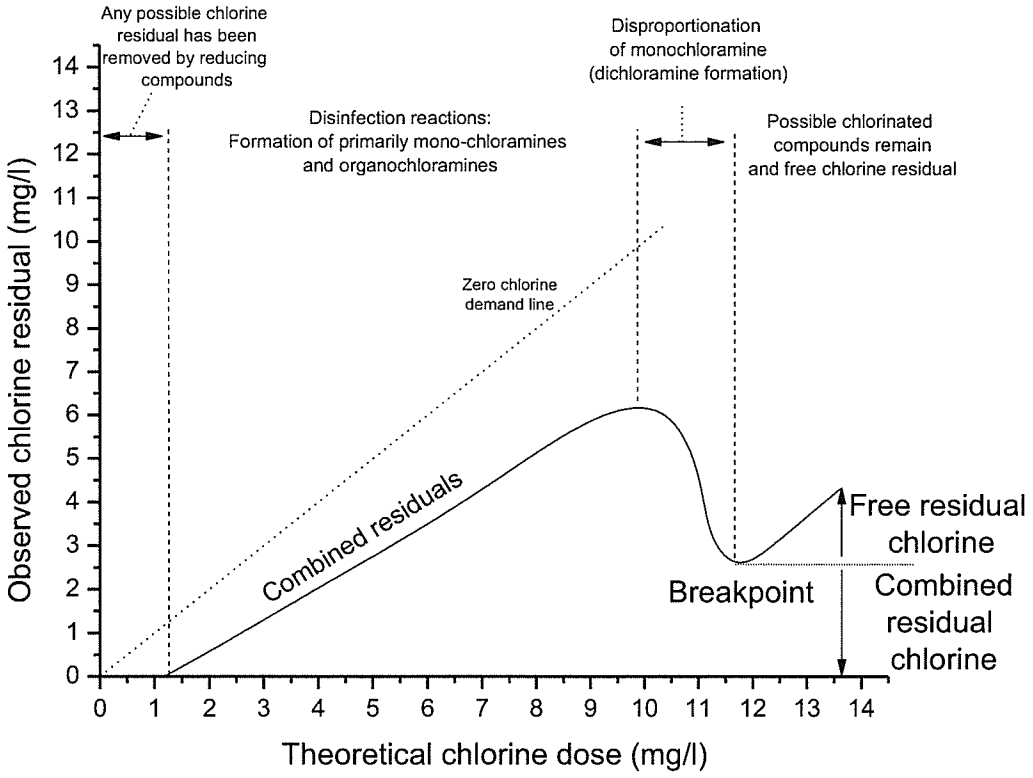


Figure 3: Theoretical illustration of the systematic approach to breakpoint chlorination.

If the conditions dictate so, the possible formation of nitrogen dichloride would occur between points (B) and (C) dependent on temperature and pH, if these conditions are not met the remaining chloramines are oxidized to gaseous nitrogen compounds, while any remaining chlorine is reduced to chloride ion as a result of oxidizing nitrogen

content (Asano, 2007). Continuing to add chlorine at this point will achieve breakpoint where most chloramines will be oxidized, and further additions will directly add to the FAC parameter. At breakpoint, theory suggests that nitrogen containing end products are released as gaseous nitrogen compounds while any carbonaceous material that has reacted with chlorine (and thus exerting a chlorine demand) is released as carbon dioxide. This is supported by observations that at breakpoint, a release of gases occurs and a significant amount of bubbles is seen in rotameters installed in chlorine solution lines downstream from the injector (White, 1999). The hypothesized overall reaction which provides an explanation for the removal of chloramines at breakpoint is presented as equation (10).

$$2NH_4^+ + 3HOCl \xrightarrow{Breakpoint} N_2 + 5H^+ + 3Cl^- + 3H_2O \qquad (10)$$

Stoichiometrically calculated, the chlorine to ammonium ratio at breakpoint is expected to be 7.6:1 (mass basis) and a mole ratio of 1.5:1.

Forecasting breakpoint chlorination parameters based upon the ammonia content in water has been previously studied (Minear and Amy, 1996, Pressley, et al., 1972), allowing for experimental results to be compared with relative confidence. In water sources where the ammonium ion was the sole contributor to the chlorine demand, breakpoint chlorination was observed in a ratio of 8:1 by weight for chlorine to ammonium in a pH range of 6-7 (Wolfe, et al., 1984). It has been noted that this ratio is only valid for ammonium concentrations lower than 1ppm, likely due to the reaction rate being a function of initial ammonia content and can range from minutes to hours for a given pH and temperature.

2.1.3 Chlorine Disinfection By-products

It was in 1974 that Bellar and Lichtenberg, followed by Rook, confirmed that the use of chlorine based oxidants, such as chlorine, for the disinfection of drinking water resulted in the presence of chloroform (a suspected carcinogen), and other undesirable disinfection by-products (DBPs) in potable waters (Rook, 1976, Bellar, et al., 1974). It was soon learned that these DBPs were the products of the reactions of chlorine with the natural organic matter (NOM) present in the water. Following these initial publications, intensive research was conducted to determine the possible reaction products of chlorinating potable waters with high concentrations of naturally occurring dissolved organic matter. Results of such studies further identified numerous chlorinated DBPs and suspected carcinogens, primarily focusing on various haloforms, with the majority of results citing elevated levels of trihalomethanes (THMs) and haloacetic acids (HAAs).

The formation of DBPs, THMs and HAAs during the chlorine disinfection process is rapidly emerging as one of the key disadvantages associated with chlorination for potable waters. Continually demanding the focus of water quality scientists and engineers, the toxic and potentially carcinogenic properties of THMs have undergone intense scrutiny throughout the last 20 years (American Water Works Association., 1990). The widespread occurrence of haloform pollutants suggests that naturally occurring humic substrates represent the dominant organic precursor to THM formation. Research has demonstrated that the chlorination of naturally occurring fulvic and humic acids have contributed to the formation of chloroform ($CHCl_3$), bromoform ($CHBr_3$), bromodichloromethane ($CHBrCl_2$), and chlorodibromomethane ($CHBrCl_2$) (Reckhow, et al., 1990, Trussell and Umphres, 1978). The corresponding bromine substituted by-

products are generally thought to be produced via parallel bromination reactions. These reactions would originate from the interaction between chlorine and the naturally occurring concentration of bromide ions present in most waters (Boyce and Hornig, 1983). This interaction is presented in equation (11).

$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad (11)$$

The exact formation mechanism of the various chlorine and bromine THMs are not well understood. The multitude of complex reactions between free chlorine and a group of organic acids commonly referred to as humic acids make it difficult to single out a precise formation mechanism. The structures of incoming humic materials continually undergo various modifications which are dependent on, yet not limited to, several natural water quality parameters. In particular, the concentration and speciation of dissolved humic materials – the available FAC, seasonal changes in temperature and pH. All of these parameters, as well as the contact time with chlorine, affect the rate, type and concentration of DBPs formed from disinfection. Efforts to understand, model and predict humic material concentrations, and accordingly adapt chlorination protocols, are normally convoluted. These models usually do not provide a substantial or feasible solution' or simply are regarded as completely ineffective likely due to the multitude of parameters required and poorly understood relationships (Gates, 1998). Current publications concerning experimental methods to resolve THM formation are extensive and vary in applicability and feasibility (Andre and Khraisheh, 2009, Kim and Kang, 2008, Liu, et al., 2008, Iriarte-Velasco, et al., 2007, Rodriguez, 2007, Adachi and Kobayashi, 1995, Reckhow, et al., 1990, Graham, et al., 1989). These methods generally range from efforts to remove THM precursors (through improved pre-chlorination

filtration processes), absorbing THMs via the use of granular activated carbon (GAC), changing disinfection procedures (Graham, et al., 1989) and lastly through changing water sources.

It was originally thought that FAC was a necessary factor in the formation of THMs, however the observation of THMs forming in the absence of FAC (notably at a reduced rate) (Asano, 2007) challenged this notion. Asano noted that initial mixing may affect THM formation due to competing reactions between chlorine and ammonia, as well as chlorine and various humic acids. Additional information on THM formation has been extensively studied and published by the United States Environmental Protection Agency (EPA) and Health Canada (Federal-Provincial-Territorial Committee on Drinking Water of the Federal-Provincial-Territorial Committee on Health and the Environment, 2006 With 2009 Addendum, 1998).

Controlling the levels of THM precursor concentrations prior to chlorination is deemed the most direct means of resolving THM problems. Investigative studies have also shown that a substantial reduction in THM formation can be achieved by the use of alternative disinfectants such as chlorine dioxide (ClO_2) and ozone (O_3), in lieu of current practices of breakpoint pre-chlorination or reduction in the pre-chlorination (Gates, et al., 2009).

With the discovery of potentially toxic DBPs and resulting government regulations outlined to limit maximum acceptable concentrations (MAC) of total trihalomethanes (tTHMs) in potable waters, scientists and engineers have taken a heightened interest in determining alternative disinfectants which may be suitable as a replacement to classical chlorination.

2.2 The Alternative Disinfectant: Chlorine Dioxide

Use of chlorine dioxide in Manitoba has been incredibly limited, largely due to the small knowledge base demographically available, and the lack of specific yet readily applicable analytical methods available for treatment facilities. Chlorine dioxide possesses superior biocidal capacity when compared to customary chlorine and chloramine disinfectants. To compare, the chlorine content is 52.6% (the amount of chlorine in chlorine dioxide) and undergoes a 5 valence electron change, giving rise the 263% more powerful disinfectant when comparing "available chlorine" content. In particular, chlorine dioxide has the ability to selectively oxidize compounds and offers an alternative to current disinfectant processes such as those which rely on chlorine, ozone and chloramines. Chlorine dioxide is not as popular as other disinfectants (ozone, chlorine, chloramines, etc.) in North American, though where is has been used, it has been applied when not only the water must be disinfected, but also when an improvement in the water's various organoleptic qualities is sought. As an example, chlorine dioxide would be used in the oxidation of the sources manganese content in order to mitigate colour. Specifically, usage of chlorine dioxide allows for enhanced control via oxidation of several major taste and odour contributing compounds such as those containing iron, manganese and sulphur.

2.2.1 Chemistry of Chlorine Dioxide

Some basic physical properties of chlorine dioxide may become evident upon synthesis. Chlorine dioxide, characteristically a greenish yellow gas, when dissolved in water produces a strong, distinctive chlorine-like, pungent odour. It is a very reactive

species; at temperatures above -40°C it is unstable and prone to explosive decomposition when concentrations exceed 10% by volume in air (Gates, 1998). By the same reasoning, highly concentrated solutions of chlorine dioxide may be dangerous if the partial pressure exceeds 10.1 kPa. Additional chemical and physical properties have been previously published by Kirk et al. (1991) and are summarized in Table 2. These parameters are characterize the uniqueness of chlorine dioxide as a molecule, as a gas stable in water, and as a potable water disinfectant.

Table 2: Selected properties of chlorine dioxide, data adapted (Kirk, et al., 1991).

Property	Value
Molecular mass	67.452 g/mol
Melting point	-59.6°C
Boiling point (At 101.3kPa)	10.9°C
Density of liquid:	
-55°C	1.773 g/mL
0°C	1.640 g/mL
10°C	1.614 g/mL
Heat of Formation	102.5 kJ/mol
Gibbs Free Energy	120.5 kJ/mol
Entropy	0.257 kJ/mol
Heat of Combustion	-102.5 kJ/mol
Dipole Moment	1.7835 D
Molar Extinction coefficient (25-50°C)	1250 (mol/L)/cm
UV Absorption Maximum	360 nm
Henry Constant	1.0 (mol/L)/atm

Chlorine dioxide is highly water soluble, yet when compared to chlorine does not undergo subsequent hydrolysis in water ($K_{Cl2,298K}=3.94x10^{4}>>K_{ClO2,298K}=1.2x10^{-7}$) and remains a gas dissolved in solution (Aieta and Berg, 1986). As such, when precautions are taken, evaporated reduction in stored solutions can be minimized. Neutral or acidic

solutions of chlorine dioxide may be considered stable for extended periods of time, if they are stored in brown glass jars, in a dark, refrigerated space with no headspace (White, 1999, Gates, 1998).

The mechanism of disinfection utilized by chlorine dioxide is based upon the principle that chlorine dioxide acts as a very strong oxidizer while maintaining some selectivity towards specific chemical attributes. The oxidation pathway is via a one-electron transfer, thus the resultant self-decomposition to the chlorite ion is generalized as in the following equation (12).

$$\begin{aligned} &ClO_2 + \text{Substrate} \rightarrow ClO_2^- + \text{Substrate}^\bullet \\ &\quad \downarrow \textit{redox} \rightarrow \begin{cases} ClO_2 + e^- \longrightarrow ClO_2^- \\ ClO_2 + H^+ + e^- \longrightarrow HClO_2 \\ ClO_2 + 4H^+ + 5e^- \longrightarrow Cl^- + 2H_2O \\ \textit{...and others} \end{cases} \\ &\quad \downarrow \hbar\upsilon \rightarrow \begin{cases} ClO + O^* \\ Cl^- + O_2 \end{cases} \end{aligned} \tag{12}$$

Chlorine dioxide does not tend to cleave carbon-carbon π-bonds, and since no chlorine is added to the molecule this accounts for the lack of halogenated by-product formation (ie. THMs) when compared to using chlorine. However, chlorine dioxide is prone to react with phenolic compounds, and rapidly reacts with organic sulfides and tertiary amines. The result of these reactions is the effective destruction of a multitude of taste and odour causing compounds (Gates, et al., 2009, Gates, 1998, Masschelein and Rice, 1979). Reactions with primary and secondary amines, alcohols, and carbonyls are considered slow, whereas reaction rates with aqueous chlorine, iron(II) and manganese(II) vary depending upon equilibrium conditions (Masschelein and Rice, 1979). From a chemical standpoint, efforts to describe the species and concentrations of

by-products produced when using chlorine dioxide are not of a straightforward stoichiometric nature. There is no single descriptor - whether functional group, reaction, or general molecule - to describe all potable water sources. One must consider several redox couples to describe the nature of the oxidation disinfection process. The primary oxidation half reactions of chlorine dioxide are presented as in Table 3. Values are reported at room temperature and standard pressure with respect to a standard hydrogen electrode and the presented data has been adapted (Lide, 1999).

Table 3: Standard reduction potentials of several oxidation states of chlorine at 25°C, data adapted (Lide, 1999).

Equation	*Standard Potential, E° (V)*	*pe (=logK)*	*Reactant Chlorine Oxidation No.*
$\frac{1}{2}\ ClO_4^- + H^+ + e^- = \frac{1}{2}\ ClO_3^- + H_2O$	1.189	20.09	7
$ClO_3^- + 2H^+ + e^- = ClO_2 + H_2O$	1.152	19.47	5
$\frac{1}{2}\ ClO_3^- + H^+ + e^- = \frac{1}{2}\ ClO_2^- + \frac{1}{2}\ H_2O$	0.33	5.58	5
$ClO_{2(aq)} + H^+ + e^- = HClO_2$	1.277	21.58	4
$ClO_{2(aq)} + e^- = ClO_2^-$	0.954	16.12	4
$\frac{1}{2}\ HClO_2 + H^+ + e^- = \frac{1}{2}\ HClO + \frac{1}{2}\ H_2O$	1.645	27.80	3
$\frac{1}{4}\ HClO_2 + \frac{3}{4}\ H^+ + e^- = \frac{1}{4}\ Cl^- + \frac{1}{2}\ H_2O$	1.57	26.53	3
$HClO + H^+ + e^- = \frac{1}{2}\ Cl_{2(aq)} + H_2O$	1.611	27.23	1
$\frac{1}{2}\ ClO^- + \frac{1}{2}\ H_2O + e^- = \frac{1}{2}\ Cl^- + OH^-$	0.810	13.69	1
$\frac{1}{2}\ Cl_{2(aq)} + e^- = Cl^-_{(aq)}$	1.396	23.59	0

The use of a Latimer diagram is normally used to convey the information contained in Table 3 in a concise manner which summarizes the standard electrode potentials relative to the element in question, chlorine. Use of the Latimer diagram can also indicate if a species has a tendency to disproportionate in solution given the conditions in which the electrode potentials in Table 3 are presented (25°C). Specifically, if the potential displayed to the right of the species is higher than the potential displayed

to the left, the species can oxidize and reduce itself, commonly known as disproportionation. The Latimer diagram for chlorine is presented as Figure 4, potentials are presented in units of Volts and has been adapted from Standard Potentials in Aqueous Solution (IUPAC) (Bard, et al., 1985).

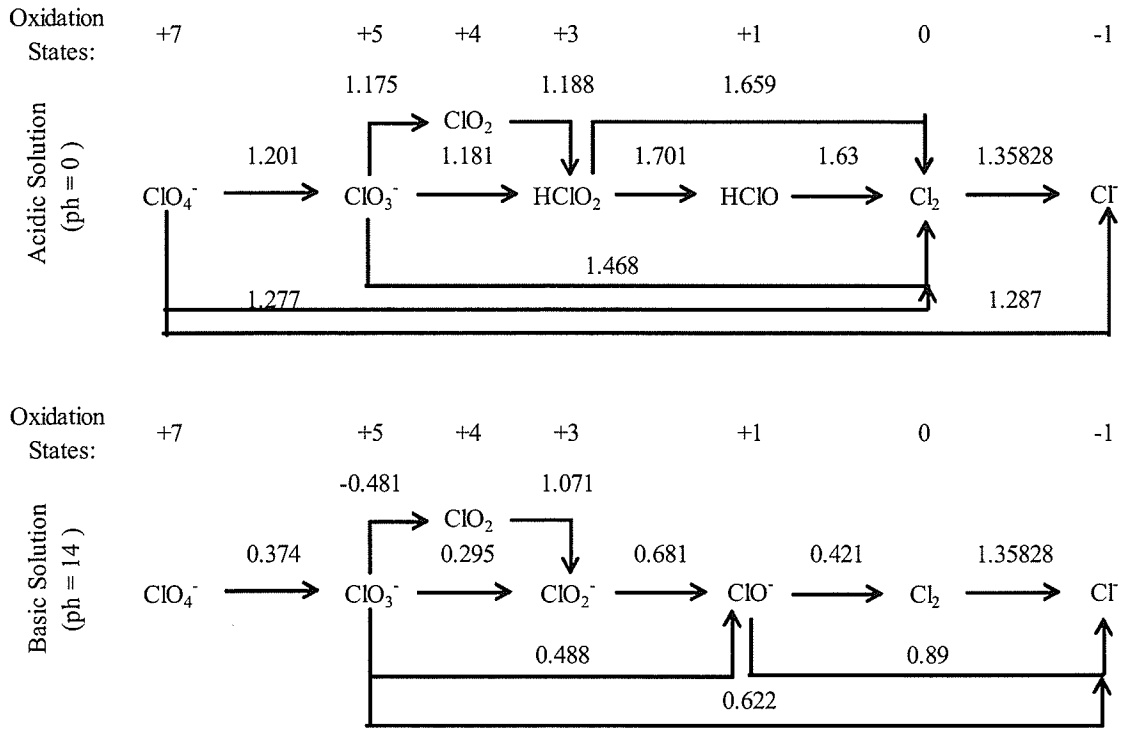


Figure 4: Latimer diagram for chlorine in both acidic and basic solution, diagram adapted (Bard, et al., 1985).

Figure 4 effectively describes the thermodynamic stability of various oxychlorine species. Variations in potentials using the two different media (ph extremes) are due to the involvement of a proton (H^+) or hydroxyl group (OH^-) in the individual standard reduction potential half reactions. If no such involvement is present, the values remain the same; as seen in for the potential describing the reduction of chlorine to chloride.

Alternatively, use of a Frost diagram can represent electrode potentials in a diagrammatic form. Frost diagrams, as in Figure 5, of chlorine provide a quick

qualitative representation as to the chemical properties of several oxychlorine species. Qualities which may be sought from Figure 5 are the following: the species with the most positive slope is a strong oxidizer, the species which lies above the line connecting two adjacent points will undergo disproportionation, and two species which lies below a line joining two terminal species will comproportionate into an intermediate species. These qualitative characteristics can describe the unique stability of chlorine dioxide, that it is a radical, kinetically existing for a prolonged period of time, yet thermodynamically unstable.

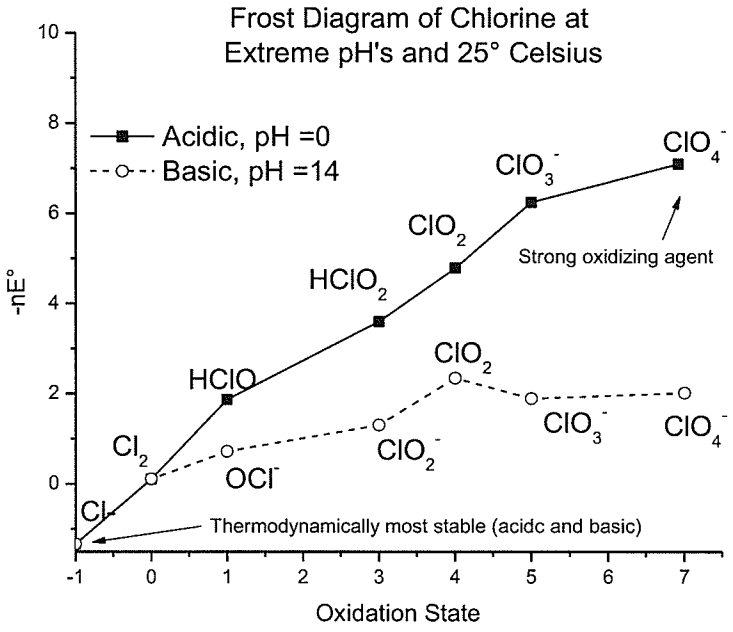


Figure 5: Frost diagram representing various chlorine species in acidic and basic conditions, values were calculated based on standard potentials, data adapted (Miessler and Tarr, 2004).

On a molecular level, chlorine dioxide corresponds to the oxidation number 5 of chlorine which provides for 263% more "available chlorine". Having an angular structure with the presence of an delocalized unpaired electron (and therefore no

tendency to dimerize), it is considered a free radical with a resonance structure as demonstrated in Figure 6.

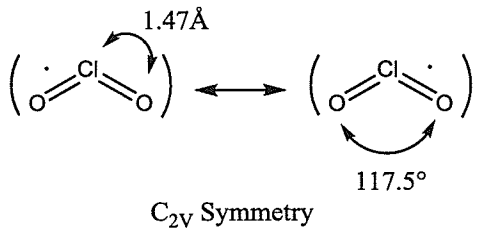


Figure 6: Free-radical monomer chlorine dioxide.

Chlorine dioxide possesses several chemical qualities that allow it to be used not only to improve overall water quality, but also to be used as an efficient disinfectant. When considering popular disinfectants, there exists a wide range of oxidation potentials without a clear trend linked to capabilities. For example, both ozone and hydrogen peroxide have high oxidative potentials, with ozone arguably being the more popular disinfectant. In comparison, chlorine dioxide has a much lower oxidation potential and yet retains admirable disinfection characteristics, as well as selective oxidizing properties (Parga, et al., 2003).

Table 4: Common disinfectants and their associated oxidation values at 25°C.

Species	*Oxidation Potential E° (Volts)*	*Half Reaction*
Ozone	2.706	$\frac{1}{2}O_3 + H^+ + e^- = \frac{1}{2}O_2 + \frac{1}{2}H_2O$
Hydrogen peroxide	1.776	$\frac{1}{2}H_2O_2 + H^+ + e^- = H_2O$
Potassium permanganate	1.679	$^1/_3\ MnO_4^- + {}^4/_3\ H^+ + e^- = {}^1/_3MnO_2 + {}^2/_3\ H_2O$
Hypochlorous acid	1.482	$\frac{1}{2}HClO + \frac{1}{2}H^+ + e^- = \frac{1}{2}Cl^- + \frac{1}{2}H_2O$
Chlorine	1.358	$\frac{1}{2}Cl_{2(g)} + e^- = Cl^-$
Chlorine dioxide	0.954	$ClO_{2(aq)} + e^- = ClO_2^-$
Hypochlorite ion	0.81	$\frac{1}{2}ClO^- + e^- + \frac{1}{2}H_2O = \frac{1}{2}Cl^- + OH^-$

*Bold face indicates common use as disinfectant

The oxidative potential values for the determination of a compound's effectiveness should not be seen as the sole criterion, as this relationship is not consistently proportional. Consider for instance the use of hydrogen peroxide (H_2O_2) and potassium permanganate ($KMnO_4$), which are both strong oxidants, yet exhibit poor disinfection potential and are thus not usually considered primary disinfectants. In contrast, chlorine dioxide has a much lower oxidative potential, yet retains significant disinfection characteristics, functioning as a highly selective oxidant following a one-electron transfer mechanism where it is reduced to the chlorite ion (ClO_2^-). The formation of both the chlorite and chlorate (ClO_3^-) ions are normally the principle by-products that must be considered when using chlorine dioxide. Chlorine dioxide undergoes a multitude of disproportionate reactions, including self-decomposition to chlorite. At a neutral pH, chlorine dioxide can dissolve into water with little hydrolysis occurring, although at a high pH decomposition occurs as the following, equation (13) (Masschelein and Rice, 1979, Gordon, et al., 1972):

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O \qquad (13)$$

2.2.2 Chlorine Dioxide for Drinking Water Treatment

Use of chlorine dioxide was first reported in 1944 at the Niagara Falls water treatment plant, located in New York State (Aieta and Berg, 1986). Since then, the adoption of chlorine dioxide, for the reduction of THMs, industrial food processing and even US National securities (for removal of Anthrax) has continually grown, reaching a much wider realm of potential applications. In 1999, the EPA estimated that 5% to 6% of all water treatment plants in the US utilized chlorine dioxide for disinfection

(Environmental Protection Agency, 1999). Despite only three Provinces acknowledging the use of chlorine dioxide in Canada (Ontario, Quebec and Manitoba) (Federal-Provincial-Territorial Committee on Drinking Water, 2005), the majority of applications occur with Quebec. In 1999, the Province of Quebec estimated that more than 600,000 people comprising approximately 10% of the population were served potable water disinfected by 12 chlorine dioxide treatment plants throughout the province (Levallois, September 2001).

Chlorine dioxide can be considered an effective disinfectant for use with drinking water treatment. When compared to chlorine, several advantages are apparent. Among these, the lack of chlorinated DBPs: chlorine dioxide does not chlorinate, but rather oxidizes organic matter present. More so, this mechanism also has the potential to reduce the THM formation potential, common to many of the surface water sources in Manitoba which contain high levels of DOC. Chlorine dioxide is more effective than chlorine for the inactivation of *Cryptosporidium* cysts that are resistant to chlorination disinfection (Gates, 1998). Notably, when compared to chlorine's pH dependency (see Figure 2), chlorine dioxide is less pH dependent, although for applications in water where the pH exceeds 9 the self-decomposition into chlorite and chlorate is significantly accelerated (Gordon, et al., 1972). Overall, to maximize the disinfection potential of chlorine dioxide, disinfecting when the pH is below 9 will maintain the chlorine dioxide concentration applied. Furthermore, chlorine dioxide is able to provide a residual, unlike ozone, and thus allows the same disinfectant to be used as both a primary and secondary disinfectant; ideal for small treatment systems.

Application of chlorine dioxide is not without disadvantages. It is naturally a radical, and although somewhat stabilized, is inevitably prone to decomposition and thus must be generated onsite for use as a disinfectant. It is unstable at high concentrations, volatile and can self-decompose due to excess light exposure requiring operators to be aware of its inherent sensitivities. Self decomposition by visible and ultraviolet light has been studied and found to produce oxygen and chlorite, as presented in equation (14) (Gordon, et al., 1972), or alternatively as presented in equation (15) (Flesch, et al., 1994).

$$ClO_2 \xrightarrow{\hbar\upsilon} ClO + O^* \tag{14}$$

$$ClO_2 \xrightarrow{\hbar\upsilon} Cl + O_2 \tag{15}$$

Furthermore, the formation of chlorite and chlorate, its principle DBPs, may be considered a large hindrance to further adoption of chlorine dioxide disinfection. Notably, it may not possible to treat waters which demand high amounts of chlorine dioxide, as the subsequent by-product formation may be substantial. The production of these by-products is regulated by Health Canada, EPA, the World Health Organization (WHO) and subsequent limits on their maximum allowable concentrations (MAC) exist. The capital investment required to meet the need for on-site generation of chlorine dioxide, as well as maintaining high generator efficiency for the minimization of forming alternative oxychlorine species, and limited operational experience results in an elevated start-up or adoption cost for chlorine dioxide when compared to chlorine. Chlorine dioxide generators operate to supply a yield of greater than 95%, providing maximum production while also minimizing free chlorine, chlorite and chlorate formation. Since the use of chlorite for generation may result in the formation of hypochlorous acid,

hypochlorite, chlorite or chlorate ions, application of equation (16) may be used to ensure that the excess of free chlorine from generator yields be less than 2% by weight (Environmental Protection Agency, 1999).

$$\frac{[ClO_2]_{ppm}}{[ClO_2]_{ppm}+[ClO_2^-]_{ppm}+[ClO_3^-]_{ppm}\bullet\left(67.45/83.45\right)_{ClO_2^-/ClO_3^-}}\bullet 100 = Generator\ Yeild \quad (16)$$

An overall simpler equation which reflects generator impurities has also been presented by the EPA which reflects the potential for FAC, chlorite and chlorate formation from generators. Equation (17) is noted to substantially resolves problems associated with different equipment-specific calibration methods for chlorine contaminated chlorine dioxide and low efficiency generators employing chlorite and chlorate as precursor reagents (Environmental Protection Agency, 1999). Equation (17) is recommended to examine generator performance using unbiased scientific principles, as oppose to non-standardized manufacturer-specific protocols (Environmental Protection Agency, 1999).

$$\frac{[ClO_2]_{ppm}}{[ClO_2]_{ppm}+[FAC]_{ppm}+[ClO_2^-]_{ppm}+[ClO_3^-]_{ppm}}\bullet 100 = Generator\ Purity \quad (17)$$

Uses for chlorine dioxide other than for disinfection are also commonly employed. Other than disinfection, chlorine dioxide is primarily used as a pre-oxidant for the removal of various organic compounds. Not only has chlorine dioxide been used for the precipitation of iron and manganese, but it is also employed for the destruction of various taste and odour causing compounds, as presented in Table 5, the data has been adapted (Zychem Technologies Ltd., 2009). In addition, several functional groups are

present in Table 5 which are known to not react with chlorine dioxide (Masschelein and Rice, 1979).

Table 5: Various chlorine dioxide reactants and non-reactants commonly found in raw waters

Species	*Mode*	*Basic Half Reaction*	*ClO_2 Dose (x Species Conc., ppm)*
Cyanide	Destruction	$CN^- + ClO_2 \rightarrow CNO^-$	2.5 (pH 7 - 8)
Disulfides	Odour Reduction	$RSR + ClO_2 \rightarrow$ Odourless	4.5 (pH 5 - 9)
Iron	Precipitation	$Fe^{2+} + ClO_2 \rightarrow Fe3+$	1.2
Manganese	Precipitation	$Mn^{2+} + ClO_2 \rightarrow Mn^{3+}$	2.5
Mercaptans	Odour Reduction	$RSH + ClO_2 \rightarrow$ Odourless	4.5
Phenol	Destruction	$C_6H_6O + ClO_2 \rightarrow H_6H_4O_2$	1.5 (pH 7 - 8)
Secondary Amines	Odour Reduction	$R_2NH + ClO_2 \rightarrow$ Odourless	5.0
Sulfide	Destruction	$S_2^- + ClO_2 \rightarrow SO_4^{2-}$	5.2
Tertiary Amines	Odour Reduction	$R_3N + ClO_2 \rightarrow$ Odourless	10

Functional Groups and Compounds Not Readily Oxidized by Chlorine Dioxide:

Ammonia	NH_3	Aldehydes	CHO
Ammonium Salts	NH_4^+	Ketones	C=O
Alkanes	C-C	Ethers	COC
Alkenes	C=C	Carboxylic Acids	COOH
Alkynes	C≡C	Primary Amines	RNH_2
Alcohols	C-OH	Unsubstituted Aromatics	C_6H_{12}
Glycols	COHCOH		

**Table data adapted from Zychem Technologies (2009) and Masschelein (1979).*

Chapter 3: Evaluation of Current Analysis Methods for Chlorine Dioxide and Its By-products

3.1 Monitoring Methods Available for Chlorine Dioxide, Chlorite, and Chlorate

The use of chlorine dioxide, for application as a drinking water disinfectant, must involve accurate means for determining concentrations. Such uses demand that reliable analytical methods be available for both large financially abundant industrial uses, as well as small inexpensive water treatment operations. Normally, chlorine dioxide concentrations are required to be monitored at several points throughout a treatment

process train: such as post generation (to observe and maintain efficiency, primarily a low chlorine and high ClO_2 generation ratio), plant effluent (post oxidation of contaminants) to ensure acceptable concentrations of residual disinfectant, and throughout the distribution network (to maintain an effective residual concentration). Reliable analytical methods are required to not only measure such concentrations, but also to maintain and abide by Provincial and Federal Regulations pertaining to the minimum and maximum (if applicable) concentrations (MAC) of chlorine dioxide present at the distribution point and throughout the system. Such examples exhibit the need for reliability over an extensive range of high and low concentration that need be analyzed; these demands are further complicated when interferences to the analytical method in question are present.

3.1.1 Current Conditions of Chlorine Dioxide Use in North America

Health Canada, in its Guidelines for Canadian Drinking Water Quality (GCDWQ), has not set a MAC for chlorine dioxide (due to its rapid decomposition), but has set the MAC of chlorite and chlorate to both 1 ppm based on a 1.5 L/day drinking water consumption rate and an average body weight of 70 kg. The EPA has adopted the Maximum Residual Disinfectant Level Goal (MRDLG) and the Maximum Residual Disinfectant Level (MRDL) for chlorine dioxide to be set at the same level of 0.8 ppm; whereas the Maximum Contaminant Level Goal (MCLG) and the Maximum Contaminant Level (MCL) for chlorite are 0.8 ppm and 1.0 ppm, respectively. Although it has been noted that a possible MCL may come into effect, the EPA does not currently regulate chlorate concentrations (Environmental Protection Agency, 1994). These health limits for chlorine dioxide, chlorite and chlorate are further reflected in the WHO's

provisional guideline for the MAC of chlorite and chlorate concentrations to be set at 0.7 ppm based on a 2 L/day drinking water consumption rate and an average body weight of 60 kg. Additionally, the WHO lacks a MAC for chlorine dioxide, presumably due to its rapid self-decomposition to chlorite and chlorate.

3.1.2 Current State of Analyses

Monitoring methods for chlorine dioxide at the operator level are commonly based upon the use of spectrophotometry due to its ease of use and relatively low-cost of reagents and equipment. However, spectrophotometry has the potential to be susceptible to a larger range of interferences (such as specific ions, temperature, light source variation, wavelength calibration, etc.).

On the contrary, instrumental methods such as those used by analytical laboratories offer a much higher degree of accuracy and precision, are less prone to interferences, yet are typically much more expensive, laborious, and require high quality standards for either calibration or use throughout their associated analytical routines.

3.1.3 Basic Spectrophotometric Analysis of Chlorine Dioxide (Operator Based)

Chlorine dioxide exhibits a wide absorbance range within the UV/visible spectrum, absorbing photons from the 280 to 490 nm range, with a maximum at 360 nm. It is widely published that the molar absorptivity, commonly referred to as ε, is 1250 $(mol/L)^{-1}$ cm^{-1} (Gates, et al., 2009, Gates, 1998) and when chlorine dioxide is the only oxidant present, direct UV standardization via Beer's Law is permissible. Beer's Law is the following:

$$A = \varepsilon bc \tag{18}$$

Beer's Law is the relationship between A, the absorbance of a particular solution at a particular wavelength, and c, the concentration of the absorbing species. The parameter b is the path length of the radiation through the absorbing medium, and ε is a proportionality constant titled the molar absorptivity constant. Therefore, as a laboratory method, the direct standardization of chlorine dioxide can be accomplished, making this method ideal for bench-top testing and research. Solutions which contain other oxidative species, particularly HOCl, OCl, ClO_2^- (present from poor generator performance or applying chlorine in conjunction with chlorine dioxide), can interfere with such direct standardization and a measurement error may be observed. Molar absorptivities for such species are presented in Table 6. Gates suggests that the use of such a direct absorbance technique be reserved for low concentration solutions (ppm range) situated in controlled laboratory settings (Gates, et al., 2009).

Table 6: Maximum wavelengths and molar absorptivities of common interfering oxychlorine compounds. Molar absorptivities are presented as $(mol/L)^{-1}$ cm^{-1}, table adapted (Gates, et al., 2009).

	HOCl	ClO_2^-	OCl^-	ClO_2
235 nm	*90.6*	69.2	9.6	167.4
260 nm	37.7	*148.2*	102.8	55.9
292 nm	23.5	90.6	*343.6*	180.5
360 nm	0	2	12.3	*1250*

From Figure 7, it becomes obvious that at lower concentrations of chlorine dioxide and higher concentrations of hypochlorous acid, chlorite, and hypochlorite there exists the potential for overlapping peaks and an inflated chlorine dioxide absorbance at 360 nm. As such, monitoring such low levels of chlorine dioxide in the presence of other oxychlorine species can easily become problematic.

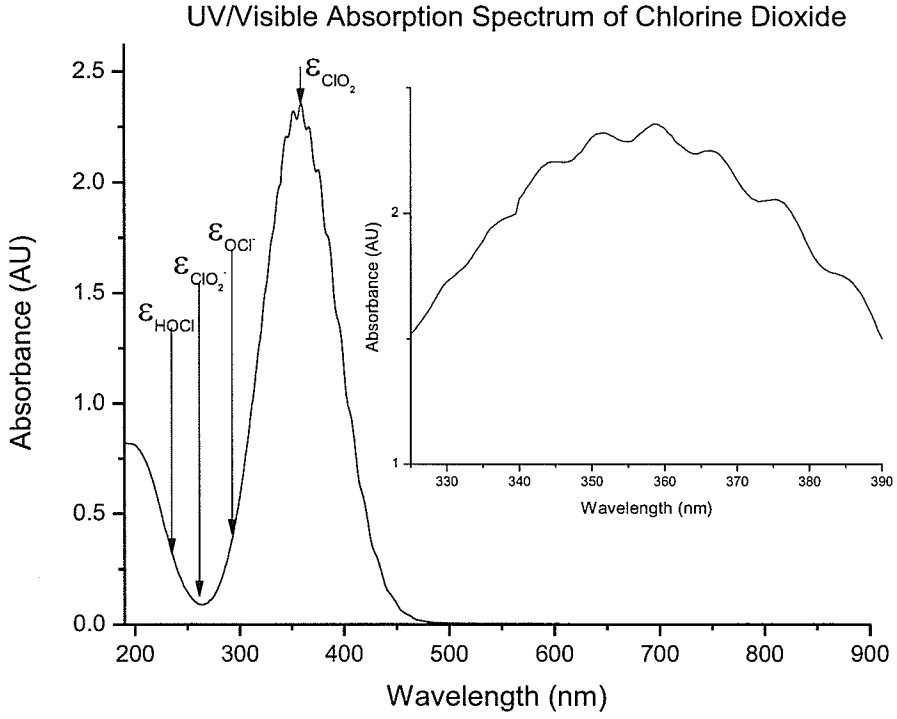


Figure 7: UV/Visible spectrum of chlorine dioxide with common oxychlorine molar absorption coefficients noted.

Maximum and minimum concentrations which can be detected via direct UV standardization are dependent upon the limits of accuracy of the spectrophotometer used, as well as the path length of the cuvette used (either 1 cm or 10 cm, the later offering increased sensitivity). Both parameters will affect the absorbance data collected and consequently affect the calculated concentration. An example calculation is as follows,

with the absorbance at 360 nm being 2.338. Using the Beer-Lambert law, equation (18), and the molar extinction coefficient of 1250 $(mol/L)^{-1}$ cm^{-1}, the chlorine dioxide concentration was calculated as shown:

$$\frac{2.338}{(1250 M^{-1} cm^{-1} \bullet 1cm)} = 0.0018704 mol/L \tag{19}$$

The chlorine dioxide concentration is then expressed as ppm by multiplying the calculated molar concentration by 67,450 ppm $(mol/L)^{-1}$.

$$0.0018704 mol/L \bullet 67450 ppm/(mol/L)^{-1} = 126.158 mg/L \tag{20}$$

3.1.4 Practical Operator Spectrophotometric Methods

The nature of these analytical methods is normally based upon the premise of chlorine dioxide reacting with an organic molecule, such as a chromophore, to either produce a colour which exhibits an absorbance at a specific wavelength; or to react with a molecule in reducing an absorbance already present at a specific wavelength. A chromophore is the part of a molecule's structure which can absorb, transmit or reflect certain wavelengths of radiation. Theoretically, these methods can be selective for chlorine dioxide, although in application, it is the combination of utilizing small residual concentrations (sub 1 ppm) and several interferences which constrain current spectrophotometric methods to a particular degree of error (method specific) and provide for difficulty when developing a flawless routine analytical method. In order to reduce possible interferences, enhance selectively, and reduce the limits of detection, researchers have coupled gas-diffusion membranes, flow-injection mechanisms, fiber optics cuvetteless CCD (charged coupled device) -based arrays, as well as a plethora of additional equipment and exotic systems to these basic methods, ultimately providing a

means to increase the selectively of the reaction of chlorine dioxide and the chromophore (Sharma, et al., 2009, Themelis and Kika, 2006, Jin, et al., 2004, Chen, et al., 1999).

Fundamentally, spectroscopic and colourimetric methods are limited in their range of detection due to the concentration of the chromophore utilized in the protocol. For example, optimizing such methods to increase the detection of chlorine dioxide can be achieved by increasing the concentration of the chromophore, while simultaneously reducing path length and sample size. Alternatively, limits of detection can be improved by reducing the chromophore concentration and simultaneously increasing the path length and the sample size. Though at first these constraints may appear easy to achieve, changing the chromophore concentration and path length do have practical engineering limits. A practical limit involves achieving a path length for a non-zero value or a length which is infinitesimally large. For these reasons, photometric methods, without the addition of equipment above and beyond fundamental photometry, may not be suited for the determination of high concentration generator production nor extremely low chlorine dioxide residual concentrations. This is because high generator effluents require a very large path length and a high chromophore concentration; whereas low chlorine dioxide concentrations require a non-zero value for path length and low chromophore concentrations.

In addition to previously noted practical limits, the issue of reagent purity should also be noted as a potential problem when relying upon photometric methods. Reagent purity is a fundamental assumption when designing, applying or testing the validity of these methods. For example, the acid chrome violet K spectroscopic method (Masschelein, 1966), the chlorophenol red method (Sweetin, et al., 1996, Fletcher and

Hemmings, 1985), the lissamine green B (LGB) method (Chiswell and O'Halloran, 1991), and the enzymatic LGB horseradish peroxidase (HRP) method (Pepich, et al., 2007) all rely on chromophoric reagents of 70% pure or less. Often the purities are expressed as a range or simply purchased as is, and arrive at either higher or lower purities than stipulated. It is this 30% impurity, as well as volatility in manufactured purity, which can account for side reactions with chlorine dioxide, and can offset any expectant oxidation to measurement calibration ratios.

Several factors may further complicate application: for instance, reagent stability can effect purity, or decomposition can reduce purity. In addition, these can elevate a multitude of alternative species which may undesirably react with chlorine dioxide. Reagent "shelf life" and desirable storage conditions should be duly noted and followed as either liquid or solid forms of the reagents can also be further affected by pre-existing impurities. These subtle variations in what is expected to be uniform reagent purities and compositions ultimately affect the sensitivity of the protocol and may lead to over-exaggeration of chlorine dioxide concentrations. Such over-estimations can lead to increased operational costs, increased lab testing analysis costs, and potentially regulatory fines.

Table 7 and Table 8 outline parameters of importance pertaining to photometric methods which have been presented in literature, Standard Methods, and by the EPA. Typical interferences to such methods include FAC, chlorite chlorate, oxidative metal ions, and potentially other oxidizing disinfectants (such as ozone).

Table 7: Meta-Analysis of Tabulated Photometric Methods for Detection of Chlorine Dioxide

Common Photometric Methods:	Direct Spectrophotometry	Acid Chrome Violet K	Amaranth	Chlorophenol Red	N,N-Diethyl-p -phenylenediamine	Lissamine Green-B	Lissamine Green-B with Horseradish Peroxidase	Rhodamine B
Alternative Name (if applicable)	*Direct Absorbance*	*ACVK*	*n/a*	*CPR*	*DPD*	*LGB*	*LGB-HRP*	*RhoB*
Measurement Wavelength (nm)	360	548	522	575	515	616	633	553
Analytical Concentration Range	5.4 - 107.9 mg/l (b=1cm)	0 - 25 mg/l	0.1 - 1.0 mg/l	0.1 - 1.9 mg/l	0.008 - 5.0 mg/l	0.03 - 0.5 mg/l	0.2 - 2.2 mg/l	0 - 1.5 mg/l
Molar Extinction Coefficient	1,250 M-1 cm-1	13,920 M-1 cm-1	66,490 M-1 cm-1	75,000 M-1 cm-1	23,000 M-1 cm-1	121,1000 M-1 cm-1	121,1000 M-1 cm-2	108,000 M-1 cm-1
Method Detection Limit	n/a	0.077 mg/l	0.02 mg/l	0.12 mg/l	0.008 mg/l	0.1 mg/l	NRL	0.02 mg/l
Cited Reagent Solution Stability	n/a	Minimum one month	Several months	Many months	Unstable	Several months	Max. two weeks (Combined LGB-HRP)	Not Reported
Commercial Available Purity (Sigma Aldrich/Fisher)	n/a	50% / n/a	90% / 85%	70% / "Pure"	98% / 98%	60% / n/a	See LGB	95% / 99%
Available Standardized Method	No	No	No	No	APHA 4500-ClO2 D	EPA 327 Rev 1.0	EPA 327 Rev 1.1	No
Available Field Method	No	No	No	No	Yes	Yes	No	No
Applicable for Chlorine Dioxide	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Applicable for Chlorite	No	No	No	No	Yes	No	Yes	No
References	Gates, 2009	Masschelein, 1989	Emmert, 2000	Fletcher, 1985	Palin, 1967 APHA, 2005	Chriswell, 1991	Pepich, 2007	Xin, 1995.

Table 8: Meta-Analysis of Noted Interferences Tabulated Photometric Methods for Detection of Chlorine Dioxide.

Noted Interferences (At Typical Concentrations)

Common Photometric Methods:	Direct Spectrophotometry	Acid Chrome Violet K	Amaranth	Chlorophenol Red	N,N-Diethyl-p -phenylenediamine	Lissamine Green-B	Lissamine Green-B with Horseradish Peroxidase	Rhodamine B
Hypochlorous Acid	High Concentrations	No	Yes (Slowly)	No (up to 5 mg/l)	Yes	Yes	Yes	No
Hypochlorite	High Concentrations	No	Yes (Slowly)	No (up to 10 mg/l)	Yes	Yes	Yes	No
Chlorite	High Concentrations	No	No	No (up to 50 mg/l)	Yes	No	No	No
Chlorate	High Concentrations	No	No	NRL	Yes	NRL	NRL	No
Ozone	Yes	No	NRL	NRL	Yes	NRL	NRL	NRL
Manganese	Yes	NRL	Yes	No (up to 10 mg/l)	Yes	No	No	NRL
References	Gates, 2009	Masschelein, 1989	Emmert, 2000	Fletcher, 1985	Palin, 1967 APHA, 2005	Chriswell, 1991	Pepich, 2007	Xin, 1995.

*NRL - No Results Found

3.1.5 Acid Chrome Violet K Method

The reaction of acid chrome violet K with chlorine dioxide is cited to occur as a 1:2 (ACVK:ClO_2) molar ratio, with decreasing absorbency (observations of this reaction is that chlorine dioxide reduces the colour of ACVK) readings being taken at 548nm (Masschelein, 1966). Although the finite mechanism for ACVK's selectivity for chlorine dioxide is not known, it is suspected that a selective attack of the anthraquinoid nucleus of the ACVK molecule is involved. This method is reported to exhibit neither fluoride nor aluminum interferences (up to 1ppm), nor interferences from active chlorine compounds, chloramines, chlorite, and chlorate. Furthermore, this method is suitable for the determination of residual chlorine dioxide concentrations as well as stock solutions and reactor operation efficiency control (Masschelein, et al., 1989). Due to the lack of a standardized method, laborious reagent preparation, and an extremely low commercial reagent purity, adoption from a Regulator's or Operator's may not provide sufficient quality control or quality assurance.

3.1.6 Amaranth Method

Given the discolourization of the organic dye, amaranth, at 522 nm, it appears to be a suitable spectrophotometric method for the determination of chlorine dioxide at residual concentrations (Emmert calibrated for a range of 0.14-1.24 ppm ClO_2) (Emmert, et al., 2000). Furthermore, this method is reported to be minimally affected by both chlorite and chlorate concentrations (up to 40 ppm), whereas introduction of up to 3.8 ppm iron(III) and FAC proved to not catalyze nor inhibit the chlorine dioxide-amaranth reaction. The reported accuracy for this method is valid in the range of 0.1-1.0 ppm

while utilizing an ammonia/ammonium chloride buffer. The authors note that this method overcomes potential interferences from FAC as it kinetically discriminates for chlorine dioxide. Specifically, it reacts faster with chlorine dioxide when compared to FAC and this method exploits such features.

3.1.7 Chlorophenol Red Method

Use of chlorophenol red for chlorine dioxide detection was first developed by Wheeler and Loft in 1978, in which they reported the measurement of residual levels of chlorine dioxide (0.5 ppm); free of interferences from chlorite, hypochlorous acid, and chlorate (Wheeler and Lott, 1978). Further investigations of this method were carried out by Fletcher and Hemmings (Fletcher and Hemmings, 1985) who showed that this method significantly reacts with both hypochlorous acid and hypochlorite. These interferences are resolved by the addition of thioacetamide, which is reported to neutralize all chlorine species, thus permitting CPR to have relatively few interferences for the spectrophotometric monitoring of residual concentrations.

3.1.8 N,N-Diethyl-p-phenylenediamine

The DPD method is well known, relatively non-laborious, and quite popular for measuring the oxidant strength of potable waters (Palin, 1967). Originally designed for the determination of FAC, its adaption as a means of measuring chlorine dioxide is facilitated by the introduction of the amino acid, glycine, to mask FAC interferences. Though once accepted by the EPA as a valid method, it has recently been rescinded due to significant interferences from common drinking water components and the possibility that glycine is not only masking FAC, but also reacting with chlorine dioxide and thus

negatively affecting residual measurements. However, the continued use of the DPD method is further discussed in Chapter 3.

3.1.9 Lissamine Green B and Lissamine Green B Horseradish Peroxidase

Originally developed as an alternative in response to the interferences the DPD method exhibited, the original LGB method proposed a detection limit of 0.03±0.01 ppm and maintained the necessary sensitivity required for residual testing. The LGB method is selective, sensitive and rapid. No interferences were originally reported from manganese dioxide or oxidized forms of iron. It overcomes all of the disadvantages of DPD: common oxychlorine species do not interfere, and only two reagents are necessary making this method much simpler. Moreover, the produced colour remains stable without manipulation of the analyte solution (Chiswell and O'Halloran, 1991).

The original LGB method was selected by the EPA as the basis for the development of a new analytical method for the detection of residual chlorine dioxide destined for further adoption by regulatory agencies. In 2007, Pepich further developed the original LGB method to include the enzyme horseradish peroxidase (Pepich, et al., 2007). The original LGB method did not have a stoichiometric reaction ratio of 1:1 between LGB:ClO_2, however this ratio is necessary for the development of an optimized sensitivity coefficient adjustment parameter. This required calibrating for the method to be reliant upon the LGB concentration used, and required an external calibration for both chlorine dioxide and chlorite. The new adapted LGB-HRP method used Type I HRP to catalyze the conversion of chlorite to chlorine dioxide (100% efficient), and permits the combined analyses of chlorine dioxide, as well as chlorite. The LGB-HRP method is a

method of difference, which first analyzes chlorite and chlorine dioxide combined, and then separately determines chlorite concentration in a second, previously sparged sample. Chlorine dioxide concentrations are then calculated by the difference. The LGB-HRP method is reported to be ideal for regulatory agencies to adopt, as both the relative time and cost associated with this method are reasonable given the performance, reagent stability, accuracy, precision, and relative interference free analysis of residual concentrations of chlorine dioxide and chlorite.

3.1.10 Rhodamine B

Rhodamine B is described as being both selective and sensitive for the residual determination of chlorine dioxide in the presence of FAC, chlorite, chloramines and chlorate. Calibration for standardization was carried out using the relatively laborious method of iodometric titration, and absorbance readings were taken at 533 nm using a 30 mm cuvette (Xin and Jinyu, 1995). It is reported that pH affects recorded absorbency significantly, and that the optimum pH value lies between 10 and 11 according to this method. Notably, a high pH accelerates the decomposition of chlorine dioxide to chlorite, although this issue is not addressed by Xin and Jinyu (1995). To ensure interferences from FAC are not possible, use of an ammonia-ammonium chloride buffer is applied, in order to mask of up to 40 ppm FAC.

3.1.11 Instrumental Methods (Other Than Spectrophotometric)

Instrumental methods for the detection of residual chlorine dioxide normally rely upon the detection of electrochemical changes whether from the oxidation-reduction potential (ORP) present in solution, electrokinetic techniques or other chemical

phenomena. Some of the most common methods based on these principles utilize detection mechanisms such as potentiometry or conductivity. More importantly, instrumental methods are not absolute and require calibration. As such, the development of accurate and high grade calibrations is required and reflected in the instrument's accuracy for measurements. Difficulty in preparation and storage of calibration standards are similar to those associated with reagent purity as outlined in Section 3.1.4. Regardless, such instruments provide a far greater scope of data concerning water components when compared to photometric methods. Instrumental analysis dramatically increases the sensitivity and accuracy of the analyses, while also reducing the required sample size, radically increasing reproducibility and increasing the rate at which samples can be analyzed. Instrumental technologies designed for the measurement of residual chlorine dioxide as well is its oxidation by-products have largely been designed utilizing electrochemical methods such as, amperometric titrations, amperometric sensors, and ion chromatographs.

The EPA currently accepts amperometry as the main instrumental method of detection for chlorine dioxide and chlorite. Though ion chromatography (IC) is the only method the EPA recommends for the detection of chlorate, it is not limited to chlorate as it can also be simultaneously used for the detection of chlorite (please see Appendix A; Tabulated US EPA Accepted Analytical Methods for Chlorine Dioxide, Chlorite, and Chlorate, June 2008).

3.1.12 Amperometry (Operator Based)

Though it is not considered a photometric method, or a classical instrumental method, given the context, an amperometric titration measures the electric current produced by a titration reaction for quantitative analysis and is thus categorized as an instrumental approach to measuring residual by-products. Commonly known as Amperometric Method I (Standard Method 4500-ClO_2 C), and Amperometric Method II (Standard Method 4500-ClO_2 E), both protocols make use of successive titrations at varying pHs and varying titrating reagents. An amperometric analyzer is employed to measure the chlorine dioxide concentration in the sample, specifically the analyzer measures the current in amperes required to maintain a constant voltage. As the concentration of the titrant increases in the sample, this can either be phenylarsine oxide (PAO) or sodium thiosulfate (NTS), the reaction with chlorine dioxide will proceed and a change is reflected in the monitored current. When the reaction has reached completion a constant current is established which signals the endpoint of the titration. Because sensitive reagents must be prepared for several titrations this method is considered quite laborious. In addition, the quality of the data ascertained will largely be dependent upon the skills of the analyst. Sequential titrations based upon the reduction of either PAO or NTS are presented as follows (Gates, et al., 2009). The initial reaction of the iodine anion with chlorine dioxide produced diatomic iodine, I_2, as in equation (21).

$$2ClO_2 + 2I^- \rightarrow I_2 + 2ClO_2^- \qquad (21)$$

The solution is then titrated with either PAO (equation (22)) or NTS (equation (23)). Once the titration is complete and a constant voltage is achieved, no diatomic

iodine remains in solution and the quantitative stoichiometric analysis is carried out for the determination of chlorine dioxide present in the sample.

$$C_6H_5AsO + I_2 + 2H_2O \rightarrow C_6H_5AsO(OH)_2 + 2H^+ + 2I^- \quad (22)$$

$$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-} \quad (23)$$

As the quality of the results is highly dependent upon the skills of the analyst, such analysis should be performed in triplicate making the procedure intensive, and prone to procedural error. The reactions are carried out at pH 7, measuring free and combined chlorine, and one fifth of the chlorine dioxide. The pH is then lowered to 2 for the analysis of all the chlorite and the remaining four fifth's chlorine dioxide. In addition to the tediousness of this method, the common copper-platinum electrode probes utilized for amperometry are easily eroded and eventually destroyed by lowering of the pH (Gates, 1998). More so, the EPA does not recommend Standard Method 4500-ClO_2 C due to the possibility for inherent errors due to competing reactions for PAO or NTS, and the high possibility of false-positive chlorine dioxide concentrations (Gates, et al., 2009). In lieu of such dilemmas, the EPA recommends the adoption of the Amperometric Method II (Standard Method 4500-ClO_2 E), although common amperometric interferences still remain. These include mono-, di-, and tri-chloramines which provide an over estimation of the residual chlorine dioxide. Commonly, free halogens other than chlorine will also titrate as chlorine, leading to an accumulating error. This method relies upon the calculation of values by difference and is at risk of being potentially inaccurate. Gates et al. (2009) recommend that when utilizing Amperometric Method II, chlorite results should be cross-referenced with IC methods for verification of standards and overall

procedural activity. This is not always a possibility in the applied field, or in some labs due to the significant investment required for an ion chromatograph.

3.1.13 Ion Chromatography (Commercial Laboratory Based)

Ion chromatography (IC) is a modern method used for the chromatographic separation of ions. Separations are performed on a column packed with a solid phase ion-exchange resin, where the migration, or more specifically, capillary electrophoresis occurs. Easily considered an indispensible tool to most laboratories, IC methods allow for complex mixtures of anions and cations to be separated precisely and quantitative amounts as small as parts per billion can be measured in a relatively short time.

The EPA calls for IC in Method 326.0 Rev 1.0 for the determination of chlorite and chlorate concentrations. There exist several variations of buffers and elution solvents which can be utilized to adjust for other ions present in the sample, ultimately this method has undergone several revisions to provide the best results. Gates and his colleagues suggest the following are typical detection limits: chlorite (3 μg/l), chlorate (9 μg/l), and that such methods are easily capable of measuring concentrations ranging from 5 ppb to 5 ppm (Gates, 1998, Pfaff and Brockhoff, 1990).

As IC is usually employed by commercial lab analysis facilities, proper sample treatment is a critical component of analysis which reflects concentrations at the time of sampling. Samples should be purged of chlorine dioxide using an inert gas and then treated with the addition of ethylenediamine (EDA) as a preservation step designated to complex chlorine which may continue to react during transportation (Wagner, et al., 2002). Furthermore, to retard additional formation of chlorite and chlorate, removal of

particulate matter and the storage of filtered liquid at 4°C are required. These storage conditions may be maintained for up to 14 days for chlorite and 28 days for chlorate, although analysis should be performed as soon as possible for optimal representation of the conditions indicative of the initial sampling. Shipped samples should be placed on ice, with zero headspace and scheduled for next day delivery and immediate analysis.

Limitations to using IC for the detection of chlorite and chlorate are that these species occur in such low concentrations that the need for postcolumn reagents (PCR) may be necessary. The use of PCR has been explored as a means to provide additional precision and accuracy for detection of not only chlorite and chlorate, but also other common drinking water ions, such as bromate and other trace oxyhalides (Snyder, et al., 2005, Weinberg and Yamada, 1998). In spite of IC providing such an immense impact in terms of selectivity, precision and accuracy for the detection of chlorite and chlorate, these instruments, like many others, require the need for extremely high purity grade reagents, solvents and calibration standards. Commercial reagent-grade sodium chlorite contains impurities, including chlorate and is prone to decomposing with time. As such, without highly stringent calibration standards, collected results may remain incredibly precise, yet ultimately inaccurate.

3.1.14 On-Line Detection (Operator Based)

Monitoring and preparation requirements for photometric or instrumental methods can be time consuming, tedious, and prone to error. Operators and regulatory agencies need to strike a balance between a practical method which provides accuracy, without compromising the importance of being maintenance friendly, and is straight-forward and

cost-effective. Though currently not validated by the EPA, the development of accurate online detection methods can be anticipated to prompt a wider adoption of chlorine dioxide by paving a pathway in which operators can focus more on the treatment process and optimization. Real-time monitoring of chlorine dioxide provides operators a means to address raw water source quality problems as they occur, facilitating adjustments to dosages in order to maintain adequate residual concentrations at a faster pace when compared to the current regulatory requirements of using manual measurements via commercial test kits throughout the distribution system (Hargesheimer, et al., 2002).

The benefits of developed on-line detection methods are significant. Records can be stored digitally and compared against dosages, providing a clearer understanding of seasonal variations in oxidant demand of the source waters. On-line monitoring allows for remote monitoring network distribution points therein providing superior modeling of disinfectant decay in real-time. Monitoring both chlorine dioxide and chlorite throughout a distribution network in real-time provides operators the ability to fine-tune dosages, save time and money, and minimize the potential for chlorite and chlorate DBP formation.

Most chlorine dioxide on-line sensor technology is based upon the use of amperometry. As previously discussed, the current flowing between two electrodes corresponds to a concentration. On-line sensors utilizing amperometry exists in two and three electrode configurations, with and without protective membrane barriers. In these configurations reference, working and zero-point electrodes are utilized. These sensors apply a gas-diffusion membrane that permits diffusion of chlorine dioxide across the membrane into the electrode chambers. An oxychlorine specific pre-defined voltage is

applied across the electrode, permitting diffusion of the species though the membrane for reduction at the working electrode. These sensors are commercially available for both chlorine dioxide and chlorite. The reduction occurs at the gold working electrode as the following half reaction, equation (24).

$$ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O \quad (24)$$

It is the combination of the pre-defined voltage and membrane which allow these methods to be selective towards a particular analyte in the presence of bromine, hydrogen peroxide, chlorite and chlorate. On-line monitoring methods are free of pH and temperature variance, as temperature is compensated by the probe, and require minimal cleaning maintenance. The electrodes are situated within an electrolyte solution which, as part of scheduled maintenance, requires the occasional replacement. Like instrumental methods, these are not absolute and require calibration using pre-established standards. Once calibrated though, their functionality is unmatched in terms of ease of use, cost and practicality.

3.1.15 Standards, Glassware and Sample Preparation

Due to the instability of chlorine dioxide, standardized solutions should be prepared as close to the time of analysis as possible. All solutions should be shielded from light, via a method such as storage in amber glass bottles using Teflon sealed caps. Sample bottles should be overfilled to minimize headspace. This will reduce the likelihood of self-decomposition, which leads to the formation of the chlorate ion, in addition to reducing the escape of volatile chlorine dioxide. Consecutive measurements spanning several hours should include periodic quality analysis checks of the stock

chlorine dioxide solution to assess concentration and the need for possible instrument re-calibration.

The source of the generated chlorine dioxide is also of concern. Bench scale synthesis methods should be free of impurities, specifically alternative oxychlorine compounds (Cl_2, HOCl, OCl^-, ClO_2^-, and ClO_3^-). One approach involves the reduction of sodium chlorate ($NaClO_3$) by potassium persulfate ($K_2S_2O_8$) (Gates, et al., 2009, Gates, 1998, Granstrom and Lee, 1958). This method utilized the addition of a solution of potassium persulfate (0.295 mmol/L) to a solution of sodium chlorate (3.5 mol/L), as presented in equation (25).

$$2ClO_2^- + K_2S_2O_8 \longrightarrow 2ClO_{2(g)} + 2K^+ + 2SO_4^{2-} \quad (25)$$

To aid in ensuring the generation is free of interferences, care must be taken to verify that the glassware is free of potential error. Glassware should be first cleaned thoroughly using soap and water, followed by an overnight soak in concentrated nitric acid and water mix (1:1 ratio). This glassware should initially be rinsed with water, followed by ample distilled/deionized water. Following a sufficient rinsing, all openings in the glassware (beakers, pipette, burette, etc.) should be covered with either a plastic wrap, paraffin or ground-glass stoppers to prohibit the entry of particulate matter (Gates, 1998). This glassware should be solely devoted to the generation of chlorine dioxide and thus cleaned as soon as possible following post-generation. Dedicated glassware reduces the possibility of cross-contamination and facilitates effective cleaning.

Sample preparation is paramount to achieving accurate testing, whether analysis is to be conducted on-site or off-site through a third party. Collection using amber glass sample bottles which should be over-filled several times, ensuring homogeneous

collection and minimization of headspace. Teflon lined caps should be used to reduce the potential of chlorine dioxide escaping. When transferring aliquots of sample solution for dilution or instrumental analysis, the recommended procedure is to aspirate from the bottom of the sample bottle, followed by draining the liquid into the receiving flask well below the surface of the reagent or dilution water (Gates, et al., 2009). In order to ensure accurate delivery and best results, an aliquot should be made using zero-headspace syringes, as the lack of headspace further deters the vaporization and reduction in expected concentration (Gordon, et al., 1972).

All samples should be analyzed as soon as possible following acquisition. Regulators typically demand that periodic testing of the water at the treatment centre and throughout the distribution system for chlorine dioxide and by-products occur. This conflicts the views of several authors which recommend not sending the sample to an outside lab, principally due to the extended period of time that occurs post sampling, and to apply an in-house analyses procedure to circumvent possible error. Specifically, the conditions in which the sample is eventually tested may not accurately reflect those at the time of sampling and thus can lead to erroneous results regardless of analytical method chosen (Gates, et al., 2009). Regardless, to conform to regulations, when sending samples to an outside lab, they should be safeguarded from light (the need for amber bottles) and placed in either cool or chilled conditions. Without proper adherence to these precautions, research suggests that photodecomposition to chlorate is possible and likely (and thus the need for on-site accurate analysis methods) (Dunn, et al., 1995, Vaida and Simon, 1995). When collecting a sample, liquid should be free flowing into the bottom of the jar, and the mouth of the delivery apparatus should remain below the

surface of the liquid. If neutralization of samples is required, the addition of thiosulfate in either solid or liquid form is recommended.

3.2 General Method Acceptance and Adoption

Due to the expensive cost of high-precision instrumentation, the adoption of spectrophotometry for the detection of residual levels of chlorine dioxide is widely maintained by regulators as a fundamental component of residual detection. Overlooking possible interferences, spectrophotometry offers the degree of sensitivity required. It is inexpensive, relatively maintenance free, and offers a straightforward procedure for the detection of residual oxidant levels (see Table 7 and Table 8). Despite this, monitoring residual chlorine dioxide concentrations from the operator's standpoint is commonly performed using the DPD method (Standard Methods 4500-ClO2 D) due to its low cost, ease of application, and support through the development of a multitude of "one step" handheld units from various commercial sources (which normally makes use of a filter photometers as oppose to a spectrophotometer). Currently, the DPD method is not recommended for residual chlorite concentrations by the EPA. A likely candidate for adoption at the operator level would be EPA method 327 Rev 1.0 or 1.1 relying upon the use of the LGB, or LGB-HRP relationship. Regardless, the EPA affirm that "if approved by the State, residual disinfectant concentrations for chlorine, chloramines, and chlorine dioxide may be measured using DPD colorimetric test kits" (Environmental Protection Agency, 2008). Thus is the link between the reliance upon the large number of handheld chlorine dioxide measuring devices which rely upon the non-discriminatory formation of the classical pink-red colour in reaction with N,N-diethyl-p-phenylenediamine (DPD) and

the ensuing optical measurement at 515 nm. The sole photometric method that the EPA continues to support is EPA method 327 Rev 1.1, which relies upon the LGB-HRP relationship for the determination of residual chlorine dioxide and chlorite and is designed for daily routine analysis.

Developed in June 2008, the Guidelines for Canadian Drinking Water Quality support the use of Standard Methods 4500-ClO_2 D, and thus permit the continued adoption of commercial handheld units or test kits throughout Canada. Though use of handheld units is nationally permitted in both Canada and the United States, provincial, state and municipal Regulatory Agencies may opt to require alternative testing procedures.

Monitoring requirements for the European countries are overseen by the European Union and are outlined in the Drinking Water Directive (DWD) 98/83/EC. The DWD is the minimum guideline for European countries to follow; it sets standards for the most common substances that can be found in drinking water. The DWD lists a total of 48 microbiological and chemical parameters to be monitored and tested regularly. In principle WHO guidelines for drinking water are used as a basis for the standards in the DWD (Europa: The European Union Online, 2008). In a recent stakeholder forum (dated June 5, 2008) entitled "Revision of the Drinking Water Directive 98/83/EC", the sole parameter associated with chlorine dioxide disinfection, namely chlorite, is noted to be likely included in a DWD revision if a Europe-wide standard is required. In the current publication, the DWD does not include any MAC for chlorine dioxide, chlorite or chlorate, nor does it provide any information pertaining to monitoring residual concentrations. Presumably residual concentration data is prescribed by the individual

country in question and often modeled after WHO guidelines, whereas the WHO lacks monitoring guidelines potentially leading to a wide variety of accepted monitoring methods.

3.2.1 Trends in Regulator Acceptance

Currently, the EPA is the only government organization in North America which has tested and validated instrumental methods. Their acceptance of the on-site operator based Standard Methods 4500-ClO_2 E (amperometry) and off-site commercial laboratory based EPA Method 326 Rev 1.0 (ion chromatography) has established a benchmark in terms of gaining the recognition of outside Regulatory agencies. Health Canada refers to the specific use of these EPA methods of testing, contrary to organizations such as the WHO and the European Union (EU) which do not acknowledge such methods at all.

Water treatment centers around the world currently rely on a multitude of on-line sensor technologies, and continuous monitoring of a multitude of water quality parameters. A logical approach would be that chlorine dioxide also be included in such monitoring. A 2007 EPA Federal Register document notes that free and total chlorine may be measured using a continuous monitoring system, although chlorine dioxide is referenced to be manually measured, no direction is offered for the continuous monitoring of chlorine dioxide (Environmental Protection Agency, 2007). Apart from the EPA providing instrumental method protocols, there appears to be very little regulatory pressure to implement online monitoring process controls in either Canada or the United States (Hargesheimer, et al., 2002). Beyond turbidity, there is no direct stipulation for continuous monitors in the Interim Enhanced Surface Water Treatment

Rule (IESWTR) or the Guidelines for Canadian Drinking Water Quality (GCDWQ), despite the recognition that a better understanding would be aided by continuous monitoring. Though not directly stated by the GCDWQ, Provincially granted operating licenses have the liberty to require on-line monitoring of finished waters.

Although the DWD currently do not outline or specify the need for on-line monitoring of drinking water parameters, a recent European Commission's Joint Research Centre (ECJRC) published a Thematic Strategy Report titled, "The Water Challenge" in January of 2000 which highlighted the need to further develop on-line monitoring technologies as a critical step towards making informed decisions on resource protection and treatment practices (Hargesheimer, et al., 2002). This is a clear Government issued acknowledgment that continuous monitors are paramount to the management of drinking water facilities for the future. Even with minimal support from North American and DWD government standards, many drinking water treatment facilities have adopted the use of on-line monitoring, for the reasons previously discussed. Yet ultimately, this move provides improved operating efficiency, and maximizes finished water quality.

3.2.2 Brief Review of Regulatory Monitoring Methods

Methods for measuring chlorine dioxide, chlorite, and chlorate are largely limited to titrimetry procedures, spectrophotometry, and ion chromatography. From a practical standpoint, daily testing procedures relying upon photometric methods would be more realistic as titrimetry is generally considered laborious and can require additional training. As with most analytical methods, the quality of the data and accuracy of the

measurements largely depends upon the skill and expertise of the analyst. The majority of Canadian drinking water treatment plants experience an aggravated potential for error in reported values due to inadequate analytical instrumentation (ion chromatography), the concurrent issue of short shelf life standards, and the inability to promptly test and analyze at the site of extraction (Hombach, 2009). As a result, the multitude of natural oxidative and reductive pathways through which chlorine dioxide, chlorite and chlorate may potentially follow (Pei, et al., 2003) logically insists that analysis be performed as soon as possible post-sampling to ensure the most accurate results. These criteria dictate that methods be made available for testing immediately following sample collection.

Many pocket colorimeters or small portable field units that make use of the diverse reagent set in which chlorine dioxide can react with Amaranth, DPD, LGB, etc. are available in the market. However, to achieve the best results, it is important to understand the potential for interferences, reagent grades and purities, as well as the necessity of standardization in order to ensure reproducibility, accuracy and precision. Even while maintaining ideal conditions for analysis, external quality control measurements should be integrated into the analysis schedule in order to ascertain what residual values are when dealing with manual field measurements.

Methods for the analysis of chlorite and chlorate are normally based on the principle of arithmetic subtraction. That is, once a total oxidant value is found the sample is further manipulated. This is then followed by an additional test to determine the chlorite concentration. The EPA recommends only one spectrophotometric method for the determination of chlorite (LGB-HRP), while listing several other titrimetric and ion chromatographic methods. While some automated titration equipment does exist to

facilitate amperometric chlorite analysis, it does not remove the potential for error due to these methods requiring several time consuming multi-step measurements, leaving it prone to accumulated errors.

A significant increase in the acceptance of chlorine dioxide as a drinking water oxidant and disinfectant in both Canada and the United States has been seen over the last twenty to thirty years. Concurrently, measurements of chlorine dioxide, chlorite and chlorate have proved to be under continual scrutiny from both regulatory agencies and operators, notably as the GCDWQ and other neighboring government legislation persistently demand the presence of less DBPs in potable waters (Environmental Protection Agency, 2009, World Health Organization (WHO), 2009, Town of Smith Falls, 2007). It is the analytical chemistry surrounding the practical application of chlorine dioxide which can be difficult to appreciate. This is largely due to its varying volatility under differing conditions, natural sensitivity existing as an oxychlorine stabilized radical, a large number of potential redox couples, and the ensuing propensity to further dissociate given a multitude of interfering reductive species. Interfering species are often categorized as the various metals and organic acids typically present in water sources. Given the diverse set of self-decomposition pathways and small residual level concentrations, producing easy, cost-effective, and relatively accurate methods for everyday operator use can be quite difficult without including generator analysis to maintain optimum efficacy. As such, the variability in analytical methods offered dictates that numerous variables, beyond solely chlorine dioxide, be considered prior to method adoption. These may include the required sensitivity, proper selectivity, availability of instrumentation (and reagents), cost effectiveness, speed of analysis,

straightforwardness, and potentially many others. Ideally, whatever method chosen is in due course a product of the skill set of the analyst, and results will be largely dependent upon attention to detail and expertise. Nonetheless, although most methods are not standardized, the disinfection literature, namely Tzanavaras, presents a wide array of analytical methods which can satisfy most demands from the operator and regulatory agency (Tzanavaras, et al., 2006).

Chapter 4: Review of Regulatory Requirements Pertaining to Chlorine Dioxide Disinfection

Microbial contamination of source waters represents a recurrently persistent high stakes issue in the effort to distribute safe and potable waters. The standard practice of utilizing chemical disinfection systems ranges between the application of chlorine, chloramines, chlorine dioxide, and ozone. Yet all of these require striking a delicate balance between the adverse toxicological risks associated with the disinfectant, the successful disinfection of the water, and the inherent potential for DBP formation from the disinfectant interacting with the raw, in process, and finished waters.

Maintaining a valid equilibrium between disinfection and DBPs requires the consideration of several parameters which should originate from a scaffold of previously reviewed, thoroughly tested, and consulted scientific works. The selection of appropriate disinfection technology, operational and maintenance protocols, instrumentation, monitoring methods, and schedule all require that such selection be incorporated into a larger, regulated, and consistently monitored support system. This support system would ideally originate from advancements that have been legitimately established to reduce

microbial contamination and minimize disinfectant toxicological risk and by-product formation. Ultimately, this would ensure that public health and safety are at the forefront of such water treatment policy.

The selection of treatment technologies, expected performance and the entire process, originating from initial disinfection to the distribution network and concluding with exit at the consumer's tap, must be meticulously planned and developed. Importantly, special consideration must be given to the abundance of varying control checks, limitations and restrictions put forth by regulatory agencies which are bound by not only technical considerations, but also the legal obligation to maintain public health and safety in the highest regard while upholding drinking water standards and guidelines.

Since colourimetric and titrimetric Standard Methods for the analysis of residual chlorine dioxide by the EPA were initially accepted in 1995, numerous changes, analytical advances, and technological developments have occurred. These changes have extended to scientific study and applied fields which have directly affected the use of chlorine dioxide as a disinfectant. It is these changes, specifically the advancement of high efficiency generators (those which exceed generator expectations outlined in Section 2.2.2), combined with the procurement of new advanced methods of analysis, the emergence of newer superior toxicological data from better human exposure evaluations, and an enhanced regulatory framework which have all culminated in providing superior disinfection methods for Municipalities and their consumers. The state of chlorine dioxide has proven to be that of a variable nature, continually calling upon Regulatory Agencies to carefully evaluate their recommendations according to best practice.

4.1 Provincial and Federal Regulations in Canada

The responsibility for the quality of drinking water in Canada is shared by all levels of government. Both the development of guidelines and scientific investigations are carried out at the federal level, in which the results assembled as the GCDWQ are disseminated to the provincial and territorial governments. This cooperation is made possible by the Federal-Provincial-Territorial Committee on Drinking Water (CDW). The remaining responsibilities are shared between the provinces and territories though the enactment of various drinking water regulations, specifically water quality standards, treatment trains, and governmental water stewardships and ministries. Further remaining responsibilities, such as the maintenance of the treatment process, adequate monitoring, sample collection and collectively ensuring that the distribution of the water is safe for public consumption, is typically maintained at the Municipal government level. The only exception involves First Nations communities located south of 60°N which are regulated primarily by the First Nation Band Councils, Health Canada, and Indian and Northern Affairs Canada (Health Canada, 2007).

As such, the quality of the public's drinking water inevitably falls under provincial and territorial responsibility within the GCDWQ. The result is the assembly of individual provincial and territorial government legislation, policy, and approval under the GCDWQ being implemented though governmental jurisdictions or individual system licenses or certificates to operate.

While there are no federal drinking water guidelines for chlorine dioxide use in Canada, monitoring requirements for its use and allowable concentrations of chlorite and chlorate vary according to the governing bodies involved and the regulations of that

government. Despite only three Provinces across Canada acknowledging the use of chlorine dioxide, namely Ontario, Quebec and Manitoba (Federal-Provincial-Territorial Committee on Drinking Water, 2005), regulations pertaining to the guidelines for monitoring dosage and residual concentrations fluctuate from province to province. A meta-analysis of national and international limits for chlorine dioxide, chlorite and chlorate is presented in Table 9, which are further discussed in subsequent sections.

Table 9: Meta-analysis of national and international regulations for chlorine dioxide, chlorite and chlorate.

	Chlorine Dioxide	*Chlorite*	*Chlorate*
Quebec	No maximum dose Distribution: 0.8 – 0.3 ppm Recommend combined residual : 1 ppm	Health Canada Values (GCDWQ)	Health Canada Values (GCDWQ)
Ontario	Only Distribution outlined: 0.8 -0.05 ppm	Not clearly stated	Not clearly stated
Manitoba	Recommend max dose: 1.2 ppm Distribution: 0.8 – 0.2 ppm	Health Canada Values (GCDWQ)	Health Canada Values (GCDWQ)
International:			
Canada	Not regulated	1 ppm	1 ppm
US EPA	MRDLG & MRDL - 0.8 ppm	MCGL - 0.8 ppm MCL - 1.0 ppm	Not regulated
WHO	Not regulated	PG – 0.7 ppm	PG – 0.7 ppm

4.1.1 Provincial Regulations

Ontario's Safe Drinking Water Act oversees the approved use and monitoring of disinfection for the Province. A subsection to this act is the "Procedure for Drinking Water Disinfection in Ontario Reference Document" which outlines specific requirements for monitoring disinfection procedures. These span chemical, ultraviolet and physical disinfection protocols. Ontario regulations permit the use of chlorine dioxide as both a primary and secondary disinfectant. The Ontario regulations further mandate that a minimum residual concentration of 0.05 ppm must be present anywhere

throughout the distribution system; whereas a maximum of 0.8 ppm must not be exceeded. Further regulations, such as provincial guidelines for chlorite and chlorate concentrations, monitoring methods, and accepted detection procedures are not clearly identified in provincial disinfection procedure documentation. Presumably, therefore, these parameters are outlined via the use of individual operational certificates of approval for chlorine dioxide treatment plants.

In 1999, more than 600,000 people were served potable water disinfected by 12 chlorine dioxide treatment plants throughout Quebec, comprising approximately 10% of the province's population (Levallois, September 2001). Chlorine dioxide has been used extensively throughout Quebec as both a primary and secondary disinfectant, while also being recommended to resolve staining from iron and manganese, as well as odour and water colour issues (Ministère du Développement durable et l'Environnement et des Parcs (MDDEP), 2006 Third Update). The MDDEP acknowledges in their design guidelines that if the water in question exceeds an oxidant demand in the range of 1-1.4 ppm, chlorine dioxide may produce by-product concentrations exceeding Health Canada's guidelines. Furthermore, these guidelines state that chlorine dioxide may be used in such a scenario if precautions are taken to reduce excessive concentrations of chlorite prior to or post-chlorination. Quebec guidelines limit the maximum allowable chlorine dioxide residual to 0.8 ppm, yet exclude parameters for chlorite and chlorate concentrations in the specific standards (Règlement sur la qualité de l'eau potable, RQEP). The REQP standards have not been set for chlorite and chlorate due to the absence of conclusive toxicological data. However, it is recommended for operators to maintain a combined maximum concentration of 1 ppm for the sum of chlorine dioxide,

chlorite and chlorate concentrations (Ministère du Développement durable et l'Environnement et des Parcs (MDDEP), 2006 Third Update).

Manitoba currently operates one chlorine dioxide plant in Holland located in the Rural Municipality of Victoria. The current operating license for the plant in Holland, dictates that the testing for residual levels of chlorine dioxide and chlorite are performed daily on waters entering the distribution system following disinfection contact time. These testing requirements are similar to other operator requirements from selected locations, see Section 4.2. The small generator footprint, dramatic THM reduction and ease of use distinguishes chlorine dioxide as a qualified disinfectant candidate for small community potable water systems in Manitoba; yet the combination of the limited dosages, high DOC values, and interference prone residual testing have significantly deterred further implementation. Testing for chlorine dioxide and chlorite levels in the water distribution system must be completed at the same times and locations as the bi-weekly bacteriological sampling. The recorded residual concentrations for both chlorine dioxide and chlorite are presented on Figure 6, daily monitoring for residual chlorine dioxide and chlorite were carried out by the operator using a commercial DPD test kit. It is important to note that a typical chlorine demand cannot be easily determined from Figure 8 in the classical sense of the term. Specifically, as chlorine dioxide does not readily react with nitrogenous compounds such as ammonia (to produce chloramines) nor other natural organic materials (humic substances, etc.) which classically present a chlorine demand, comparing a hypochlorous acid chlorine demand to a chlorine dioxide "chlorine demand" can become quite difficult due to the differences in reaction types

(oxidation versus chlorination) and the subsequent compounds in which chlorine dioxide selectively reacts with.

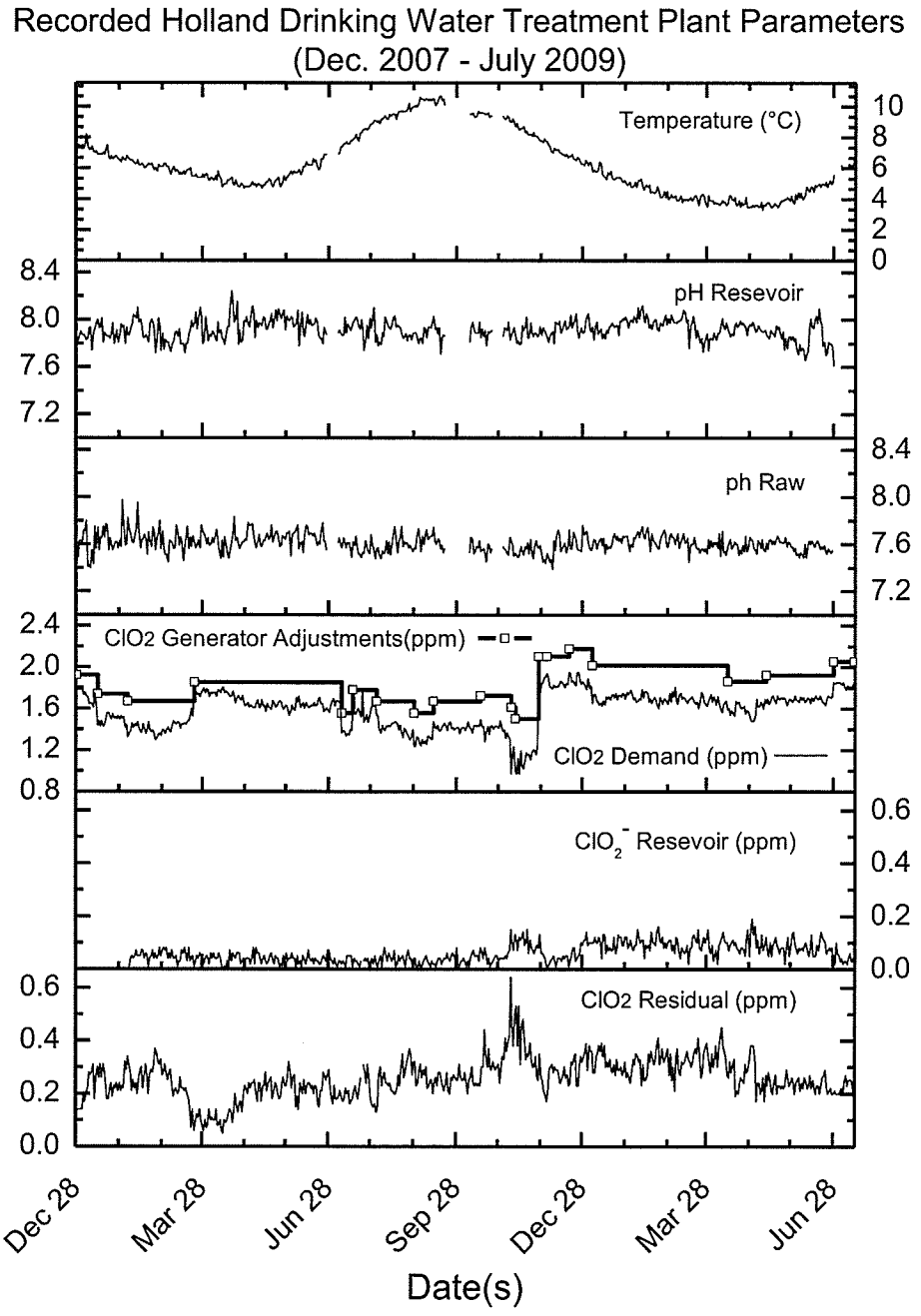


Figure 8: Recorded parameters for the Town of Holland from December 2007 to July 2009 (Tested using a commercial DPD test kit).

The operating range of allowable residual chlorine dioxide concentrations for Holland's water treatment plant (0.2-0.8 ppm) is based on disinfection contact time (CT) calculations completed by the design engineer and limits suggested by the Province of Ontario's Ministry of the Environment Drinking Water Office and Health Canada recommendations (Manitoba Stewardship, 2009). The maximum recommended dosage for chlorine dioxide is 1.2 ppm, which abides by a 50-70% "conversion ratio" set forth to limit possible residual chlorite concentrations in the distribution system below the limit of 1 ppm (Manitoba Stewardship, 2009). Chlorate concentrations are difficult to accurately detect onsite as they commonly require lab testing via ion chromatography, and elevated chlorite levels are indicative of a problematic issue, testing for the chlorate anion has been identified as part of the general laboratory chemical analysis protocol required once every three years (Barlishen, 2009).

4.1.2 A Canadian Perspective

Contributing factors such as the established relationship existing between chlorine dioxide disinfection by-products (DBPs), pre-existing organic matter content, and the dosages of chlorine dioxide, have been well documented for their ability to substantially affect the remaining residual chlorine dioxide, chlorite and chlorate concentrations observed post-application (Gates, et al., 2009, White, 1999, Aieta and Berg, 1986). Health Canada's guidelines are established in part due to the results of Korn's work (1998). These results suggest that average ratios for the "conversion" of chlorine dioxide to chlorite and chlorate have been reported to vary from approximately 0.39 to 0.70 for chlorite and 0.04 to 0.21 for chlorate with little change occurring from varying pH for

chlorate (Korn, 1998). Notably, Korn agrees that while only observational data involving cause and effect prognosis has been collected to this point, little information about cumulative stoichiometric relationships exists to accurately predict DBPs resulting from chlorine dioxide. Apart from various studies which focus on specific functional groups and the associated formation of their subsequent chlorine dioxide DBPs, existing information about predictive by-product modeling is limited. In part, this is because the treatment of drinking water requires the consideration of a multitude of organic and inorganic matter as well as their associated functional groups and intricate molecular relationships, and thus leaves predicting by-product concentrations an extremely strenuous task. Ideally, these parameters would be best met through individual treatment center modeling based on the needs of the local water source, rather than a set value which fails to recognize the variant nature of water sources. Commonly, to meet MACs of chlorate and chlorite in finished waters, regulatory agencies have chosen to set a chlorine dioxide residual limit (both Health Canada and the EPA have a MAC of 1.0 ppm), which reflects a combination of human health risk assessments data and an observed approximated 50-70% conversion ratio from dosage to chlorite by-product (Federal-Provincial-Territorial Committee on Drinking Water of the Federal-Provincial-Territorial Committee on Health and the Environment., 2008, Korn, et al., 2002, Korn, 1998). Thus forms a fundamental predicament of utilizing chlorine dioxide: the hypothetical dosage level which is targeted at meeting oxidant demand and achieving effective disinfection may very well be impossible to apply, given that increased dosages may potentially lead to the consequent formation of increased chlorite and chlorate concentrations unequivocally exceeding GCDWQ, USEPA and WHO guidelines. Again,

this scenario of dose versus MCL may be potentially elevated with the adoption of more accurate on-site analytical methods thereby maximizing the applied dose. Such difficulties in meeting demands may be observed in Table 10, as this table highlights current regulations from several Regulators which are further discussed in the following sections.

Table 10: Tabulated summary comparing current Manitoba regulations to those of other Regulators.

	Manitoba	*Ohio EPA*	*California Dept. of Health*	*EU DWD*	*UK*	*Germany*	*Australia*	*New Zealand*
ClO_2 Range:	0.8 - 0.2 ppm	0.8 /0.8 ppm	0.8 /0.8 ppm	-	Combined max of 0.5 ppm	0.5 -0.05 ppm	1 ppm	? - 0.2 ppm
ClO_2^- Max:	1 ppm	0.8 / 1 ppm	0.8 / 1 ppm	-		0.2 ppm	0.3 ppm	0.8 ppm
ClO_3^- Max:	1 ppm	-	-	-		-	No data	0.8 ppm
Accepted ClO_2 Methods:	EPA Approved	Amp., LGB-HRP, DPD	EPA Approved	-	DPD, on-line sensors	Membrane selective electrodes, DPD	Only cite DPD	Requires continuous monitoring (5min freq.)
Accepted ClO_2^- Methods:	EPA Approved (DPD included)	Amp., LGB-HRP, IC	EPA Approved	-	DPD, on-line sensors	Membrane selective electrodes, DPD	Only cite DPD	Requires continuous monitoring (5min freq.)
On-line Analysis?	No reference	Referenced for Ozone	No reference	-	Yes, recommended	Yes, recommended	No reference	Yes, recommend
Other:	Recommends max dose of 1.2 ppm ClO_2.	State dictates acceptable methods.	Chlorate is on a notification list at 0.8 ppm.	Possible inclusion of chlorite and chlorate at 0.7 ppm.	Cannot exceed 0.5 ppm at tap	Max dose is 0.4 ppm ClO_2.	Currently under revision	Notes DPD, suggests alternatives such as IC, amp, and CPR.

4.2 United States Environmental Protection Agency (EPA) Regulations

As previously noted, the MRDLG and the MRDL for chlorine dioxide is set at 0.8 ppm; whereas the MCLG and the MCL for chlorite are 0.8 ppm and 1.0 ppm, respectively. The EPA does not currently regulate chlorate concentrations, although

there is evidence that this parameter may receive a MCL in due course (Environmental Protection Agency, 1994).

Probably the most significant contributor to the development of chlorine dioxide in the US is advancement of the Microbial and Disinfection By-product (MDBP) Rule originating from the Safe Drinking Water Act of 1986. The MDBP implementation guidelines list the Stage 1 Disinfectants/Disinfection By-products Rule (DDBR) to further minimize chances of elevated levels of chlorine dioxide and chlorite in finished waters. Though the original set of guidelines of 1986 cited levels of 0.3 ppm and 0.8 ppm for chlorine dioxide and chlorite respectively; it is the DDBR (1998) which became the first enforceable ruling to set a MRDL for chlorine dioxide and a MCL for chlorite concentrations (Environmental Protection Agency, 1998). This amendment originated from a change in the calculated uncertainty factor for the risk model and suggested that the MRDL and MCL for chlorine dioxide and chlorite be elevated to 0.8 ppm and 1.0 ppm, respectively. This aided in placing the MRDL as close to the MRDLG as possible (Environmental Protection Agency, 1999). Furthermore, the adoption of these MRDL and MCL rulings well protected consumers. Specifically, the result of the widespread use of the DPD method and its relatively inflated levels of positive errors in recorded values resulted in false positives in practice and therefore enforced lower levels of chlorine dioxide than what was actually present in tested samples (Gates, et al., 2009).

Future regulations will most likely take into account the improved selectivity and sensitivity offered by EPA Method 327 Rev 1.0 or Rev 1.1 (LGB or LGB-HRP), conceivably providing new lower MRDL and MCL parameters for chlorine dioxide and chlorite. In light of newer toxicology studies on the effects of chlorate (Chhabra, et al.,

2003, Booker, 2000), such findings may also suggest a MCL of chlorate will also come into effect. The combination of better methods and superior human risk assessment modeling may possibly provide newer, relatively higher MRDL and MCL values which would likely advance the use of chlorine dioxide for potable waters in North America.

4.2.1 Ohio Environmental Protection Agency

The State of Ohio is actively pursuing environmental protection issues through the Ohio Environmental Protection Agency (Ohio EPA). Ohio EPA's goal is to protect the environment and public health by ensuring compliance with local environmental laws. The Division of Drinking and Ground Waters (DDGW) ensures compliance with the federal Safe Drinking Water Act and evaluates potential threats to source waters of Ohio's 1,500 public water systems. The Ohio EPA provides MRDL and MCL values for chlorine dioxide, in addition to readily available documentation suggesting the best obtainable technologies and the latest rule making in progress in either draft or proposed forms.

Current State legislation permits the use of chlorine dioxide as a disinfectant, with a MRDL of 0.8 ppm (reported as ClO_2), and an MCL of 1.0 ppm for chlorite. An MCL for chlorate does not currently exist. The MCL for chlorite applies to all community and non-transient, non-community public water systems that treat their water with chlorine dioxide. The Ohio EPA suggests that controlling the treatment processes to reduce disinfectant demand, and that controlling disinfectant treatment processes to reduce disinfectant levels, is the "best available technology" to reduce and maintain minimal levels of chlorite at the entrance to the distribution network and throughout.

The monitoring requirements set forth by the Ohio EPA are similar to those in Manitoba. Systems serving more than 3,300 consumers require the construction of a director-approved monitoring plan. Such a plan should include specific locations and schedules for collecting samples for chlorine dioxide and chlorite, and clearly outline how the public water system will calculate compliance with the MCL for chlorite. Regardless, while routine daily monitoring of chlorine dioxide is required, routine monthly monitoring is required for chlorite within the distribution network. Specifically monthly distribution sampling should include three samples taken from the first customer, a location representative of the average residence time, and a location reflecting the maximum residence time. The Ohio EPA provides reduced monitoring programs, when qualified, for systems to monitor their distribution system on a quarterly basis presuming the chlorite MCL has not been exceeded over the last year.

The currently accepted methods for the residual analysis of chlorine dioxide originate from various editions of Standard Methods (APHA). Approved Standard Methods are 4500-ClO_2 C (amperometric titration; 18th, 19th, and 20th editions), 4500-ClO_2 D (DPD; 18th, 19th, and 20th editions), and 4500-ClO_2 E (amperometric titration; 18th, 19th, and 20th editions). The online version of Standard Methods is also approved, specifically methods 4500-ClO_2 C-00, 4500-ClO_2 D-00 and 4500-ClO_2 E-00. EPA Method 327.0 Rev 1.1 is also deemed acceptable for chlorine dioxide. Interestingly, the Ohio EPA specifically outlines the acceptance of on-site operator maintained online automated residual analyzers for ozone using amperometric electrodes, yet there is no such equivalent legislation of chlorine dioxide.

The Ohio EPA's currently accepted methods for the daily residual analysis of chlorite are Standard Methods 4500-ClO_2 E (amperometric titration; 19th, and 20th editions) and 4500-ClO_2 E-00 (online). These two methods are designed to be used for testing at the entrance of the distribution system. For routine monthly monitoring, EPA method 300.0 Rev 2.1 (ion chromatography), 300.1 Rev 1.0 (ion chromatography), 317.0 Rev 2.0 (ion chromatography), and 326 Rev 1.0 (ion chromatography) are all accepted. These methods are further suggested for the additional monitoring throughout the distribution network, following method's sampling procedures.

At this time there are no drafted rulings which pertain to the use of chlorine dioxide, nor its DBPs, although proposed ruling changes do exist there is no date for when these proposed rulings will be finalized. Proposed changes to the current rulings concerning chlorine dioxide usage are minimal, but should be noted. For instance, one suggestion involved the removal of the 3,300 person limit to reflect that any community using chlorine dioxide shall comply with a proper monitoring schedule, where others more significantly impact the analytical methods. These include the addition of the 21st edition and removal of the 18th edition of Standard Methods to the previously outlined protocols for chlorine dioxide and the removal of Standard Method 4500-ClO_2 D-00.

One particular change affecting residual chlorite analysis is the 21st edition of Standard Methods meant to supplement previously discussed protocols, and most importantly, the adoption of EPA Method 327 Rev 1.1 for the on-site determination of chlorite using the LGB-HRP method. This is ideal as the operator need only prepare three samples with small aliquots of reagent added. Analysis is performed by a handheld

spectrophotometer (facilitated by the use small handheld commercial units adapted to measure at 633 nm).

4.2.2 California Department of Public Health

The California Department of Public Health's (CDPH) Drinking Water Program (DWP) is politically situated within the Division of Drinking Water and Environmental Management. The DWP regulates public drinking water systems and potable water standards for California. Separate branches comprising the DWP are responsible for enforcing both federal and state regulations (California Safe Drinking Water Acts, SDWAs). Furthermore, the DWP acts as the regulatory agency which governs the safe distribution of drinking water from approximately 7,500 public water systems.

The DWP permits use of chlorine dioxide at a MRDL of 0.8 ppm (reported for ClO_2), and a chlorite MCL of 1.0 ppm. Although no MCL is presented for chlorate concentrations, the DWP has acted to add chlorate to a notification levels list. Contaminants on the notification levels list do not possess a MCL as a formal regulatory process is required prior to transitioning to a MCL. The CDPH provides a health based notification list which outlines advisory levels for certain drinking water contaminants which do not currently have a federally regulated MCL. If concentrations exceed allowable limits outlined in the notifications list, certain state regulated requirements and contaminant-specific recommendations are then implemented, yet all require that the utility inform the public about the associated health risks. The notification level for chlorate is 0.8 ppm. Utilities which exceed notification-list parameters by ten times or

more are augmented to a response level where the utility may be immediately taken offline.

In order to abide by the MRDI, the CDPH requires daily testing for systems using chlorine dioxide, and waters must be drawn from the entrance to the distribution system. When chlorine dioxide is used as a residual disinfectant, and booster stations are not present either within the distribution system or alternative injection points within the system, samples should be taken in triplicate at a minimum of at least six hour intervals as close to the first customer as feasible.

Chlorite concentrations are to be tested daily at the entrance to the distribution system. Any sample found to exceed the MCL require additional chlorite sampling be performed within the distribution system (in triplicate) at a location as close as possible to the first customer, at a location that represents the average residence time and a location that reflects the maximum residence time. Monthly monitoring of chlorite concentrations within the distribution system is required, across three locations three times over as presented above. Systems which use chlorine dioxide may apply for reduced distribution system monitoring schedules based on a quarterly basis when the MCL is not found to exceed chlorite limits. MCL compliance is based upon the arithmetic average of any given distribution set sampling, effectively, certain locations can exceed the MCL through the average throughout the distribution system must remain below MCL.

The CDPH accepts monitoring methods which follow EPA approved methods, including the common operator method Standard Methods 4500-ClO_2 D (DPD) for chlorine dioxide. The CDPH does not accept Standard Methods 4500-ClO_2 D (DPD) for chlorite (California Code of Regulations, 2009). However, the CDPH does accept EPA

Method 327 Rev 1.1 for the both determination of chlorine dioxide and chlorite using the LGB-HRP method. There are no current drafts or proposed rulings which affect chlorine dioxide or its DBPs publically offered by the CDPH.

4.3 European Union Regulations

Due to the natural diversity that the EU represents, setting overly stringent regulations could yield not only a negative economic effect, but also some unimagined pressures or demands upon its members, or members in consideration. It is important to properly consider which parameters should be applied to all members and those which should be applied on an individual basis. As a result, the EU outlines water quality parameters which are based on more generally accepted parameters, and closely follow the guidelines set forth by the WHO. The WHO's guidelines are based on average weighted risk values calculated based on the risk of a lifetime exposure, and thus such adoption provides an extra safeguard as the EU accepts these values as their maximums though their Drinking Water Directive (DWD), presented as Council Directive 98/83/EC. This directive sets the minimum drinking water quality parameter objectives; whereas participating member states can choose to include additional requirements relevant to their communities. This results in a greater number of parameters being listed and the potential for increasingly stringent MACs, or both, in member state regulations. Regardless, member states are not allowed to set lower standards than those which were previously outlined in directive 98/83/EC.

Though the 98/83/EC directive lacks several common parameters (DBPs, THMs, etc) found in North American guidelines, the functionality of the DWD operates on a

precautionary principle ensuring safe water is available. That is, a zero tolerance approach should be taken with those parameters which are not found in the 98/83/EC directive and have little scientific data to support any conclusion (Gates, et al., 2009). This translates to member states setting a maximum based upon the limits of detection available for the particular analyte of interest, effectively minimizing concentrations of those contaminants.

Although this directive presents no information pertaining to the use of chlorine dioxide, chlorite or chlorate, it is currently under significant review. The initial framework development of a new directive began in 2000, and as recently as 2007 and 2008 had been forwarded to member states, various stakeholders and the scientific community for consultation. This new directive attempts to harmonize a standard for drinking water quality, sampling procedures and chemical constituents among the countries in the European Union.

Although the directive is not yet completed, a final report targeted at establishing a list of chemical parameters for inclusion into the DWD is available from the European Commission, and was commissioned by DHI, an independent consulting and research organization within the EU. This report outlines individual MACs of chlorite and chlorate at 0.7 ppm and further proclaims that these species are controlled by-products which require monitoring compliance (DHI, 2008). The report further specifies that the largest source of chlorite is from chlorine dioxide applications and chlorate due to the use of hypochlorites for disinfection, and as no parametric values are present in directive 98/83/EC, any revisions should include both values.

4.4 Regulations for Selected Countries

4.4.1 United Kingdom

In the United Kingdom (UK), the Building Services Research and Information Association (BSRIA) advocates for chlorine dioxide as the best available technology for control of Legionella in both hot and cold water systems. Their publication is cited as being the most comprehensive independent record of chlorine dioxide effectiveness carried out in the UK. The BSRIA has studied the efficacy of chlorine dioxide in the temperature range of 20-45 °C, and concluded that it remains an effective disinfectant. Use of chlorine dioxide is controlled by the Secretary of State and is authorized for use in public water supplies on the condition that the combined concentrations of chlorine dioxide, chlorite and chlorate not exceed 0.5 ppm (Pavey and Roper, 1997). Though relatively dated, this legislation calls for the use of the DPD test method for the daily monitoring and determination of the ratio of dosing relative to water usage, which is cited to provide for rapid adjustment accordingly. On the contrary, the legislation also imparts the acceptance of automatic online monitoring; that is the acceptance of automatic residual analysis of chlorine dioxide via amperometric sensors. However, the policy acknowledges that while a 0.5 ppm combined residual may be exceeded within the process train and distribution network, it must not be exceeded at the exit point, especially at the consumers tap where the sample is representative of the distribution network. Consequently, utilities are required to measure outgoing plant waters for chlorite and chlorate concentrations.

4.4.2 Germany

As previously noted, the EU establishes the initial framework and guidelines for the minimum drinking water qualities of its member states. In Germany, working under the Federal Ministry of Health, it is the Federal Environment Agency (Umweltbundesamt - UBA) which holds authority over drinking water regulations and standards. As of June 2009, German Drinking Water Regulations currently regulate chlorine dioxide for disinfection purposes; regulating its dosage, minimum and maximum concentrations throughout the distribution system (Umweltbundesamt, 2009). The maximum allowable chlorine dioxide dose is 0.4 ppm, with a distribution network minimum of 0.05 ppm and a maximum of 0.5 ppm. Furthermore, regulations state that chlorite concentrations cannot exceed 0.2 ppm measured as chlorine dioxide (though chlorite would provide the same limitation), because if this concentration is exceeded; the formation of chlorate ions is possible.

Chlorine dioxide use in Germany is almost exclusively used in scenarios where the water is unpolluted and relatively clean (and thus a very low oxidant demand) with feed rates ranging between 0.1 and 0.2 ppm, so that the limit of chlorite, 0.2 ppm can never be reached (Ritter, 2002). Regulations state that samples should be measured quickly after acquisition using a membrane electrode sensitive to chlorine dioxide. The regulation offers supplementary material regarding accepted methods of analysis, while referencing methods outlined in the German standard for the determination of chlorine dioxide, DIN 38404 Part 5 (Deutsches Institut für Normung, ie. German Institute for Standardization), or the more recent DIN 38408-G 5 which is valid between 2009-01-20 to 2012-01-14) (Johann-Sebastian-Bach-Straße, 2009). The Standard DIN 38408-G5,

titled "German standard methods for the examination of water, waste water and sludge; gaseous components (group G); determination of chlorine dioxide (G 5)" is a titrimetric procedure based upon the oxidation of DPD by chlorine dioxide. The coloured DPD solution resulting from the reaction of chlorine dioxide is then back titrated with ammonium iron(II) sulfate, and the chlorine dioxide concentration is calculated from these titrations. This standard also provides for the spectrophotometric detection of chlorine dioxide using DPD, making it analogous to Standard Methods 4500-ClO_2 D.

4.4.3 Australia

The use of chlorine dioxide in drinking water was evaluated by the National Health and Medical Research Council (NHMRC) and approved for drinking water use in 2005. Current Australian Drinking Water Guidelines (ADWG) only recently adopted the use of chlorine dioxide as a primary disinfectant in 2004, dictating that a weekly sampling and testing frequency representative of the quality of water supplied to consumers be adhered to (Natioanl Health and Medical Research Council, 2004). While insufficient data prevents the existence of health guidelines for the maximum concentration of chlorate, a maximum of 1 ppm health guideline and a maximum of 0.4 ppm aesthetic guidelines are stipulated for chlorine dioxide. The ADWG prohibits concentrations greater than 0.3 ppm of chlorite to be present in finished waters. The following calculation demonstrates the ADWG chlorine dioxide guideline assuming all chlorine dioxide intake originates from drinking water:

$$\frac{3\,{}^{mg}/_{kg}\,(\text{body weight per day}) \bullet 70\text{kg}(\text{body mass})}{2l/day(\text{consumption rate}) \bullet 100(\text{safety factor})} = 1ppm \qquad (26)$$

The chlorite guideline is calculated as the following (assuming that 80% of the daily chlorite intake originates from water):

$$\frac{1\,{}^{mg}/_{kg}\,(\text{body weight per day}) \bullet 70\text{kg(body mass)} \bullet 0.8}{2l\,/\,day(\text{consumption rate}) \bullet 100(\text{safety factor})} = 0.3ppm \qquad (27)$$

In contrast to the GCDWQ, there is no reference or discussion pertaining to a 50 to 70% conversion ratio of chlorine dioxide to chlorite. The ADWG's reference to the formation of these equations is similar to those enacted by the WHO. The WHO has established a set guideline value of 0.2 ppm for chlorite, based upon a body mass of 60 kg, whereas these parameters are known to not provide a significant difference in contrast to the ADWG's use of 70 kg.

The ADWG highlights the efficacy of chlorine dioxide for the inactivation of various microorganisms at 5 °C which is a relatively average drinking water source temperature, elaborating that the preferred pH for the application of chlorine dioxide falls between 6 and 7. Ideally, this value should be less than 8 as its effectiveness is amplified three-fold in a pH range of 6 to 9. Furthermore, the ADWG remarks that use of chlorine dioxide is ideal for small to medium sized plants and that the technology is moderately complex. Regardless, the regulations further state that a moderately persistent residual is achievable, although the process control is still developing. The largest disadvantage is the rapid consumption of chlorine dioxide when applied to raw waters, a finding which again emphasizing the suitability for relatively pure waters (also noted by the German Drinking Water Regulations). This is likely a leading reason as to why chlorine dioxide is rarely used as a disinfectant in Australian reticulated supplies, although when used,

typical chlorite residual between 0.2 and 0.4 ppm is observed (Natioanl Health and Medical Research Council, 2004).

The ADWG cited one prescribed measurement method, namely the use of Standard Methods 4500-ClO_2 Part D (1992). However, the ADWG is currently under a revision period with an expected update to be released in 2009, thus this recommendation may change.

4.4.4 New Zealand

Through the Ministry for the Environment, the current New Zealand Drinking Water Standards, NZDS (DWSNZ2005) came into effect December 31, 2005 (Ministry of Health, 2005). Their regulatory focus has shifted from quality control, to quality assurance and is targeted at maintaining standards for providing quality drinking water to New Zealand residents.

While there is growing concern that it is impacting public health, there is no set maximum acceptable value (MAV) for chlorine dioxide in New Zealand . The reasoning provided is that chlorine dioxide rapidly breaks down, and an established MAV for chlorite provides adequate protection from any potential toxicity. In contrast, both chlorite and chlorate concentrations are regulated at 0.8 ppm as chlorine dioxide, though the regulations specify that disinfection should never be compromised. These regulations further require that if the MAV of chlorite is to likely exceed 0.8 ppm chlorine dioxide cannot be used in such a system, and a monitoring program complacent with the drinking water assessor's (DWA) standards is established.

The NZDS requires continuous monitoring systems with the use of chlorine dioxide, such that the separation between individual data records may not be exceeded by more than 5 minutes. The minimum chlorine dioxide concentration which must be present in the drinking water supply distribution system is 0.2 ppm, whereas the NZDS considers the efficacy of chlorine dioxide equivalent to that of chlorine. As such, the minimum concentration of 0.2 ppm is expressed as 0.2 ppm of free available chlorine equivalent (FACE). In addition, NZDS provides ample information pertaining to log credit deactivation scenarios using chlorine dioxide, more than what is presently publically available when considering the European Union, the United Kingdom, Germany, and Australia.

In addition to requiring the continuous monitoring of chlorine dioxide, protozoal compliance monitoring requires that sampling occur at a site where the adequacy of the residual present and the minimum disinfection contact time can be clearly demonstrated. Additional monitoring requirements specify that the flow and water temperature are continually measured.

These regulations also provide sampling protocols for both chlorite and chlorate. That is, NZDS requires sampling be collected in plastic containers for both species. Chlorite sampling must be taken throughout the distribution zone, whereas chlorate should be taken at both the exit of the treatment plant and throughout the distribution zone. As of July 2005, the refereed method for analysis of both ions is EPA Method 300.0 which employs ion chromatography and therefore samples must be sent to a commercial lab for analysis.

Other than the refereed method, alternative methods noted for the detection of chlorite include: amperometric titration (Standard Methods 4500-ClO_2 D); DPD titration (Standard Methods 4500-ClO_2 E); polarography; specific ion electrodes (for chlorite) and flow injection analysis. For continuous monitoring compliance, the only legitimately acceptable method would be via use of specific ion electrodes.

The abundance of previously noted methods for chlorite detection is a stark contrast to a refereed method for the detection of chlorine dioxide. The NZDS state that due to the absence of a MAV for chlorine dioxide, and thus the unknown degree of sensitivity, no analytical method is adopted. However, as no alternative recommended methods are available, the NZDS does highlight other methods; specifically, the amperometric method (Standard Methods 4500-ClO2 C), the DPD method (Standard Methods 4500-ClO2 D), and the chlorophenol red method.

These standards also point to a common flaw exhibited by not only many simple test kit methods but also the approach of some drinking water regulations. This flaw is that some methods measure chlorine dioxide as a chlorine equivalent, and regulations are at times vague to such differentiation. Thus to abide by regulations, operators must be aware of this and properly convey the correct units. This conversion of data expressed as chlorine dioxide in units of milligrams of chlorine per litre to chlorine dioxide expressed as milligrams of chlorine dioxide per litre is present in equation (28).

$$\frac{mg}{L} Cl_2 \Big/ 2.6 = mg\, ClO_2 \Big/ L \tag{28}$$

Equation (28) presents the theoretical translation of chlorine dioxide in terms of a 100% oxidative capacity conversion, which may not necessarily be the case. The

predicament of knowing how the chlorine dioxide concentration expressed as a chlorine concentration was determined, provides a strong rational for ensuring that all the subsequent variables are expressed in units of their own weight per volume (or molarity), rather than that of an equivalent weight of chlorine per volume.

4.5 The World Health Organization (WHO)

It was not until 1993 that the WHO's Guidelines for Drinking-water Quality began to include chlorite as a monitored parameter. At that time, it included a provisional guideline of 0.2 ppm for chlorite, and no mention of chlorate (due to lack of data), and chlorine dioxide (due to its rapid decomposition). Currently, the WHO does not regulate chlorine dioxide dosage concentrations, but provides provisional guidelines for both chlorite and chlorate concentrations at 0.7 ppm (World Health Organization (WHO), 2008). The WHO deems these values as provisional because the use of chlorine dioxide may result in these values being exceeded, and the difficulty in meeting these rulings does not justify failure to compromise. No provisional guideline is set for chlorine dioxide due to its rapid decomposition, although the WHO notes a typical conversion of 60-70% chlorine dioxide to chlorite is expected. It is the relatively low provisional guideline for chlorite which acts to protect against the potential toxicity of chlorine dioxide.

The WHO estimates a tolerable daily intake (TDI) for chlorite be 30 μg/kg of body weight based on a no observable adverse effect level (NOAEL) of 2.9 mg/kg body weight per day. The NOAEL originates from a two-generation study in rats, based on a decreased brain weight in the F_1 and F_2 generations and altered liver weights in the

second generation. The result is an uncertainty factor of 100 (World Health Organization (WHO), 2008). The WHO allocates 80% of the TDI to water. As such, the provisional guideline for chlorite at 0.7 ppm is presented as equation (29).

$$\frac{2.9\,{}^{mg}/_{kg}\,(\text{body weight per day}) \bullet 60\text{kg(body mass)} \bullet 0.8}{2l/day(\text{consumption rate}) \bullet 100(\text{safety factor})} = 0.696\,ppm \qquad (29)$$

The WHO sets a TDI of 30 μg/mg for chlorate, based upon a NOAEL of 30 mg/kg. This NOAEL is drawn from a 90-day study in rats in which thyroid gland colloid depletion was observed at the next higher dose, resulting in an uncertainty factor of 1000 (World Health Organization (WHO), 2008). The calculated parameter using the data available is presented as equation (30).

$$\frac{30\,{}^{mg}/_{kg}\,(\text{body weight per day}) \bullet 60\text{kg(body mass)} \bullet 0.8}{2l/day(\text{consumption rate}) \bullet 1000(\text{safety factor})} = 0.720\,ppm \qquad (30)$$

It is unclear whether the WHO provides or suggests specific monitoring methods for compliance with their standards. The current Guidelines for Drinking-water Quality do not provide such information, rather focusing entirely on standards and the inherent justification for those parameters.

Chapter 5: Improving the Accuracy of N,N-Diethyl-p-phenylenediamine (DPD)

Although some established authors, such as Gates, Ziglio, Ozekin and the EPA do not advocate the continued use of DPD for the measurement of chlorite or chlorine dioxide concentrations, its use is still prevalent throughout North America and Europe. While this is likely due to the low cost of reagents and relative simplicity in application,

the transition to commercial adoption as the primary test for FAC to chlorine dioxide is aided by the provision of easily administered test kits. Such tests kits, offered by various manufacturers, remove any need for understanding the underlying chemistry involved, and individually vary in their methods; thus limiting the potential for reproducibility.

In contrast, as the development of oxychlorine detection instrumentation continues to improve in accuracy and precision, originally accepted methods which were considered interference free may necessarily not be the case. Such large scale advocacy for the use of DPD is conceivably due to this method being the original method designed for chlorine dioxide detection (Palin, 1957), the production of profitable test kits and handheld testing computers, and the establishment of a diverse knowledge base. These have all been influential in justifying organizations such as the EPA and standards such as the NZDS to reference to the DPD method without being proponents of its continued use. It is important to note that a single method to provide accurate results for any circumstance concerning source waters has not been developed at this point. As such, determining the appropriate method for a given water source is a crucial decision when examining chlorine dioxide in portable waters.

5.1 An Introduction to DPD

Chapter 1 presented the history of the DPD method, which was originally developed for the detection of FAC, as well as combined chlorine (Palin, 1957). At a later point, this method was adapted for measuring chlorine dioxide (Palin, 1975).

Upon reaction with an oxidant, DPD will form a pink colour, with quantifiable absorbencies considered to be the doublet peaks at 515 and 555 nm. Most methods

which employ DPD measure its absorbance at 515 nm, although, measurements can also be performed at 555 nm; it is at the researchers' discretion (Hirayama, et al., 2000). Both the structure of DPD and the generalized equation of its oxidation are presented in Figure 9.

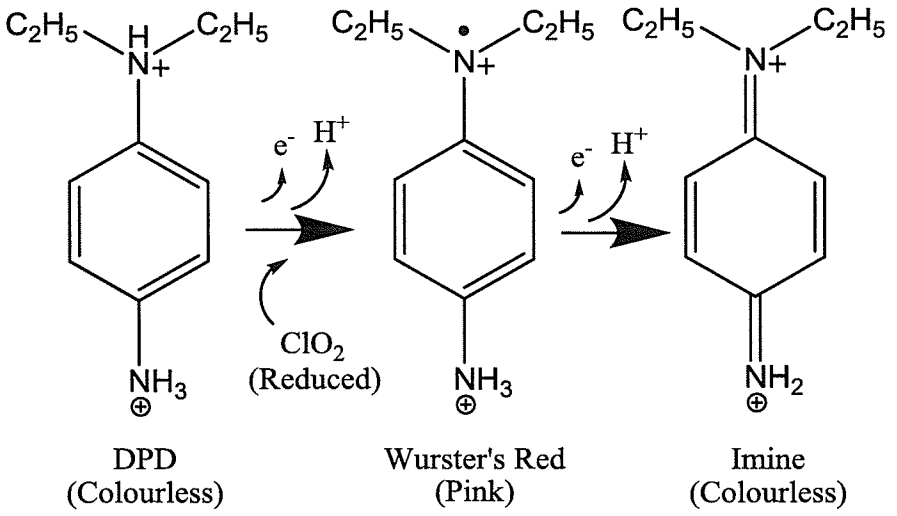


Figure 9: The generalized equation to the oxidation of DPD to the Wurster's dye (pink) quantifiable product.

While commercial and standard methods employing DPD have been developed to estimate the residual concentrations of chlorine dioxide and free available chlorine - due to its ease of use, low-cost and rapid quantification - literature has also advised against possible interferences (APHA, Moberg and Karlberg, 2000) and potentially misleading results (Gordon, 2000, Gordon, 1999).

Chlorine dioxide DPD test kits are typically based upon the same chemistry employed in the EPA accepted Standard Method 4500-ClO_2 D for chlorine dioxide. As such, they are susceptible to many interferences due to manganese (II), chlorine, hypochlorite, and other possible oxidative species.

Of these potentially interfering species, Standard Method 4500-ClO_2 D masks FAC with the addition of the amino acid glycine. Measuring mixtures of FAC (HOCl and OCl^-) and chlorine dioxide using DPD may lead to overestimation of chlorine dioxide concentration. This is important to consider, as systems which make use of both chlorine dioxide and chlorine and systems which exhibit poor generator performance may experience error in analysis when using DPD if the masking agent is not 100% effective.

5.2 The Chemistry of DPD

Figure 10 depicts the possible oxidation mechanisms of DPD by chlorine dioxide. Under most circumstances, DPD is oxidized to form two compounds: Wurster's dye, and an colourless imine compound.

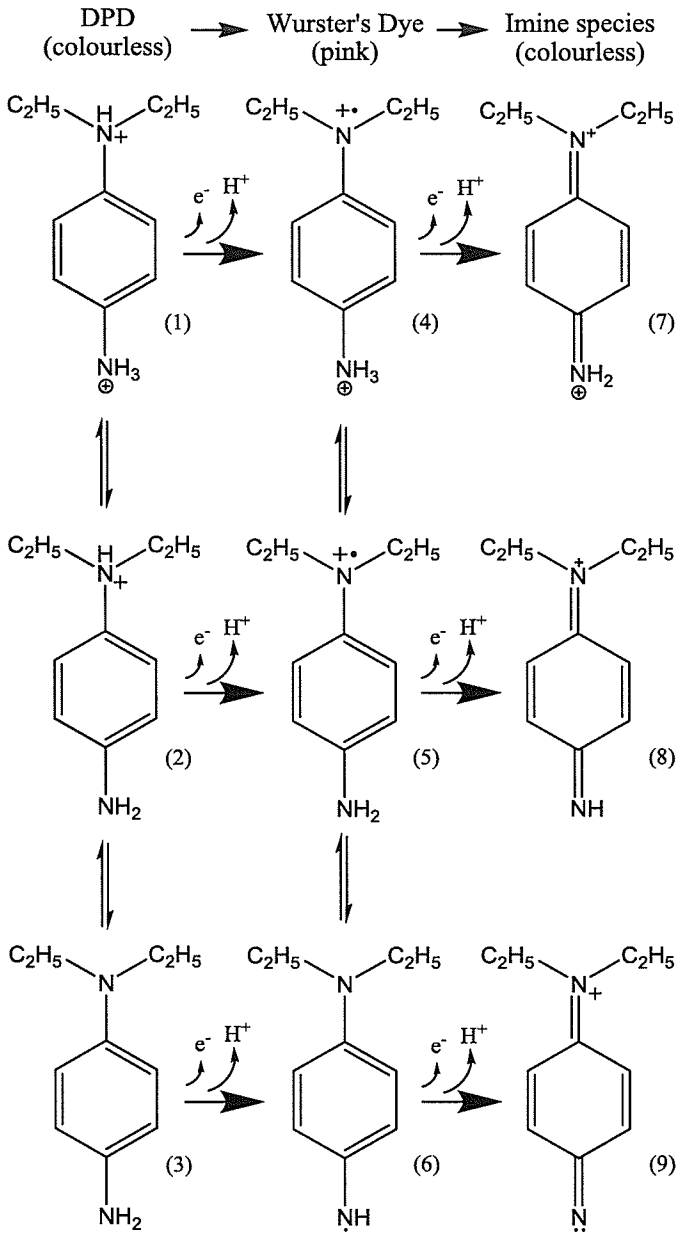


Figure 10: Oxidation pathway of DPD to Wurster's dye and its imine complex, mechanism adapted (Moore, et al., 1984).

Compounds 1, 2 and 3 depicted in Figure 10 represent the initial colourless DPD reagent prior to oxidation in various protonated forms, whereas compounds 4, 5, and 6 are species of Wurster's dye. As any formation of the colourless imine species (compounds 7, 8, and 9 in Figure 10) are not reversible, this marks a fundamental

problem associated with the use of DPD. Furthermore, these compounds are not formed equally and their yields vary given differing conditions. The adapted method for chlorine dioxide detection utilizes a phosphate buffer which buffers the systems pH within the 7.2 range to eliminate the potential interference of varying pH and subsequent error in analysis. For example, at a pH around 7, the semiquinoid cationic species, Wurster's dye, is present in high yields (represented as structures 4, 5 and 6 depicted in Figure 10). It is this species which forms the bright pink colour commonly associated with DPD, and although it is a relatively stable free-radical, may be further oxidized to the colourless imine and is not reversible. As such, high oxidant concentrations force the production of the imine and cause the resultant reaction to fade in colour.

5.3 Recommendations Regarding the Continued Use of DPD

Use of DPD for low-level oxidant measuring is chemically problematic as the rapidly formed quantitative Wurster's dye may be interpreted as an intermediate product, destined to fade to the imine. The fading of the intermediate is considered relatively slow in comparison to the initial formation of colour because the development and the subsequent absorbance at 515 nm only require a few seconds to achieve completion. The transition from coloured intermediate to colourless end product dictates that spectrophotometric analysis must be completed promptly after initial reagent mixing. Conversely, very high oxidant concentrations resulting in little colour being present may be interpreted by an operator as having very little oxidant present. Furthermore, spectrophotometric methods for low level chlorine dioxide detection can be problematic if the DPD protocol relies upon the combination of interference masks, the formation of a

coloured intermediate and the establishment, as well as reliance of calibration data correlating absorbencies to residual values. Moreover, spectrophotometry has the potential to be sensitive to temperature changes that can affect absorption readings which is critical considering that the natural variance of source waters may retain sufficient oxidative capacity to also promote reduction of DPD. As such, the resulting application of the DPD protocol is under much debate. Furthermore, the low oxidation reduction potential (ORP) of DPD leaves it susceptible to a high degree of interference from unintended oxidizing reactants such as common oxychlorine compounds (chlorites, hypochlorites, monochloramines, etc.) and metal ions (iron, manganese, copper and permanganate). Theoretically, by establishing DPD spectrophotometric calibration data (dose vs. response) these interferences could be minimized through the development of an internal standard to minimize or eliminate matrix effects, though such a method may not be deemed suitable for field analysis.

5.4 Investigations of the Calibration for the Standard DPD Chlorine Dioxide Method

Studies concerning the validity of calibrating in accordance with Standard Method 4500-ClO_2 D were investigated. Given the chemical instability of oxidized DPD and the latent formation of the imine product, such a scenario calls for an evaluation of the model of calibration used in the Standard Method. This method cites that as an alternative to titrating with DPD, the analyst may opt for calibrating a colourimeter using standardized potassium permanganate ($KMnO_4$) solutions, as directed in Standard Method 4500-Cl.G.4a (APHA, 2005). The result is a solution where one milliliter is the equivalent of 1 ppm Cl_2, and the appropriate dilutions are made to achieve the desired calibration range.

The potassium permanganate effectively acts as a chlorine dioxide surrogate for the construction of calibration data and the subsequent measurement of samples, providing results as per-weight equivalents of chlorine (ppm Cl_2).

Equation (31) demonstrates the permanganate half reaction which occur to reduce DPD to Wurster's red as illustrated in Figure 10. Notably as the permanganate ion is a strong oxidant, both Wurster's red and the colourless imine complex are expected to be a product of this oxidation. The manganese(II) ion is expected to be the sole reduction product for any of the oxidized species in Figure 10, given that the manganese(II) ion, equation (31), is colourless and the most thermodynamically stable ion of manganese. No precipitate is observed as the Wurster's red transitions to the colourless imine, which draws the conclusion that the redox conditions are favorable to manganese(II) rather than the insoluble MnO_2 complex.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad (31)$$

5.5 Spectrophotometric Agents Alternative to DPD for Potential Operator Use

5.5.1 Use of N,N,N',N'-Tetramethyl-p-phenylenediamine (TMPD) and Cerium(IV) for Detection of Chlorine Dioxide

TMPD, also commonly known as Wurster's blue, was discovered in 1879, and undergoes a one electron oxidation of tetramethyl-phenylendiamine to form a dark blue cation. Use of TMPD in exchange for DPD is hypothesized to provide superior oxidization specificity as well as colour stabilization; both shortcomings of the current spectrophotometric DPD protocol. This hypothesis is rooted in the differing molecular structure, as TMPD is symmetrical, having an additional tertiary amine substituent, and

thus not only providing an increase in electron density, but also potentially being less reactive to hypochlorous acid. As such, investigation to the application of TMPD within chlorine dioxide detection system appears to be well suited. As with DPD, the mechanism for the oxidization of TMPD relies upon the loss of an electron forming a radical cation and giving rise to a bluish hue, as opposed to the classical pink colour associated with DPD.

TMPD has been traditionally used as either an oxidant or acid-base indicator, though it is only slightly soluble in water. TMPD provides three wavelengths at which a recorded absorbance may be observed upon formation of Wurster's blue, namely at 328, 564 and 612 nm.

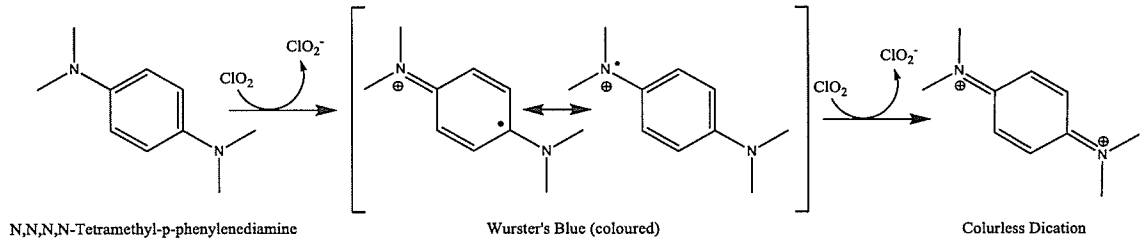


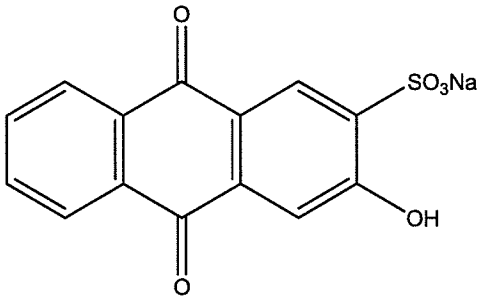
Figure 11: Reduction of TMPD to Wurster's blue, and further reduction to the colourless dication.

The colour development originating from the two para-tertiary amine groups' di-cations in the TMPD molecule is hypothesized to provide greater sensitivity when compared to the tertiary amine group's mono-cation present in DPD. When comparing DPD to TMPD, the formation of Wurster's Blue is based solely on the transfer of electrons, whereas DPD requires the loss of both an electron and proton. This difference provides for the hypothesis that TMPD would be less influenced by due to the lack of proton dependence.

Incorporation of a small amount of cerium has been shown to provide increased sensitivity to TMPD spectrophotometric reactions; as such the addition of cerium in this method is also investigated (Mori, et al., 1997). The use of DPD for spectrophotometric residual testing is common in water treatment throughout the Manitoba yet similar protocols involving TMPD are largely unknown. This is possibly due to the ubiquitous relationship DPD has established in the detection of oxidants by eclipsing the use of similar molecules for detection and the prevalent use of DPD for measuring free and total chlorine (as well as monochloramine) throughout the Province.

5.5.2 Use of 1,2-dihydroxyanthraquinone-3-sulfonate (Alizarin Red S) for the Detection of Residual Chlorine Dioxide in the Presence of Chlorite as an Interference

Alizarin red S (ARS) is a water soluble anthraquinone, primarily used in the dye industry, as well as an acid base indicator (Figure 12). Between the pH range of 3.5 to 6.5 the colour ranges from yellow to red, however given a pH range of 9.4 to 12 the colour ranges from orange to violet (Sabnis, 2007). Applications for ARS range from use as a calcific deposition indicator, or fluoride detection in potable waters, to the cyclical voltamic detection of chlorine dioxide in the ppb range (Quentel, et al., 1994). ARS is commonly used a spectrophotometric reagent for the analytical detection of fluoride based on either complexometric or signaling ligand exchange systems.



Alizarin Red S

Figure 12: The molecular structure of ARS.

Voltamic detection is based on the pre-concentration of ARS on a mercury drop electrode in which the observed stripping peaks are correlated to a chlorine dioxide concentration. Such methods provide increased sensitivity and selectivity for chlorine dioxide (Quentel, et al., 1994). This procedure was also demonstrated using ARS in combination with an indigo carmine dye.

5.5.3 Use of Copper(II) Sulfate for the Residual Detection and Discrimination of Chlorite from Chlorate

The use of copper sulfate for the detection of chlorite was noted by Morodant and Duval, who observed the differentiation of the reaction of copper sulfate producing a green colour with chlorite, yet not with chlorate (Morandat and Duval, 1950). Such differentiation serves as the basis for further development of a potential stereoscopic method for the selective detection of chlorite without interference from chlorate. Ideally, chlorine dioxide is be removed by bubbling an inert gas through the sample followed by the application of a potential differentiation method.

Efforts to find similar work in published literature were unsuccessful, and furthermore, research pertaining to chlorites of copper does not provide any reference to the potential selectivity between chlorite and chlorate. As such, the green colour is spectroscopically observed to provide quantification at 387 nm, just within the ultraviolet region. The wide absorbance peak extends between the ultraviolet and visible spectrum, while the observed colour is the sum of the cyan copper sulfate colour provided in the range 700 nm and the peak in the 400 nm range.

5.6 Free Chlorine Masking

As both chlorine and chlorine dioxide may be used in the same system for the purpose of source water disinfection and distribution system management (or from plant generators), the exact analysis proves difficult when presented individually or as a mixture. The Standard Method 4500-ClO_2 D utilizes glycine as an FAC oxidant mask in the presence of chlorine dioxide. The assumption is that glycine reacts with FAC to form

N-monochloro glycine. Alternative masking agents such as oxalic acid, or malonic acid, have also been suggested, although not adopted by Standard Methods (Masschelein and Rice, 1979). Utilizing a masking agent for FAC allows for the measurement of the chlorine dioxide concentration to be selectively analyzed, whereas determining FAC concentration is the product of an arithmetic subtraction of the chlorine dioxide concentration from the total oxidant value. It has been reported however, that chlorine dioxide present within a sample may potentially react with the addition of glycine underestimating the concentration of chlorine dioxide using the DPD method (Gates, et al., 2009). An alternative suggestion would be to purge any chlorine dioxide present in a sample, and subtract the FAC concentration from a total oxidant value, yielding a chlorine dioxide concentration. It is noted that such an alternative is quite time-consuming and requires approximately 30 minutes of gas-purging time, whereas the use of a handheld kitchen beater may also be effective (Hombach, 2008). As such, quantitative determination in the presence of FAC necessitates an adjustment of reagents used, however if chlorite is present in the sample (which is common when using chlorine dioxide), the result of the developed colour may not be solely representative of the analyte under scrutiny.

Many researchers note that glycine is one of several amino acids which are somewhat resistant to chlorine dioxide, and thus provides the differentiation needed for analysis (Tan, et al., 1987, Masschelein and Rice, 1979). The assumption is based upon the relative simplicity that glycine presents: its R-group consists of only a hydrogen atom, leading to a composition which lacks more reactive side chains such as sulfides and aromatic groups, and consequently resists potential oxidation by chlorine dioxide. In

later work Masschelein noted that such a reaction rate would be a product of experimental conditions, is considered slow, and therefore can promote secondary losses of chlorine dioxide (Masschelein, 1984). In contrast, other researchers have shown that chlorine dioxide can substantially react with glycine, potentially obscuring analysis (Taymaz, et al., 1979, Taymaz, et al., 1979). Interestingly, Taymaz and colleagues reported that within one hour at room temperature, in the presence of a five-fold molar excess, 50% of chlorine dioxide had reacted with glycine. Furthermore, using a three-fold molar excess, 35% of the chlorine dioxide had reacted after 80 minutes. Apart from potential reactions and differing views, glycine has a limited shelf life and commonly requires the addition of mercuric (II) chloride as an antiseptic. Further studies regarding the potential of alternative masking agents are described in this manuscript.

5.7 Masking Agents Alternative to Glycine

Several masking agents have been proposed throughout literature although their widespread adoption has been curtailed due to their lack of specificity, as well as deficiency of properly masking FAC. It is important that an ideal mask suppress any reaction of FAC or additional oxychlorine compounds, and that this be accomplished without reacting with either chlorine dioxide or the chromophoric compound. As part of the initial development of the use of CPR for chlorine dioxide detection, Fletcher also investigated the use of alternative masking agents. These were glycine, ammonium sulphate and sodium cyclamate. The results of Fletcher's work agree with results reported by Taymaz, that glycine is ill suited as a free available chlorine masking agent as

a 50% loss of a 0.4 ppm solution of chlorine dioxide was recorded after a period of 30 minutes at a pH of 7 (Fletcher and Hemmings, 1985).

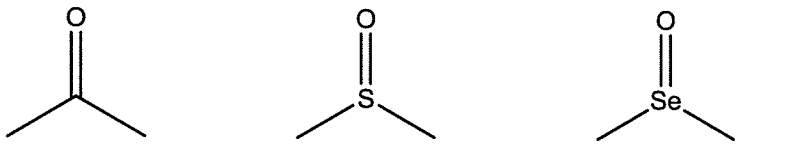
Ammonium sulphate was observed to react directly with FAC at a pH of 7 to form monochloramine. At small concentrations, Fletcher observed that ammonium sulphate did not react with chlorine dioxide, and thus partially satisfied the criteria as an ideal masking agent. Though chlorine dioxide was observed to not react with ammonium sulphate, the monochloramine produced through the masking process may potentially react with chlorine dioxide, and thus the possibility of using it as an alternative masking agent was abandoned.

Fletcher describes the use of sodium cyclamate as an effective FAC masking agent, which, when compared to the original development of the CPR method provides superior results including masking chlorine interferences up to 20 ppm. Unfortunately, Fletcher did not provide any reasoning for selecting these reagents nor was any premise given to explain their effectiveness when compared to each other or other reagents available.

It has been reported that use of acetone has successfully been applied to mask free chlorine, while leaving combined chlorine completely unaffected (Pandey, et al., 1998). Pandey's team suggested that the addition of a very small amount of acetone (1 ml of a 1% solution in water) reacts with FAC to form chloroacetone, a non-oxidizing product. They also investigated the use of sodium cyclamate to mask FAC. Results suggested that the product of the masking reaction still provided enough oxidizing capacity to produce a response from the chromophoric compound chosen for analysis. As such, there existed the need to obtain a FAC masking agent which did not produce an oxidizing product, as

Pandey, Gosain, Sahasrabuddhey and Verna (1998) have suggested using acetone to accomplish this.

Structurally similar to acetone, dimethylsulfoxide (DMSO) has also been suggested as an excellent FAC masking agent by Imaizumi and colleagues. (Imaizumi, et al., 1993). Their results note that with the addition of excess DMSO, the absorbance associated with free chlorine had completely disappeared. Moreover the oxidation of iodide to iodine was totally inhibited. Imaizumi's team found that chlorine dioxide, chlorite, and chlorate concentrations did not react even when co-existing in the presence of excess DMSO in solution, a finding verified by ion chromatography. Furthermore, the use of ion chromatography verified the proposed reaction of reducing chlorine or sodium chlorite to chloride, with the recommendation of following a 1:2 ratio respectively. Such findings are ideal as chloride is known for not interfering with the DPD method of measuring chlorine dioxide. Results concerning the use of DMSO as a masking agent were similar to reduction using sodium thiosulfate (Na_2SO_3). Conclusions suggest that DMSO selectively reduces chlorine, while not interfering with chlorine dioxide. As both acetone and DMSO have shown promise in functioning as effective FAC masking agents, no results in literature pertaining to a similar alternative, dimethyl selenoxide have been found (Figure 13). Selenium is the next logical substitute when following the carbon-sulphur trend. Interestingly, Pandey and colleagues (1998) do not reference Imaizumi's work, and thus the possibility of an effective masking agent structural trend may have been potentially overlooked.



Acetone	Dimethylsulfoxide	Dimethyl selenoxide
C_3H_6O	C_2H_6OS	C_2H_6OSe
Exact Mass: 58.04	Exact Mass: 78.01	Exact Mass: 125.96

Figure 13: Both acetone and DMSO have shown FAC masking characteristics, yet similar results for a selenium substitute have not been found.

Because commercially available sources for dimethyl selenoxide are lacking, efforts to obtain an alternative suitable FAC masking agent proved difficult, and investigations concerning the suitability of di- and tri- ethanolamine were carried out. Their molecule structures are presented in Figure 14.

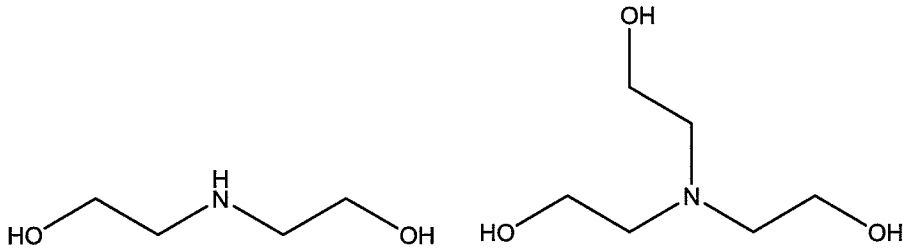


Figure 14: The structures of both DEA and TEA.

5.8 Examination of Using an Alternative FAC Masking: a Mixture of Di- and Tri-Ethanolamine

Both diethanolamine (DEA) and triethanolamine (TEA) have a wide variety of commercial uses which range from applications in cosmetics, foaming agents, or soaps, to uses as a complexometric agent in titration or industrial applications. The use of a mixture of di- and tri- ethanolamine in a mixing ratio of 20:80 (di-/tri-) as a FAC suppressant was reported by Hombach (Hombach, 2009).

Both DEA and TEA have desirable characteristics for use as a masking agent. In particular, they are economical, widely available for commercial use, have extended shelf lives and do not require antiseptic additives to maintain quality.

While both species have active hydroxyl groups (-OH) and have been considered to be a weak base, it was hypothesized that hydroxyl groups of the alcohol could react with FAC. The hydroxyl groups could be replaced with a halogen atom in order to form the resultant haloalkane - in this case, the chlorine from FAC would be the replacement. The haloalkene, is assumed to react slowly with chlorine dioxide, thus allowing a kinetic window of opportunity for possible further masking agent development. Accordingly, this hypothesis provides for a sufficient FAC mask and, given that both compounds are known to exhibit antioxidant characteristics, could potentially resist any reactions between chlorine dioxide and DEA or TEA. These qualities theoretically provide a means of differentiating between FAC and chlorine dioxide, the key criterion of an ideal masking reagent. This hypothesis is tested.

Part 3: Experimental

Chapter 6: General Materials and Methods

The objectives' of this study were to evaluate the DPD protocol for measuring residual levels of chlorine dioxide, specifically it's spectrophotometric calibration procedures, as well as its use of glycine as a FAC masking agent. Additional objectives included establishing possible alternative spectrophotometric reagents platforms which

may lead to further development of possible operator-based field methods for the detection of residual chlorine dioxide and its by-products.

Common to all experimental work was the use of MilliQ water used throughout all experiments (including spectrophotometric banks and dilutions unless otherwise stated). In addition, absorption spectra were recorded using a BioChrom model 2100 UV-VIS spectrophotometer using 1cm Hellma quartz cuvettes when appropriate. A Thermo-Electron model 230A pH meter was used for pH measurements. All time trials were established using the BioChrom time delay software.

Chapter 7: DPD for Chlorine Dioxide Analysis

7.1 Experimental Method for Analysis of Calibration using DPD for Chlorine Dioxide

The effects of reaction time and subsequent absorbance at 515 nm for the calibration of the DPD procedure with standardized potassium permanganate were investigated. The Standard Methods protocol 4500-ClO_2 D 3d (APHA, 2005) outlines procedures for calibration which require formulating all the necessary solutions and then spectrophotometrically measuring to form the appropriate calibration data.

7.2 Materials and Reagents (Analysis of the DPD for Chlorine Dioxide Method Calibration)

All reagents used were obtained from Sigma (St. Louis, MO, USA) unless otherwise noted. Chlorine demand free Milli-Q water (Millipore, Bedford, MA, USA) was used in preparation of all solutions, including the spectrophotometric blanks. All

glassware was thoroughly cleaned and soaked in a 1:1 solution of nitric acid and water for 12 hrs and then rinsed several times with Milli-Q water prior to use. All reagents were used without further purification.

7.2.1 Experimental Method for Use of Diethanolamine and Triethanolamine as an Alternative FAC Mask

The objective was to determine if a mixture of DEA and TEA could effectively suppress FAC in synthetic samples containing only FAC and chlorine dioxide. Calibration and concentration analysis of both FAC and chlorine dioxide were measured as outlined in Standard Methods protocol 4500-ClO_2 D 3d (APHA, 2005) through the use of spectrophotometry . Concentration ranges of 0, 0.25, 0.5 and 1 ppm of oxidant were evaluated; however, of these concentrations, only varying the ratio of chlorine dioxide to chlorine from 0:0 to 100:0 and 0:100 were investigated. The manipulations were designated to provide observations as to the effectiveness of small or large concentrations of oxidant, as well as provide some inclinations as to an appropriate mixture ratio.

As per Standard Methods protocol 4500-ClO_2 D 3d, calculations pertaining to chlorine dioxide, FAC, total available chlorine and chlorite concentrations are based on the recording of five variables, A, B, C, D, and G at multiple stages throughout the method. These variables originate from the initial publication by Palin which applies this method for the analysis of FAC (Palin, 1957). Variables A, B, and C relate to the FAC concentration, D pertains to the total available chlorine, including chlorite content, and G correlates the chlorine dioxide concentration post masking agent addition and mixing.

Standard Methods protocol 4500-ClO_2 D 3d applies glycine as the masking agent (0.0285 mol/L), though reasoning as to how or why such a concentration is recommended

is not provided. A search through literature did not provide sufficient reasoning for such a concentration. Accordingly, this experiment maintained the same molar concentration which was originally applied and subsequently fractioned the DEA to TEA ratio.

In the absence of chlorite, the calculations were as follows:

$$\text{Free Available Chlorine} = A - G \tag{32}$$

$$\text{Total Available Chlorine} = C + 4 \bullet G \tag{33}$$

$$\text{Chlorine Dioxide} = 5G \,(\text{or } 1.9\text{G if expressed as } ClO_2) \tag{34}$$

As chlorite is a key product from the reduction of chlorine dioxide, it is necessary to check for this variable. This method notes that the chlorite is present if reading D is greater than the product of C+4G. If such is the case, chlorite is calculated as equation(35), and the total available chlorine parameter also changes, as in equation(36).

$$\text{Chlorite} = D - (C + 4G) \tag{35}$$

$$\text{Total Available Chlorine} = D \tag{36}$$

Therefore by calculating the FAC, chlorine dioxide, chlorite, and total available chlorine content, and comparing it to similar results with use of a masking agent, the potential for FAC suppression may be observed.

7.2.2 Materials and Reagents (Alternative FAC Mask Experiments)

Materials, reagents and glassware were prepared as previously presented in section 7.2. All reagents were used without further purification. Standardized solutions of hypochlorite and sodium thiosulfate were also purchased from Sigma (St. Louis, MO, USA). Spectrophotometry was carried out as in Chapter 6.

Chlorine dioxide was generated using a bench-top gas train as in Figure 15. This method utilized the addition of a solution of potassium persulfate (0.295 mmol/L) to a solution of sodium chlorate (3.5 mol/L), as presented in equation (37). This method is recommend for research scale synthesis of chlorine dioxide as it produces relatively pure product, but is considered to be slow in terms of reaction rates, product yield and is therefore not favorable from a plant generator standpoint.

$$2ClO_2^- + K_2S_2O_8 \longrightarrow 2ClO_{2(g)} + 2K^+ + 2SO_4^{2-} \quad (37)$$

The round bottom flask reaction vessel was connected to a packed column containing solid sodium chlorite which was connected to the final collection flask. The final collection flask was wrapped in aluminum foil and chilled to minimize photolytic decomposition and to improve adsorption of the gas into solution; respectively. The generated gas was purged from the reaction vessel for approximately 20 minutes, producing a yellow-green solution.

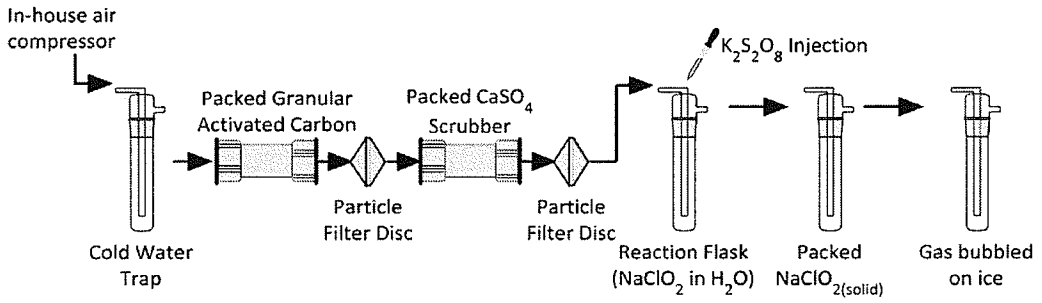


Figure 15: Gas train setup for the generation of chlorine dioxide. The collected gas was bubbled through water, collected, and standardized

This method of generation is reported to be free of residual chlorite, chlorate and other by-products and is capable of being used directly for potable water treatment (Deshwal, 2005, Gates, 1998). The working chlorine dioxide solution was standardized

at 360 nm according to Beer-Lambert's Law using a molar absorptivity constant of 1225 $(mol/L)^{-1}cm^{-1}$ (Masschelein and Rice, 1979) yielding a final concentration in the range of 2 ppm. Solutions were appropriately diluted using a zero-head space syringe and spectrophotometrically standardized daily prior to experimentation.

Chapter 8: Potential Spectrophotometric Chlorine Dioxide Detection Methods Alternative to DPD (Operators Based)

8.1 Alternative Spectrophotometric Methods for Chlorine Dioxide Residual Analysis Research

Spectrophotometric methods alternative to DPD for the detection of chlorine dioxide and chlorite have been explored. Though such research is far from complete, the purpose of these studies was to determine possible candidates for further investigation and exploration. Reaction candidates within the current study examined the results of the relationship between chromophoric agent, chlorine dioxide and chlorite as potential detection systems alternative to DPD. Three possible reagents are presented as an initial detection framework, demonstrating quantitative and relatively non-laborious characteristics providing the intended application ideal for operators.

In the first trial, chlorine dioxide was measured using N,N,N,N′-tetramethyl-p-phenylenediamine (TMPD) in the presence of cerium(IV). This was followed by investigation of whether 1,2-dihydroxyanthraquinone-3-sulfonate (alizarin red S) could be used as a chlorine dioxide colorimetric agent. The final trials sought to determine if the levels of the by-product chlorite could be measured using the introduction of copper(II) sulfate. These trials hypothesized that by measuring a combined residual

(chlorite and chlorate) using standard DPD method, and chlorite using copper(II) sulfate concurrently, one could establish a chlorate concentration based on logical subtraction.

8.1.1 Materials and Reagents of Alternative Spectrophotometric Work

All reagents used were obtained from Sigma (St. Louis, MO, USA) unless otherwise noted. Chlorine demand free Milli-Q water (Millipore, Bedford, MA, USA) was used in preparation of all solutions, including the spectrophotometric blanks. All glassware was cleaned and then soaked in nitric acid water bath (1:1) (12 hrs) and then rinsed several times with Milli-Q water prior to use. All reagents were used without further purification. Solutions of chlorite were standardized as published by Philippi (Philippi, et al., 2007). Spectrophotometry was carried out as in Chapter 6. Chlorine dioxide was generated as in Section 7.2.2.

8.1.2 Experimental Work for Chlorine Dioxide Residual Detection using TMPD and Cerium(IV)

TMPD was substituted for DPD following the procedures outlined in Standard Methods protocol 4500-ClO_2 D 3d. Other changes were the addition of 4.104 mg TMPD just prior to final dilution in a 25 ml volumetric flask containing a 7.5 ml of a pH 5.5 acetate buffer (0.1 mol/L), 7.5 ml of a certified stock of $Ce(SO_4)$ (0.001 mol/L) solution, and the appropriate amount of the working chlorine dioxide solution. Absorbencies were immediately recorded post-mixing at 328, 563 and 612 nm in a 1 cm pathlength quartz cuvette. Blanks controls contained no chlorine dioxide.

8.1.3 Experimental for the Detection Chlorine Dioxide Residuals using Alizarin Red with Chlorite as an Interference

In this study, ARS was used to probe for a spectrophotometric quantitative reaction with chlorine dioxide, or with chlorine dioxide in the presence of typical chlorite concentrations at 516 nm.

A buffered stock solution of 0.002 mol/L alizarin red S was prepared by mixing 0.6845 g of solid alizarin red S, 20 mg of sodium phosphate (tri-basic), 48.5 g of ammonium chloride and 1.78 mL of concentrated ammonium hydroxide. All reagents were diluted to 1 L, stirred overnight and filtered using Whitman No. 1 filter paper to remove any un-dissolved materials. The final pH of the red stock alizarin red S solution was 7.73. Standardization of chlorite solutions was spectrophotometrically carried out using a molar absorptivity constant of 154.0 L mol^{-1} cm^{-1} at 260 nm using sodium chlorite in Milli-Q (Philippi, et al., 2007). Again, blank controls contained no chlorine dioxide or chlorite.

8.1.4 Experimental for the Measurements of Chlorite Concentrations with Copper(II) Sulfate

Investigations concerning the practicality of using a copper sulfate system to detect chlorite concentrations in waters disinfected with chlorine dioxide were also examined. Such a system theoretically could provide an alternative means to detect chlorite either spectrophotometrically, or with further research, via cyclic voltammetry using a mercury drop electrode similar to that of Quentel's work (1994).Stock solutions of copper sulfate (0.00125 mol/L) and sodium chlorite (0.00025 mol/L) were appropriately diluted in Milli-Q water and buffered using an acetic acid acetate buffer to

pH 6.5. Working solutions consisted of mixing varying amounts of both stock solutions and diluting with Milli-Q water. Absorbencies at 387 nm were recorded after approximately 5 minutes post mixing.

Part 4: Results and Discussion

Chapter 9: On the Use of DPD for Residual Chlorine Dioxide Detection

9.1 Observations Using Potassium Permanganate for DPD Calibration

Analyses of the use of potassium permanganate as a calibration standard for chlorine dioxide measurements are presented on Figure 16. Specific efforts to measure the temporal sensitivity of utilizing potassium permanganate as a DPD calibration standard are presented.

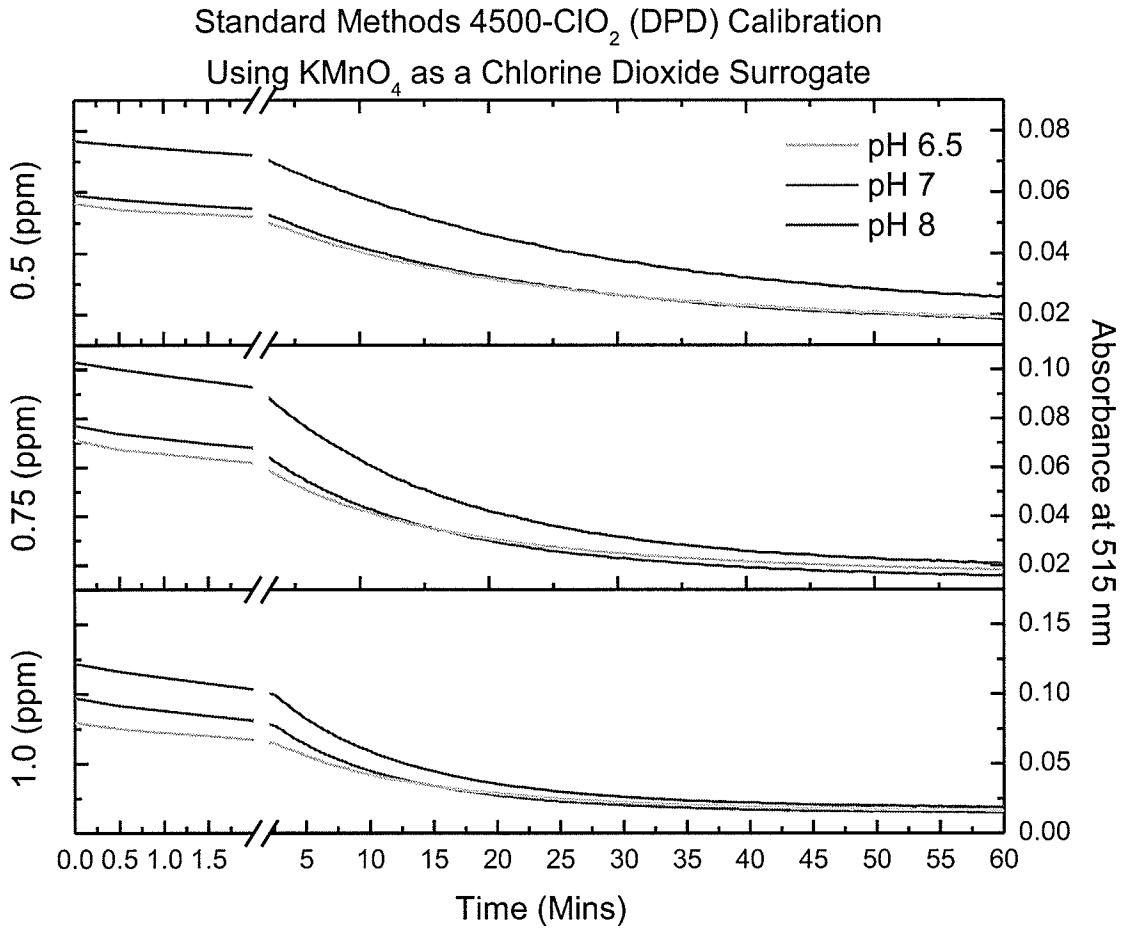


Figure 16: Results of using $KMnO_4$ as a chlorine dioxide surrogate for DPD calibration.

Figure 16 illustrates differing results given at three different pH's; the observed absorbencies increased with an increase to the pH. As per Figure 10, most commercial methods employ a buffer to eliminate pH effects, through when the pH is slightly altered, as seen in Figure 16, a significant change in absorption can be observed. Consequently, if changes in commercial reagent preparations occur, or even if manufacturers select alternative buffering reagents (which could vary around an approximated pH), comparison between DPD tests can be either under- or over- estimated based solely on

the system's pH. Figure 16 exemplifies the need for accurate pH buffering, reproducible every time and indifferent of manufacturer test kit design.

In addition to the affects of pH, Figure 16 highlights the increasing loss in absorbency with higher oxidant concentrations applied causing the subsequent calibration curve to be susceptible to variance. The observation of low stability in the coloured reaction product (as described in Section 5.2) suggests that at high concentrations of the oxidizing species, the colour observed at 515 nm may be radically reduced within a time period of less than 15 minutes. An examination of the fluctuations in pH ranges is presented in Table 11. This Table highlights an increasing rate of change in absorbance. For the first two minutes from initial mixing, a change in absorbance of between approximately 10-20% can be observed. The concentration of 0.025 ppm is not included in Figure 16 as it exhibits little change in comparison.

Table 11: The rate of change for the calibration of DPD using $KMnO_4$ at 0.025, 0.5, 0.75, and 1.0 ppm.

		Absorbance			Change in Absorbance		
	Time	*pH 6.5*	*pH 7*	*pH 8*	*pH 6.5*	*pH 7*	*pH 8*
0.025 ppm	0:00:00	0.005	0.0031	0.0124	-	-	-
	0:00:30	0.0055	0.0034	0.013	9%	9%	5%
	0:01:00	0.0059	0.0035	0.0131	15%	11%	5%
	0:01:30	0.006	0.0037	0.0133	17%	16%	7%
	0:02:00	0.0058	0.0038	0.0134	14%	18%	7%
	0:10:00	0.0061	0.0035	0.0138	18%	11%	10%
	0:20:00	0.0057	0.0038	0.0139	12%	18%	11%
	0:30:00	0.0057	0.0038	0.0142	12%	18%	13%
	1:00:00	0.0054	0.0039	0.0142	7%	21%	13%
0.5 ppm	0:00:00	0.0767	0.059	0.0767	-	-	-
	0:00:30	0.0753	0.0575	0.0753	-2%	-3%	-2%
	0:01:00	0.0742	0.0564	0.0742	-3%	-5%	-3%
	0:01:30	0.0731	0.0554	0.0731	-5%	-6%	-5%
	0:02:00	0.072	0.0546	0.072	-7%	-8%	-7%
	0:10:00	0.0584	0.042	0.0584	-31%	-40%	-31%
	0:20:00	0.046	0.0323	0.046	-67%	-83%	-67%
	0:30:00	0.0377	0.0263	0.0377	-103%	-124%	-103%
	1:00:00	0.026	0.0184	0.026	-195%	-221%	-195%
0.75 ppm	0:00:00	0.1031	0.0771	0.1031	-	-	-
	0:00:30	0.1	0.0737	0.1	-3%	-5%	-3%
	0:01:00	0.0975	0.0716	0.0975	-6%	-8%	-6%
	0:01:30	0.0951	0.0696	0.0951	-8%	-11%	-8%
	0:02:00	0.0928	0.0679	0.0928	-11%	-14%	-11%
	0:10:00	0.0425	0.0444	0.0818	-143%	-74%	-26%
	0:20:00	0.0308	0.03	0.0421	-235%	-157%	-145%
	0:30:00	0.0249	0.0228	0.0316	-314%	-238%	-226%
	1:00:00	0.018	0.0158	0.0206	-473%	-388%	-400%
1.00 ppm	0:00:00	0.0796	0.0972	0.1218	-	-	-
	0:00:30	0.0749	0.0916	0.1161	-6%	-6%	-5%
	0:01:00	0.0722	0.0879	0.1116	-10%	-11%	-9%
	0:01:30	0.0699	0.0842	0.1075	-14%	-15%	-13%
	0:02:00	0.0671	0.0809	0.1035	-19%	-20%	-18%
	0:10:00	0.042	0.0448	0.0588	-90%	-117%	-107%
	0:20:00	0.0287	0.0272	0.0355	-177%	-257%	-243%
	0:30:00	0.0223	0.0202	0.0261	-257%	-381%	-367%
	1:00:00	0.0164	0.015	0.0188	-385%	-548%	-548%

9.2 Calibration of the DPD Method Using Potassium Permanganate

Figure 16 illustrates that the standard potassium permanganate calibration method provides a large degree of variance. Table 11 further demonstrates that the changes in

absorbance, which can be interpreted as changes in reaction rates, appears to effect what absorbency is measured at the given concentration and pH. From observations, one could potentially model this data to construct a predicative theory of absorbance reduction per unit of time. Though this may be plausible, such a model would likely differ among treatment plants as operators typically construct calibration data using their in-house water and consequently the variation in chemical makeup (and possible interferences), temperature and pH would likely create a large degree of divergence (including seasonal) from such a model.

Table 11 highlights the magnitude of possible error as the pH and oxidant concentration increase. Initial small concentrations (0.25 ppm) of the oxidant do not appear to substantially vary, although as the concentrations are increased to 1 ppm, a rapid change in absorbance is observed. Such degree of variance is notably a large source of error when constructing calibration data and operators need be aware that timing is an important factor in this method.

An ideal calibration would initiate a stable absorbance which could be maintained over a satisfactory period of time for measurement. From the observed data such stability is not available, given that within five minutes of initial reagent mixing a significant change in absorbance occurs, and that more than one fourth of the initial absorbance is lost after five minutes. Possible consequent results would be the inaccurate calibration of absorbance to concentration calibration data and the subsequent measurements made against such calibration. This would subsequently lead to the possible underestimation of residual concentrations when analyzing and subsequent infringement upon Regulatory standards. Such calibration could be improved by an internal additions protocol for

spectrophotometric calibration. Such a method "spikes" a sample with a known amount of a particular analyte, where the ratio of the spiked analyte response is compared to the unknown sample and used to calculate concentrations. This method effectively negates matrix effects, yet assumes a linear response between analyte response and concentration. Though such a method may yield value from a laboratory setting, actual methods using raw and/or untreated waters will undoubtedly contain a multitude of organic or inorganic species which are may also absorb in the measurement wavelength, and not necessarily provide a linear response; thus interfering with such a detection method. Overall results presented in Figure 16 and Table 11 indicate that the calibration of the DPD protocol using potassium permanganate standards is not advisable due to rapid changes in absorbance, thus misrepresenting an accurate calibration between analyte and absorbance.

Chapter 10: An Alternative FAC Mask for Chlorine Dioxide DPD Analysis

10.1 Observations on the Use of Di- and Tri- ethanolamine (DEA and TEA) as an Alternative Masking Agent

As a reference for determining the FAC and chlorine dioxide content throughout this experiment, the need to calibrate for DPD was required. Sources of error as those previously discussed in Chapter 9 were not evaluated through this experiment. The results of calibrating using increasing dosages of potassium permanganate as a chlorine surrogate are presented in Figure 17. The calibration range was from 0.05 to 4 ppm, with the stock concentration standardized to provide 1 ppm of chlorine per milliliter of potassium permanganate stock solution.

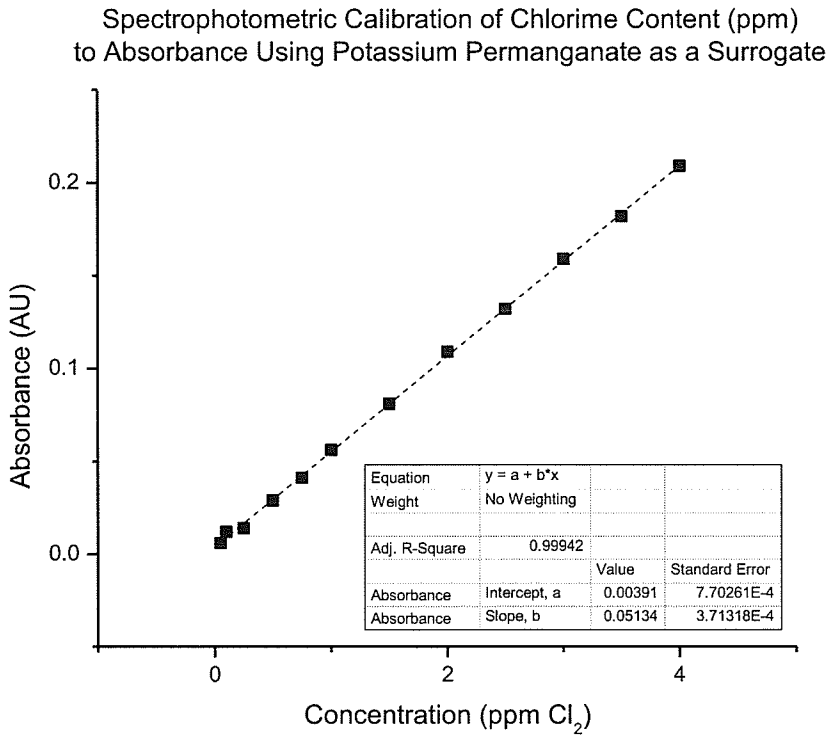


Figure 17: Spectroscopic calibration of a surrogate oxidant to provide a correlation between chlorine content and absorbance,

Table 12 presents the results of varying the oxidant volume, as well as the chlorine dioxide to chlorite ratio and using glycine as a FAC mask. No DEA, TEA or glycine masking agents are introduced in the experiments in Table 12, all raw data and recorded values for readings A,B, C, D, and G can be found in Appendix B. Only the varying ratios and resultant FAC, chlorine dioxide, total available chlorine and chlorite concentrations are presented.

Table 12: Estimation of chlorine dioxide and chlorine content using DPD and glycine masking.

Oxidant Volume (ppm Cl_2)	% ClO_2	% OCl^-	*FAC (ppm Cl_2)*	*Chlorine Dioxide (ppm Cl_2)*	*Total Available Cl_2 (ppm)*	*Chlorite (ppm Cl_2)*
0	0	0	0.0001	0.0153	0.0155	0
0.25	0	100	-0.0001	0.0193	0.0194	0
0.5	0	100	0.0014	0.0165	0.0179	0
0.75	0	100	0.0002	0.0260	0.0260	0
1	0	100	0.0021	0.0193	0.0215	0
0.25	25	75	0.0000	0.0201	0.0201	0
0.5	25	75	0.0010	0.0206	0.0216	0
0.75	25	75	0.0010	0.0255	0.0264	0
1	25	75	0.0019	0.0252	0.0271	0
0.25	50	50	0.0004	0.0201	0.0205	0
0.5	50	50	0.0007	0.0247	0.0254	0
0.75	50	50	0.0010	0.0298	0.0308	0
1	50	50	0.0011	0.0329	0.0339	0
0.25	75	25	0.0002	0.0227	0.0227	0
0.5	75	25	0.0004	0.0280	0.0283	0
0.75	75	25	0.0006	0.0344	0.0347	0
1	75	25	0.0005	0.0410	0.0414	0
0.25	100	0	-0.0002	0.0255	0.0253	0
0.5	100	0	0.0003	0.0326	0.0328	0
0.75	100	0	0.0004	0.0400	0.0403	0
1	100	0	0.0001	0.0487	0.0486	0

Results from substituting glycine in the procedure at the same molarity are presented. The variance in substitution was investigated using a ratio of 0% DEA: 100% TEA. The results are presented in the subsequent tables, Table 14, Table 15, and Table 16. A summary of these results is shown in Figure 18, noting the differences observed for FAC and chlorine dioxide with and without the mask applied.

Table 13: Results of the potential use of 0%DEA:100%TEA for FAC suppression.

Oxidant Volume (ppm Cl_2)	% DEA	% TEA	% ClO_2	% OCl^-	*FAC (ppm Cl_2)*	*Chlorine Dioxide (ppm Cl_2)*	*Total Available Cl_2 (ppm)*	*Chlorite (ppm Cl_2)*
0	0	100	0	0	0.0000	0.0168	0.0168	0.0000
0.25	0	100	0	100	0.0007	0.0163	0.0170	0.0000
0.5	0	100	0	100	0.0013	0.0163	0.0177	0.0000
0.75	0	100	0	100	0.0020	0.0165	0.0186	0.0000
1	0	100	0	100	0.0026	0.0165	0.0193	0.0000
0.25	0	100	25	75	0.0008	0.0165	0.0174	0.0000
0.5	0	100	25	75	0.0015	0.0165	0.0183	0.0000
0.75	0	100	25	75	0.0027	0.0165	0.0193	0.0000
1	0	100	25	75	0.0035	0.0163	0.0199	0.0000
0.25	0	100	50	50	0.0010	0.0168	0.0179	0.0000
0.5	0	100	50	50	0.0020	0.0173	0.0195	0.0000
0.75	0	100	50	50	0.0033	0.0176	0.0207	0.0000
1	0	100	50	50	0.0044	0.0176	0.0219	0.0000
0.25	0	100	75	25	0.0010	0.0183	0.0193	0.0000
0.5	0	100	75	25	0.0024	0.0155	0.0181	0.0000
0.75	0	100	75	25	0.0036	0.0158	0.0192	0.0000
1	0	100	75	25	0.0054	0.0155	0.0227	0.0018
0.25	0	100	100	0	0.0016	0.0158	0.0174	0.0000
0.5	0	100	100	0	0.0034	0.0153	0.0185	0.0000
0.75	0	100	100	0	0.0050	0.0158	0.0230	0.0024
1	0	100	100	0	0.0063	0.0160	0.0275	0.0052

Table 14: Results of the potential use of 25%DEA:75%TEA for FAC suppression.

Oxidant Volume (ppm Cl_2)	% DEA	% TEA	% ClO_2	% OCl^-	*FAC (ppm Cl_2)*	*Chlorine Dioxide (ppm Cl_2)*	*Total Available Cl_2 (ppm)*	*Chlorite (ppm Cl_2)*
0	25	75	0	0	0.0000	0.0155	0.0155	0.0000
0.25	25	75	0	100	0.0008	0.0153	0.0161	0.0000
0.5	25	75	0	100	0.0014	0.0158	0.0172	0.0000
0.75	25	75	0	100	0.0021	0.0158	0.0180	0.0000
1	25	75	0	100	0.0030	0.0158	0.0187	0.0000
0.25	25	75	25	75	0.0010	0.0153	0.0163	0.0000
0.5	25	75	25	75	0.0019	0.0155	0.0174	0.0000
0.75	25	75	25	75	0.0030	0.0158	0.0186	0.0000
1	25	75	25	75	0.0039	0.0160	0.0199	0.0000
0.25	25	75	50	50	0.0012	0.0160	0.0172	0.0000
0.5	25	75	50	50	0.0023	0.0165	0.0188	0.0000
0.75	25	75	50	50	0.0033	0.0173	0.0205	0.0000
1	25	75	50	50	0.0045	0.0168	0.0213	0.0000
0.25	25	75	75	25	0.0015	0.0168	0.0184	0.0000
0.5	25	75	75	25	0.0030	0.0181	0.0207	0.0000
0.75	25	75	75	25	0.0042	0.0178	0.0215	0.0000
1	25	75	75	25	0.0053	0.0181	0.0230	0.0000
0.25	25	75	100	0	0.0018	0.0153	0.0170	0.0000
0.5	25	75	100	0	0.0032	0.0155	0.0186	0.0000
0.75	25	75	100	0	0.0050	0.0155	0.0230	0.0026
1	25	75	100	0	0.0065	0.0155	0.2804	0.2584

Table 15: Results of the potential use of 50%DEA:50%TEA for FAC suppression.

Oxidant Volume (ppm Cl_2)	% DEA	% TEA	% ClO_2	% OCl^-	*FAC (ppm Cl_2)*	*Chlorine Dioxide (ppm Cl_2)*	*Total Available Cl_2 (ppm)*	*Chlorite (ppm Cl_2)*
0	50	50	0	0	0.0000	0.0153	0.0153	0.0000
0.25	50	50	0	100	0.0007	0.0158	0.0165	0.0000
0.5	50	50	0	100	0.0014	0.0158	0.0172	0.0000
0.75	50	50	0	100	0.0021	0.0160	0.0182	0.0000
1	50	50	0	100	0.0029	0.0160	0.0189	0.0000
0.25	50	50	25	75	0.0011	0.0153	0.0163	0.0000
0.5	50	50	25	75	0.0018	0.0158	0.0177	0.0000
0.75	50	50	25	75	0.0029	0.0155	0.0184	0.0000
1	50	50	25	75	0.0039	0.0158	0.0197	0.0000
0.25	50	50	50	50	0.0012	0.0160	0.0173	0.0000
0.5	50	50	50	50	0.0025	0.0160	0.0186	0.0000
0.75	50	50	50	50	0.0037	0.0158	0.0217	0.0022
1	50	50	50	50	0.0048	0.0163	0.0211	0.0000
0.25	50	50	75	25	0.0014	0.0158	0.0171	0.0000
0.5	50	50	75	25	0.0031	0.0153	0.0183	0.0000
0.75	50	50	75	25	0.0000	0.0155	0.0187	0.0032
1	50	50	75	25	0.0055	0.0155	0.0232	0.0023
0.25	50	50	100	0	0.0016	0.0155	0.0171	0.0000
0.5	50	50	100	0	0.0033	0.0155	0.0189	0.0000
0.75	50	50	100	0	0.0046	0.0163	0.0226	0.0017
1	50	50	100	0	0.0059	0.0163	0.0262	0.0040

Table 16: Results of the potential use of 75%DEA:25%TEA for FAC suppression.

Oxidant Volume (ppm Cl_2)	% DEA	% TEA	% ClO_2	% OCl^-	*FAC (ppm Cl_2)*	*Chlorine Dioxide (ppm Cl_2)*	*Total Available Cl_2 (ppm)*	*Chlorite (ppm Cl_2)*
0	25	75	0	0	0.0000	0.0158	0.0157	0.0000
0.25	25	75	0	100	0.0008	0.0150	0.0157	0.0000
0.5	25	75	0	100	0.0014	0.0153	0.0167	0.0000
0.75	25	75	0	100	0.0022	0.0155	0.0177	0.0000
1	25	75	0	100	0.0029	0.0153	0.0182	0.0000

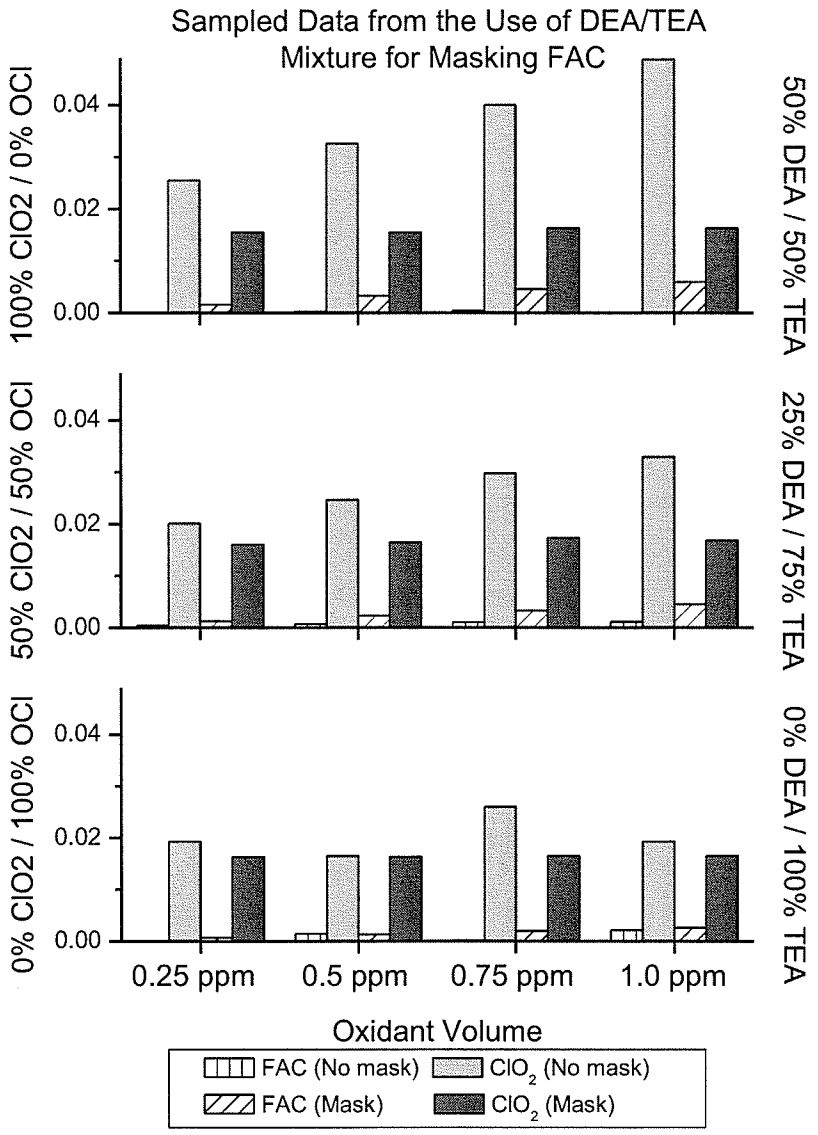


Figure 18: Observed Trends in Varying both the Oxidant Ratios, as well as, the Masking Agent Ratios.

10.2 Discussion of Using DEA and TEA as Prospective FAC Masking Agents

The results presented in Table 13 through Table 16 suggest that using a mix containing DEA and TEA intended as an oxidant mask, as tested, has been achieved, though not as anticipated. FAC still provides a response after addition of the mask. Specifically, the findings also suggest that chlorine dioxide is reacting with the mask in

all the ratios of DEA to TEA tested. Figure 18 highlights changing the type and ratio of oxidant, with the largest concentration providing the largest response. Even while no chlorine dioxide was applied, the method still provided a substantial response for chlorine dioxide. When compared to no mask application, the FAC response is observed to be larger when the mask is applied. This presents the hypothesis that the mask is reacting with the FAC, though initial it was expected to reduce FAC response, the results present an increase.

Alternative results are found for chlorine dioxide. When the mask is introduced, the chlorine dioxide response is subsequently reduced. Furthermore, when no chlorine dioxide was applied, observed responses reflected similar results as if there was chlorine dioxide applied. The chlorine dioxide content was anticipated to remain the same, as any viable mask would be required to not react with the oxidant. The continuation of sampling at more DEA to TEA ratios should be considered, as experimentation at alternative total molar concentrations may provide alternative results.

The use of either a 100% TEA, or a 25% to 75% ratio of DEA to TEA has been shown to rapidly reduce chlorine dioxide in the presence of FAC and chlorite (as observed with a decrease in chlorine dioxide content). Masking agent concentrations remained at the same molarity used for glycine in the Standard Methods protocol 4500-ClO_2 D 3d. Further development may provide means to confirm or contribute to the development of a stoichiometric reaction ratio between the masking agents and chlorine dioxide response.

Chapter 11: Novel Use of TMPD and Cerium(IV) for Sub 1 ppm Chlorine Dioxide Detection

11.1 The Results of Using TMPD and Cerium for Chlorine Dioxide Detection

The colour developing reaction between TMPD and chlorine dioxide with and without the addition of cerium sulfate was systematically investigated in a weakly acidic buffered media. As shown in Figure 19, the addition of chlorine dioxide promotes an absorbance throughout the ultraviolet and visible spectrum, which observed as a blue colour, hypothesized to be representative of the semiquinone radical cation intermediate product. Absorbencies were recorded at three wavelengths, 328, 564 and 612 nm, with 328 nm consistently providing the highest absorption.

The direct substitution of TMPD for DPD in the Standard Methods protocol 4500-ClO_2 D 3d did not provide any means for further quantification at any of the published wavelength associated with TMPD. Upon the addition of a small amount of chlorine dioxide to solutions of TMPD, a blue colour change did occur (Figure 19), although the absorbencies at 328, 564 and 612 nm did not remain stable enough for further analysis. Such volatility is presented in Figure 20, where the reading continually increased thus failing to provide any further means for quantification.

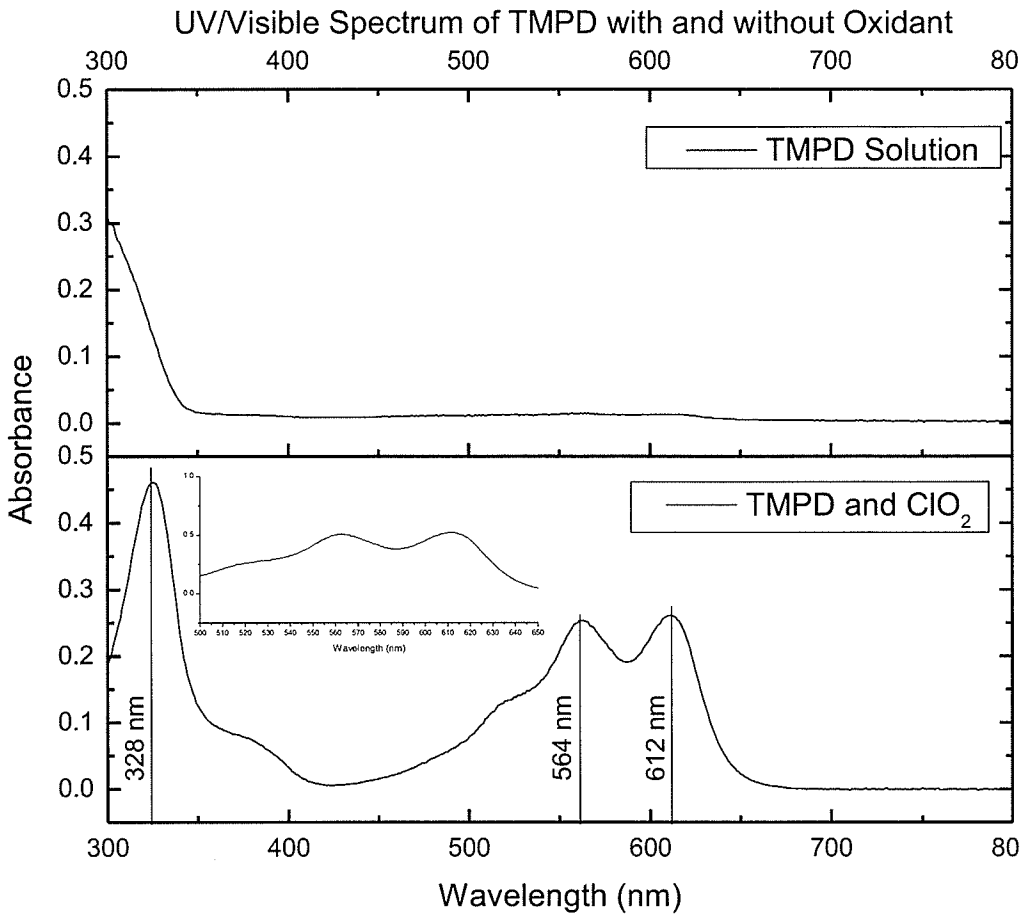


Figure 19: A comparison between a solution of TMPD in water, and its oxidized form using chlorine dioxide

Readings taken at 328, 564, and 612 nm for the duration of 45 minutes were recorded to observe the amplitude of change at a particular wavelength, given the direct substitution of DPD for TMPD. These results are presented on Figure 20.

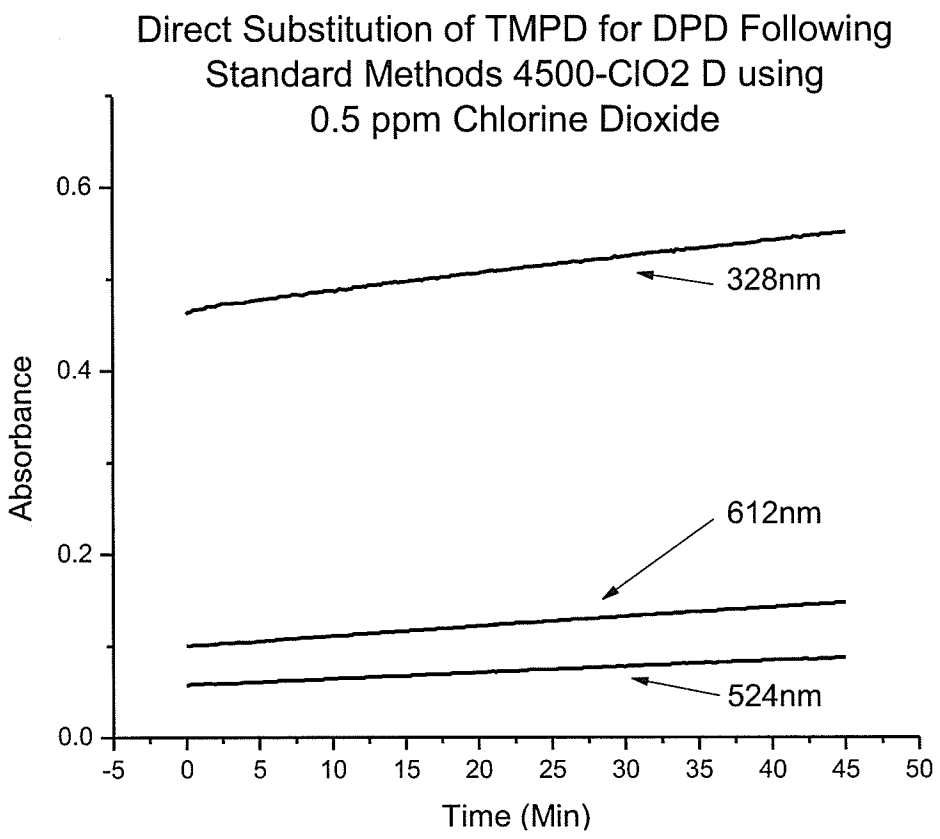


Figure 20: Observed changes in absorbance from substituting TMPD for DPD in Standard Methods.

Early observations suggest that the use of TMPD as a direct replacement does not provide satisfactory results. Consistent with most handheld spectrometers utilizing light emitting diodes as their light source, quantification was carried out at 612 nm, under the supposition that any potential application would be facilitated by utilizing a wavelength in the visible spectrum. As the reading at 612 nm provided the highest absorbance at all concentrations tested when compared to 524 nm, its use was selected for further investigations. Therefore, the results derived from varying the concentrations of chlorine dioxide at 612 nm are presented in Figure 21. In this figure, the reference blank contained only deionized water, while the reference did not contain any chlorine dioxide. These results suggest that an increase in absorbency occurs regardless of the

concentration applied. In contrast to using DPD and forming to the colourless imine complex, the gradual increase in absorbance provides the hypothesis that no imine complex forms when using TMPD, a potentially key advantage over the use of DPD. Alternatively, the continual increase in absorbance was unexpected and can be theorized to be a matter of oxidation kinetics. Further study beyond the scope of this work would be required to accurately evaluate such observations.

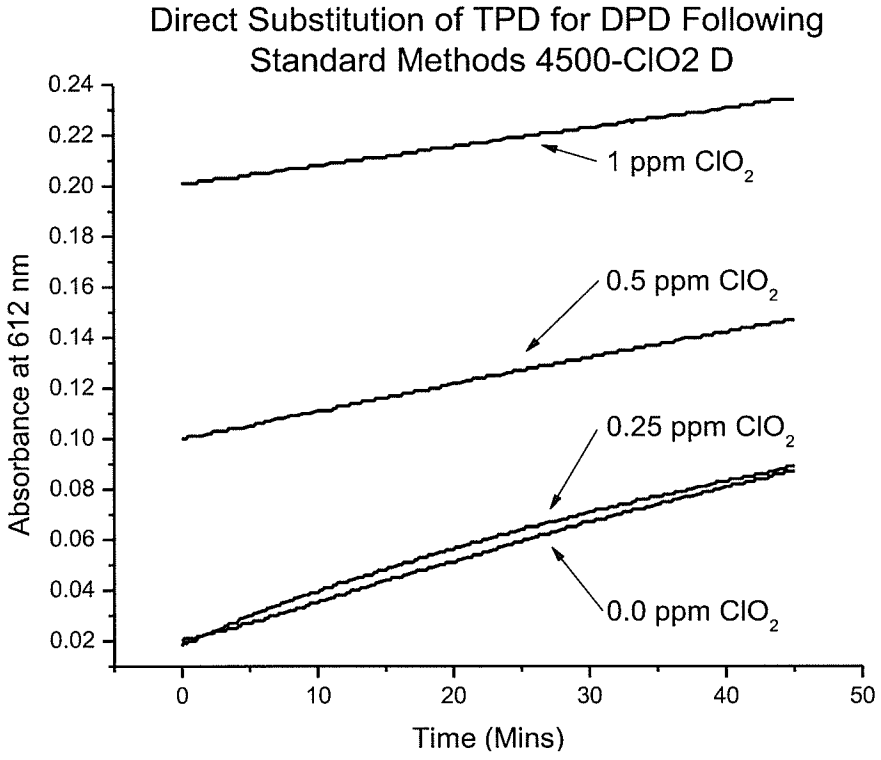


Figure 21: Effects of increasing the chlorine dioxide content when using TMPD for detection at 612 nm.

The requirement to review which wavelength is best suited for further investigation following the addition of cerium necessitated a re-evaluation of the wavelength selection, with and without cerium. The comparative data is presented on Figure 22.

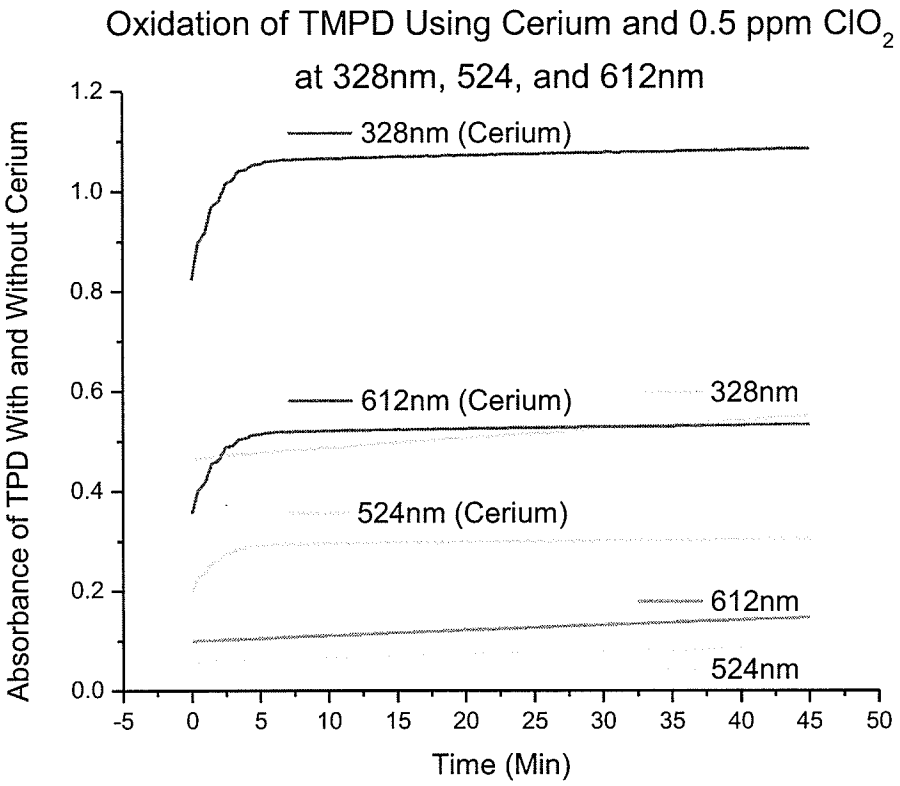


Figure 22: Wavelength selection comparing results from the inclusion of cerium, and without.

Figure 22 highlights the difference between trials which were conducted with and without the addition of cerium. The addition of small amounts of cerium was hypothesized to catalyze the oxidation of TMPD by chlorine dioxide, given that similar methods employing cerium has been reported to accelerate the spectrophotometric determination of alkaloids, steroids (Nemcova, 1996) and benzoylperoxides (Mori, et al., 1997). By utilizing the 612 nm wavelength, investigative trials incorporating cerium for the detection of residual levels of chlorine dioxide in conjunction with TMPD are presented on Figure 23.

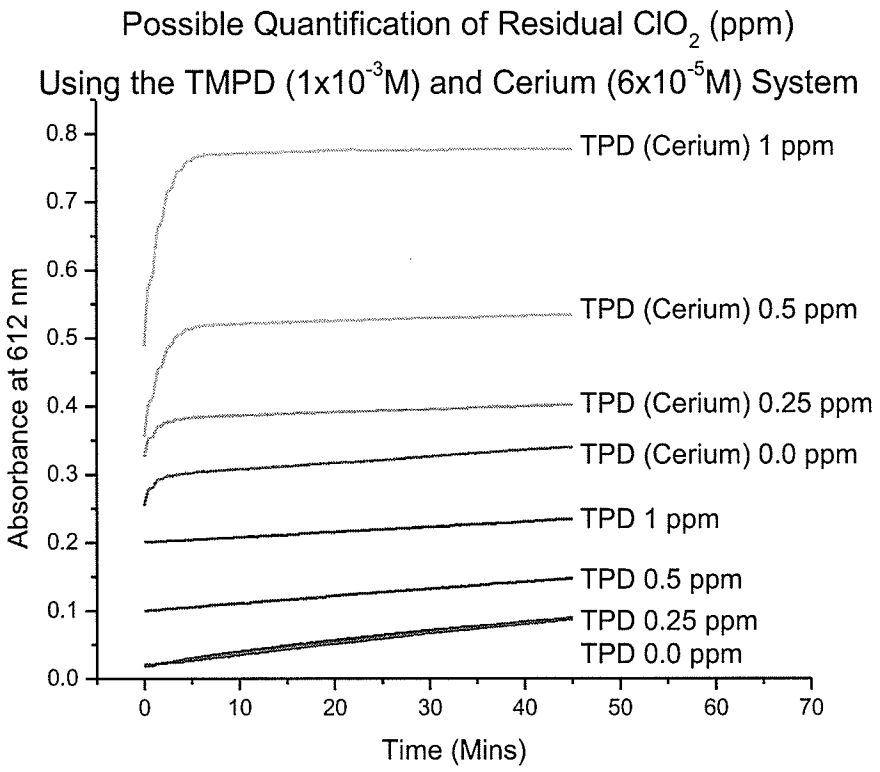


Figure 23: Application of a potential TMPD and cerium system for residual chlorine dioxide analysis,

It was observed that the addition of small amounts of cerium inhibited the continual increase in absorbance observed at all three wavelengths as compared to trials which did not include cerium (Figure 22 and Figure 23). The addition of cerium can also be interpreted as accelerating the precursor of formation of the final products. The observed results cannot provide a means to distinguish between an inhibiting or accelerating scenario. The observed plateau in absorbance facilitated quantification following approximately a 10 min post mixing delay.

Final investigations included a brief verification to determine if similar results from the addition of cerium also occurred when adhering to the use of DPD in the Standard Methods protocol (Figure 24).

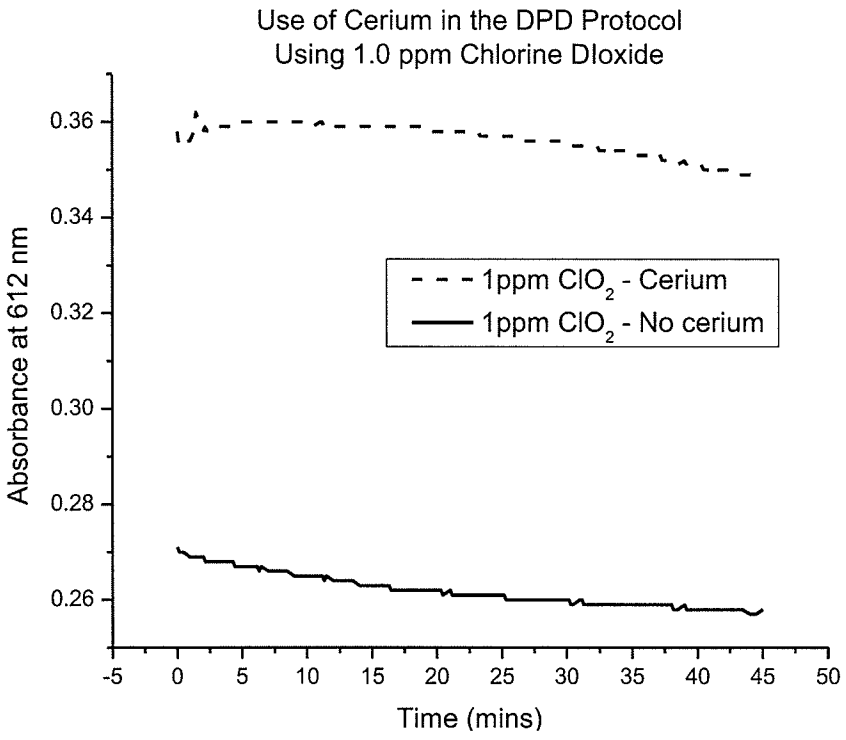


Figure 24: Comparison of incorporating cerium with DPD and without.

11.2 TMPD and Cerium Detection System for Chlorine Dioxide

Though TMPD is structurally similar to DPD and its application is found as an enzymatic oxidant indicator in microbiology, use within the field of drinking water for detection application is currently unknown. Use of TMPD in exchange for DPD was hypothesized to provide superior oxidization specificity as well as colour stabilization - both established limitations to the current application of DPD for residual chlorine dioxide detection. It was observed that using three published quantifiable wavelengths (328, 564 and 612 nm) following post dilution of the salt and reagent mixing allows continual increase in the recorded absorbencies for the observed time frame (Figure 21). Unfortunately, this volatility provides little basis for further quantification without additional method derivatization steps. As such, with the addition of a small amount of

cerium sulfate prior to diluting to the final volume it was observed that such temporal absorbance volatility appeared suppressed, as demonstrated in Figure 22. Two hypotheses can be drawn from the addition of cerium(IV). First, that the cerium(IV) provides sufficient "radical cation stability" to effectively curtail the transition from the blue radical cation to the colourless di-cation via resonance stabilization, in essence, that the cerium is directly interacting with TMPD. Second, it is hypothesized that the cerium is not a true catalyst and is continually oxidized and reduced between cerium(IV) and cerium (III), thereby providing an electron source for TMPD to achieve rapid absorbance stabilization. Specifically, such mechanism is hypothesized to occur by the reduction of cerium(IV) to cerium(III) via TMPD, while chlorine dioxide oxidizes cerium(III) back to cerium(IV). This hypothesis could explain the observed stabilization in absorbance from the addition of cerium(IV). Similar results are not observed with using the same molarities of DPD and cerium(IV), and thus suggesting that the mechanism is TMPD specific. Either theory may explain the observed acceleration in absorption and the subsequent possibility for chlorine dioxide quantification.

Figure 23 illustrates the sensitivity for detection of residual concentrations of chlorine dioxide (0-1 ppm) as well as the ability to record a stable absorbance following approximately a post-10min mixing time. In order for this method to be viable, however, interference testing has to be established. Although further investigation is necessary for the development of these methods, experimental results suggest the capacity to accurately measure low residual concentrations of chlorine dioxide (0-1 ppm).

Chapter 12: Use of Alizarin Red S for Chlorine Dioxide Detection in the Presence of Chlorite

12.1 Results on the use of Alizarin Red for Chlorine Dioxide Detection in the Presence of Chlorite

The ultraviolet and visible spectrum of ARS was recorded to have a quantifiable absorbance at 516nm (Figure 25). Figure 26 and Figure 27 illustrate the results of experiments on the application of alizarin red for the detection of small residual concentrations of chlorine dioxide in the presence of chlorite.

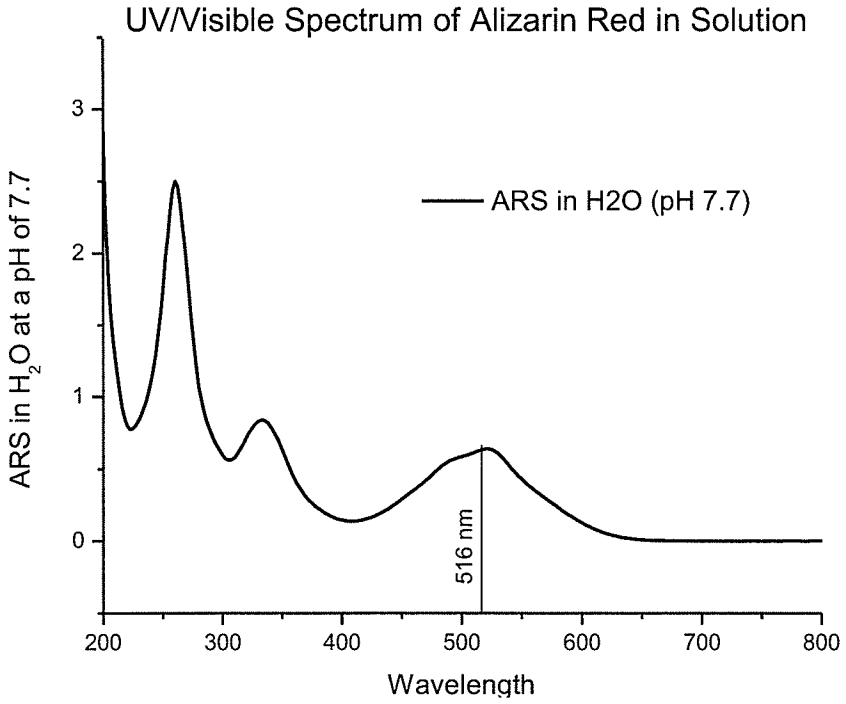


Figure 25: UV/Visible spectrum of alizarin red, buffered to a pH of 7.7, absorbance readings were taken at 516nm.

As such, the introduction of increasing aliquots of chlorine dioxide presented a hyperchromic shift in absorbance at 516 nm. These observations are recorded in Figure 26. This illustrates the visible absorption spectrum of varying concentrations of chlorine dioxide and alizarin red. Optimum quantification was at wavelength of 516 nm. A linear

reduction in absorbance with increasing concentrations of chlorine dioxide was observed. Such a hyperchromic shift occurs throughout the entire ultraviolet and visible range, signifying a reduction in the chromophore content analogous to bleaching colour.

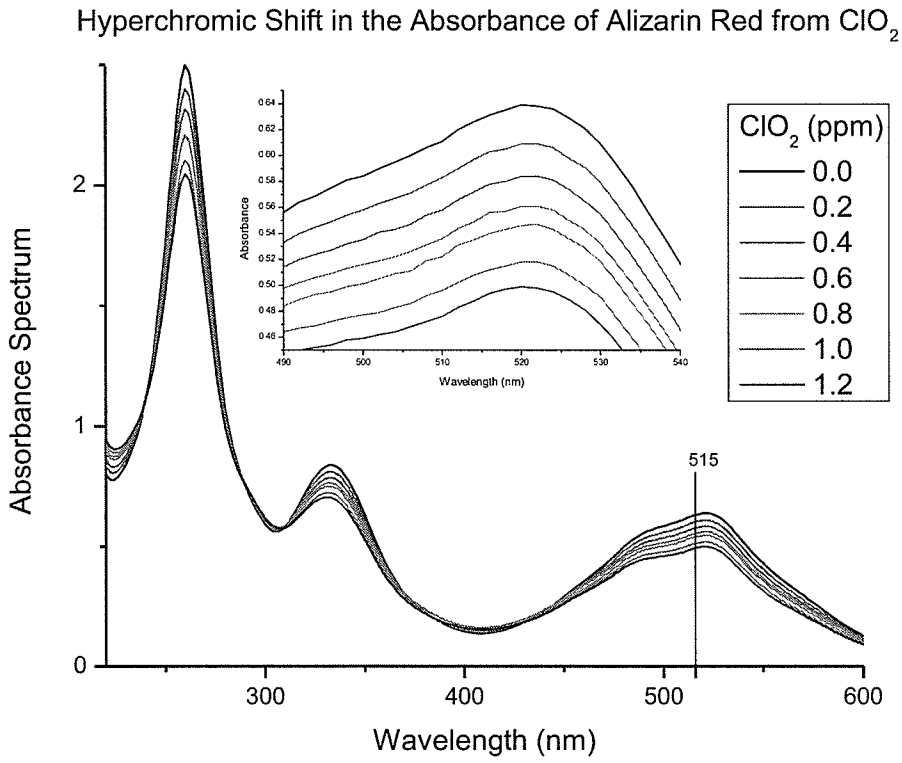


Figure 26: The observed reduction in absorbance at 516 nm due to increasing concentrations of chlorine dioxide used.

The introduction of small concentrations of chlorite was used to observe any potential changes which could be associated as chlorite interference as chlorite will always be present where chlorine dioxide is applied. Figure 27 provides the initial basis for the possible quantification of residual levels with minimal interferences from chlorite; up to 0.5 ppm. The apparent molar absorptivity constants were calculated in accordance with Beer-Lambert law in which absorbance is expressed as a change from initial value

and were found to be 11142±1118, 10372±839, and 10906±1721 L mol^{-1} cm^{-1} for chlorine dioxide (0-4 ppm), chlorine dioxide in the presence of 0.2 ppm chlorite and 0.5 ppm chlorite, respectively. These findings suggest ϵ is constant, specifically, constant within experimental error. These results are depicted in Figure 27.

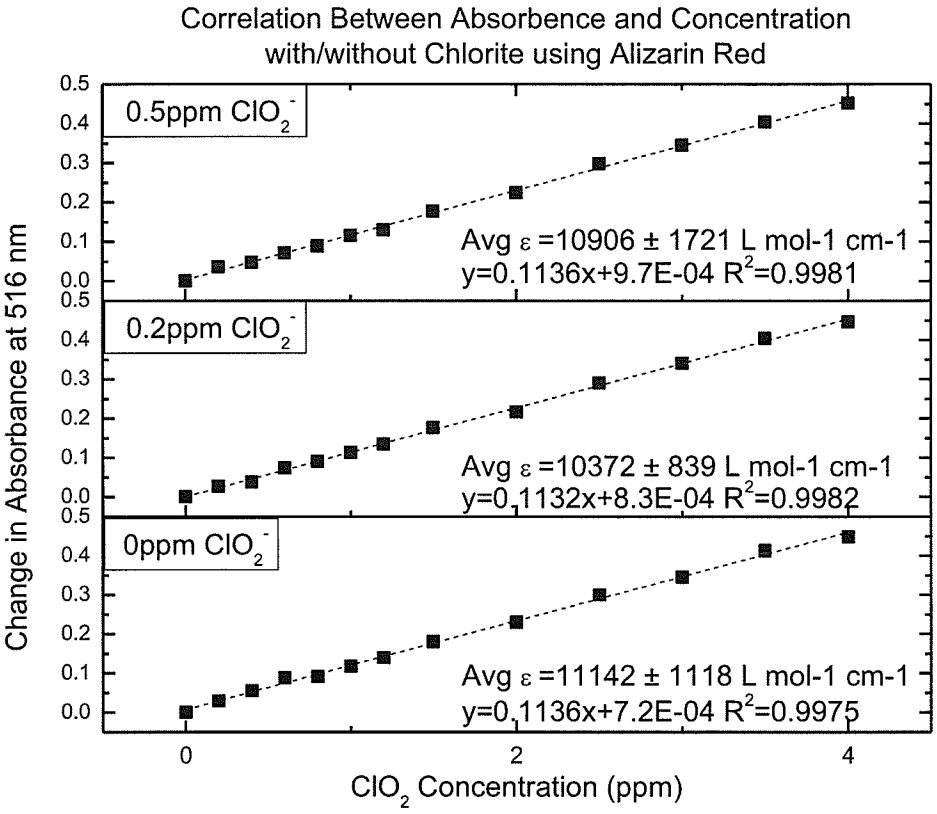


Figure 27: Use of alizarin red for chlorine dioxide detection with and without potential chlorite interferences.

12.2 The Alizarin Red S System for Chlorine Dioxide

Alizarin red has been shown to provide residual chlorine dioxide concentrations in the presence of chlorite, giving rise to the possibility of a potential detection system (Rak-Banville, 2008). Application of alizarin red for detection is observed for a concentration range of 1 to 5 ppm chlorine dioxide (though residual concentrations may range from sub 1 ppm to above 5 ppm as GCDWQ do not apply an MCL to chlorine

dioxide), whereas chlorite concentrations of 0.2 and 0.5 ppm chlorite ion do not appear to interfere. Straight-forward quantification at 516nm was possible when the solution was buffered accordingly, as high alkaline (pH≥10) conditions favor rapid decomposition. Though ideal synthetic samples of deionized water with appropriate reagent dilutions were used, the progressive introduction of common drinking water metal ions culminating in the inclusion of natural or raw water samples should be further analyzed to verify if the method remains applicable. Furthermore, it should be noted that phosphate ions are a likely candidate for the further discolouration of alizarin red (Abdallah, et al., 1991), as such these interferences and others previously outlined should be further tested.

Chapter 13: Detection of Chlorite from Chlorate Using Copper(II) Sulfate

13.1 Findings from the use of Copper sulfate for Chlorate Detection in Presence of Chlorite

Results of the unique application of copper sulfate for the detection of chlorite yielded molar absorptivity constants of 117±38 L mol^{-1} cm^{-1} for low concentration trials (0-10 ppm) and 6.49 ±0.42 L mol^{-1} cm^{-1} for high concentration trials (1:1-1:10 molar ratio of $CuSO_4$:ClO_2^-, 269 ppm – 2690 ppm). These results are presented in Figure 28 and Figure 29. No colourimetric responses were found when replacing the same concentration of chlorite with chlorate (potassium chlorate), thus providing the potential to discriminate between chlorite and chlorate ions.

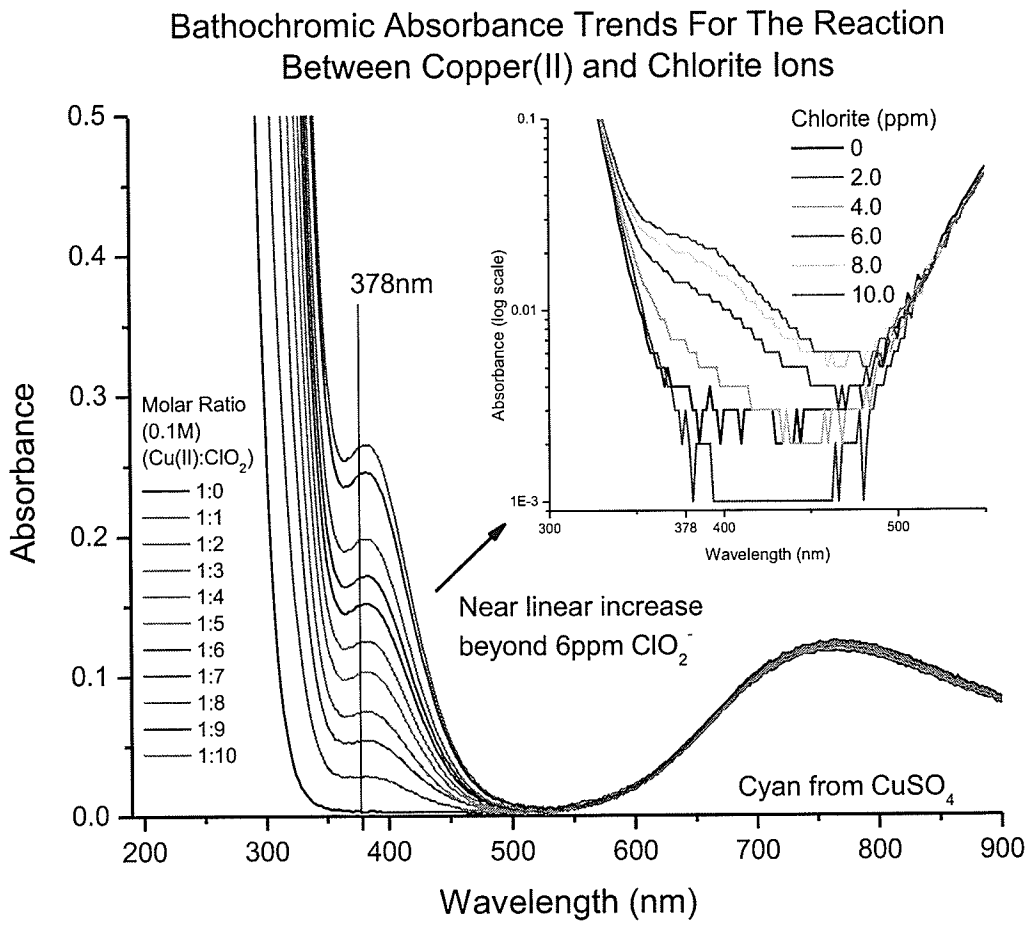


Figure 28: Observed non-linear increase in spectrum absorbance from increasing chlorite concentrations tested.

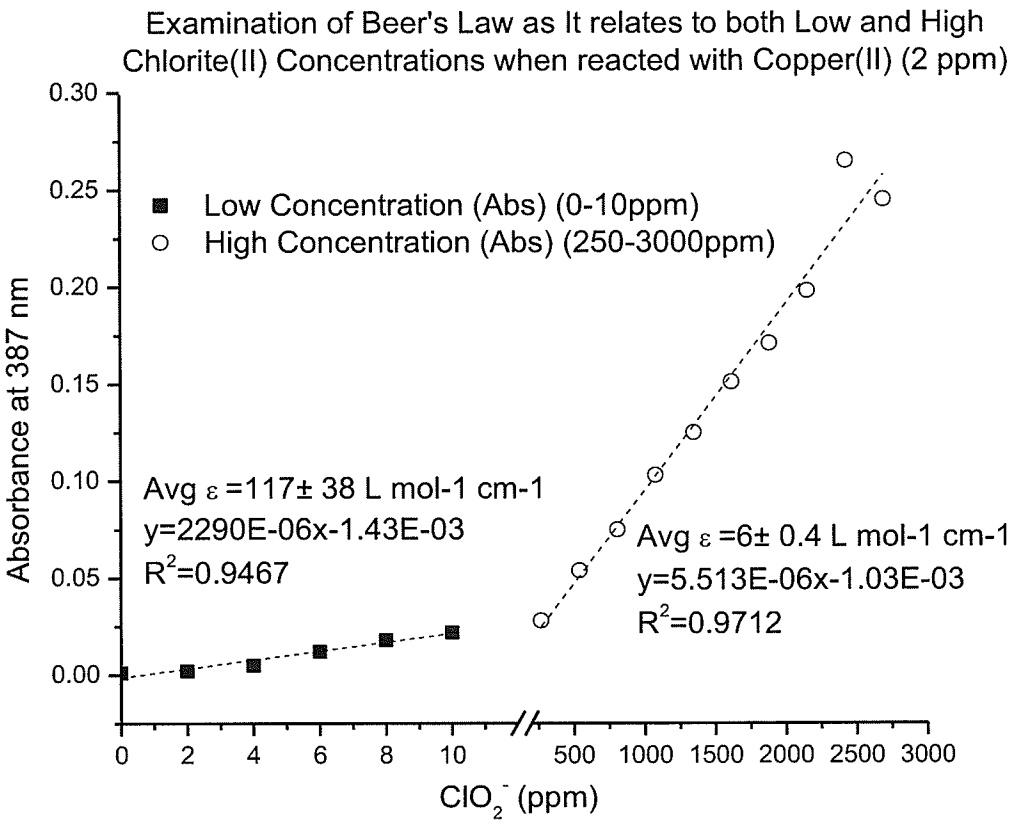


Figure 29: Molar absorptivity constant calculations based on low and high chlorite concentrations.

13.2 The Copper(II) Sulfate System for Chlorite

This research sought to determine if the levels of the by-product chlorite could be measured using the introduction of copper(II) sulfate to differentiate between the presence of chlorite and chlorate. As most field analyses utilize some form of a masking agent or arithmetic subtraction from a total oxidant value for the detection of chlorite, the ability to selectively analyze its concentration can be considered favorable. Interestingly, the mixture of copper and chlorite yields a green colour, though when substituting chlorite by chlorate no colour is observed. This differentiation may provide the possibility for the development of a chlorite selective spectrophotometric protocol. Copper has been established for its ability to catalyze the decomposition of hypochlorite

to chloride (Church, 1994); whereas the similar decomposition of chlorite has not been reported. Plausible method development could allow measurement of a combined residual of chlorite and chlorate using standard DPD methods, followed by measurements of chlorite using copper(II) sulfate, which could potentially establish a chlorate concentration based on a logical subtraction. The data presented here suggests that the development of a viable protocol for the quantification of chlorite in the presence of chlorate at concentrations between 6-10 ppm may be possible (Figure 28). Though these concentrations exceed those commonly found in drinking water applications, possible uses for monitoring discharge originating from the pulp and paper industry where chlorine dioxide is used as a bleaching additive may be suitable for further investigation of said method. Lower concentrations appear to fail Beer's Law, yet this could possibly be linked to the low molar absorptivity constant of the product from the chlorite and copper ions (Figure 29). As such, no absorption coefficient may be calculated and thus makes use of this method at such low concentration a poor candidate for spectrophotometric analysis. This could be rectified by the use of an extended cuvette path length (10 cm as oppose to 1 cm) which would increase sensitivity 10 fold. The pH was buffered to approximately 5.5, as this provided the highest absorbance when compared to a range of pH values tested (5-8). At a pH of 7 precipitates began to form in solutions, presumably from copper hydroxide complexes. Further work should include using extended path length cuvettes, as well as possible interference testing and efforts to determine the origin of the observed absorbance at 387 nm.

Though it would be considered ideal to have a direct spectrophotometric detection method for chlorate ions, the small number of methods available for the detection of

these ions relies on methods other than spectrophotometry . If development of a universal protocol were successful, a possible route for analyses could be based upon arithmetically subtracting from a total oxidant value (usage of DPD for the formation of a total oxidant parameter could be considered). As chlorate is normally found in much smaller concentrations when compared to chlorine dioxide or chlorite, the identification of low concentrations need be a concern for the risk of rendering the development vulnerable to interferences. The possibility of cascading error would also need to be considered. Regardless, all currently EPA accepted methods for chlorate detection rely solely on ion chromatography, requiring samples to be sent away to commercial labs for analysis.

Part 6: Conclusion

Chapter 14: Final Thoughts

Drinking water is a fundamental human need, and the methods used in disinfecting drinking water directly impact the quality of the water consumed. Where THM levels are elevated, water system owners and operators are exploring alternative disinfection practices. One such alternative is the use of an alternative disinfectant, such as chlorine dioxide. While chlorine dioxide has been proven to not produce THMs, its North American application is relatively small in part due to difficulties and established interferences associated with accurately monitoring residual levels and principle by-products: in this case, chlorite and chlorate.

Of several methods available in literature, the most standardized spectrophotometric analysis method in North America is the N,N-diethyl-p-

phenylenediamine (DPD) method. This method has been adapted by inclusion of the amino acid glycine acting as a FAC masking agent, to allow chlorine dioxide concentrations to be evaluated. Furthermore, in addition to monitoring issues and hindering wider adoption, the elevated chlorine dioxide demand in waters high in natural organic matter (NOM) elicits the need to be cognizant of the possibility of creating elevated concentrations of by-products. Due to the oxidative nature of chlorine dioxide, specifically the numerous reductive half reactions that may occur with organic and inorganic compounds as well as within the distribution system, it is critical that simple and accurate residual analysis methods be available. As is the challenge with many potable Canadian Prairie water sources which may exhibit chlorine dioxide demands greater than 1.2 ppm (which is the maximum dose recommended by the Guidelines for Canadian Drinking Water Quality), there is a need to provide operators with proper residual analysis tools in order to maximize their dosages and provide an effective residual throughout the distribution system.

Objectives of this work were to study the effectiveness of the standard DPD method for the detection of chlorine dioxide in potable waters, including an evaluation of the spectrophotometric calibration using potassium permanganate and masking free available chlorine. Furthermore, development of potential alternative spectrophotometric reagents was explored to provide a foundation for additional research.

Promising candidates, such as alizarin red, copper(II) sulfate, and N,N,N',N'-tetramethyl-p-phenylenediamine were investigated for their potential to measure chlorine dioxide and chlorite for typical drinking water treatment residual concentrations (sub 1ppm).

Following the prescribed Standard Methods for DPD calibration, investigative studies were carried out as to the stability and practicality of applying low concentrations of potassium permanganate as a chlorine dioxide surrogate. Conclusions are that DPD calibration with potassium permanganate does not appear reliable due to the time-sensitive volatile absorbencies observed post reagent mixing. Absorbance reduction up to 20% were observed after 2 minutes at a pH of 7 when applying a dosage of 1 ppm. This can result in a serious underestimation of disinfectant concentration when reporting to regulating agencies. The observed decrease in DPD absorbance when calibrating is due to the continued non-reversible formation of the colourless imine product. The initial imine product formation is dependent on variables such as pH, temperature, oxidant concentration, etc, but is always initially formed, though usually in small concentrations (Gordon, et al., 1972). Initial imine formation is largely due to the continued oxidation of DPD by chlorite, as chlorite is immediately produced from the chlorine dioxide-DPD reaction. As such, with time, the conversion from Wurster's red to the imine compound is unavoidable, and is observed with the fading of the coloured solution to transparent. Such uncertainty in calibration will provide for considerable error when calibrating for a concentration range as small as 0.8 to 0.2 ppm in Manitoba. .

Alternative spectrophotometric reagents such as TMPD, alizarin red and copper(II) sulfate, were investigated for their potential to measure chlorine dioxide and chlorite for typical drinking water treatment residual concentrations.

The TMPD and cerium method which provides for accurate sub-1 ppm chlorine dioxide concentration detection may provide a platform for an alternative method upon which operators and regulators could potentially rely. As the loss of a proton to form the

coloured product is not required for TMPD, the hypothesized mechanism that TMPD could provide for improved pH independence is an additional benefit to this method.

Alizarin red was observed to measure chlorine dioxide residuals in the presence of low concentrations of chlorite from 0-4 ppm in the presence of 0.2 and 0.5 ppm chlorite ion. Further investigations as to the use of copper(II) sulfate for residual chlorite determinations are warranted, as detection below 6 ppm was not reproducible.

Copper sulfate was successfully used to measure concentrations of chlorite ranging from 6 to 10 ppm. Concentrations below 6 ppm were not distinguishable likely due to a low molar absorptivity constant. Such results warrant further investigations as to the sensitivity of the molar extinction coefficient, as well as alternative interferences.

The cumulative results of the potential applications of alternative detection agents such as alizarin red, copper sulfate, TMPD and cerium matrices, that when applied in tandem, can be hypothesized to provide spectrophotometric detection of low concentrations of chlorine dioxide (TMPD/cerium alizarin red) and chlorite (copper sulfate results subtracted from a total chlorite and chlorate oxidant concentration).

Applications of di- and tri-ethanolamine as an alternative masking agent for hypochlorite have been also been explored as an alternative substitute to glycine. Results suggested that use of such a mixture provided an oxidant mask which appeared to underestimate the concentration of chlorine dioxide more than hypochlorite. When compared to glycine, this mixture is considered inferior as a reaction with chlorine dioxide significantly deters measurements. Details as to such mechanism are unknown.

Part 7: Recommendations

Chapter 15: Potential Directions

One avenue to providing a successful analogue to current chlorine based disinfection is the use of chlorine dioxide. Although in some ways it can even be considered a successor to current chlorine based disinfection practices, its production, detection and by-product formation characteristics as presented have been highly debated and at times criticized. Chlorine dioxide has been adapted for use as a potable water disinfectant. For these purposes, this study aimed to examine its current legislative acceptance and recognized methods of analysis, while also making efforts to establish new possible residual and by-product detection methods. Although this area has grown in recent years as a direct response to the need to decrease THM content in finished waters, continued research concerning alternative disinfectants such as chlorine dioxide is indeed warranted. Among future directions, experimentation employing the use of solid-phase extraction (SPE) methods should be evaluated. SPE cartridges provide a means to remove, concentrate, or purify samples prior to analysis, making them ideal for isolating numerous of compounds interest from bulk samples.

Currently, in the context of drinking water, no literature was readily available employing SPE methods for use with chlorine dioxide, chlorite or chlorate. As their application requires the mobile sample phase to be passed through a stationary phase (usually by applying pressure through a syringe), chlorine dioxide detection may be ill suited due to the natural volatility of the compound. Nonetheless, possible uses of SPE

range from the extraction of chlorite and chlorate, separation of the two species, and the possibility for pre-concentration of each species and thus enablement of methods which could not originally be used due to their limits of detection or potential interferences experienced at low concentrations (such as spectrophotometry). Considering the practical applications of using SPE for these purposes is one proposal for continued work.

15.1 Suggestions for the Continuation of Additional Experimental Work

The results presented involving a mixture of both DEA and TEA can be further continued using alternative ratios, yet more importantly varying total molarities of the masking agent used to determine any subsequent effects on FAC content. This may incite alternative results, or allow for a superior understanding alluding to a potential stoichiometric relationship. Such experimentation could be rapidly accomplished with an automated flow injection analysis instrument setup.

Further research into the experimental spectrophotometric detection systems (TMPD and cerium, ARS, and copper sulfate) is warranted, and at minimum, span much smaller and larger concentrations of chlorine dioxide, with and without the inclusion of FAC, chlorite, and chlorate as interferences. Following such testing, typical drinking water components should be introduced, including chlorate, hypochlorous acid, manganese, etc. Establishing interferences with these methods should be considered a priority to any further development.

Lastly, the development of a subtractive chlorate determination using copper sulfate should be pursued. By measuring a total oxidant parameter, for instance through the DPD method, followed by measurement of chlorine dioxide and chlorite (via TMPD

and alizarin red S), an arithmetic subtraction can theoretically provide an experimental chlorate concentration. This method would be initially restricted to experimental samples, though if successful, may provide the initial basis for an alternative chlorate detection system. All potential methods investigated still require an in-depth evaluation using alternative confirmatory methods such as LGB-HRP, ion chromatography and other analytical methods for a complete comparison.

15.2 Chlorine Dioxide in Manitoba

15.2.1 Efforts to Reduce THM Content: Use of Chlorine Dioxide and DOC Reactivity

The chemical characteristics of DOC are not only influenced by the source material, but are also influenced by all the biogeochemical processes involved in the natural carbon source and sinks of a particular body of water. As such, the variety of organic components, be it humic acids, fulvic acids, and others, and their characteristic chemical makeup, hydro-, hypo- lippo-, philic, and etc features constituent the terms dissolved organic carbon. Importantly, each of the natural anabolic and catabolic biogeochemical pathways occurring within a water source are likely to affect the DOC chemistry in a differing way.

Many water supplies within Manitoba contain high amounts of DOC, which through a series of multi-step reactions, is the principal pre-cursor of several chlorination by-products. Focusing upon the exact chemical makeup of local DOC content (likely via fractionation) may provide a potentially significant contribution to understanding THM formation which has been largely overlooked, in part, due to the natural complexity of

these systems. Understanding the principle functional groups which provide for THM formation, when using chlorine, may provide for a major comparison intended to reducing THM formation upon disinfection with chlorine dioxide. Results may provide for an evidenced based practice to low-THM disinfection; via chlorine or via the adoption of chlorine dioxide for both disinfection and easily maintaining residual concentrations throughout the distribution network.

15.2.2 Residual Analytical Detection

As per possible recommendations surrounding the use of chlorine dioxide, the WHO offers a quantitative reason for a MAC 0.7 ppm for chlorite and chlorate based upon NOAEL studies. These values are reflected in the CGDWQ, as similar reasoning is used to calculate the MAC in Canada. Most developed nations applying chlorine dioxide restrict chlorite and chlorate concentrations to the sub-1 ppm range.

Although the CGDWQ provides MACs which are similar to those presented in many governmental legislations (with the exception of California), the protocols offered for chlorine dioxide, chlorite and chlorate detection are not as widely common. In comparison, the NDWS provides the most exhaustive outline of recording and monitoring requirements. Specifically, the NDWS demands that continuous monitoring of chlorine dioxide and chlorite be employed, thus procuring the use of on-line amperometric probes. Not only is the operator and regulatory agency offered a magnitude of selectivity and relatively interference free measurements, amperometric probes provide the ability to rapidly adjust application parameters based upon changes

observed in residual readings. Similar legislation could be considered ideal for Manitoban systems, as surface waters continually change characteristics (such as DOC, temperature and pH). On-line chlorine dioxide and chlorite amperometric sensors to complement routine operator testing methods (such as the LGB-HRP method) may become considerably important in future expectations concerning chlorine dioxide application for potable water disinfection.

Appendix A:

Tabulated US EPA Methods for Chlorine Dioxide, Chlorite and Chlorate, June 2008 (Environmental Protection Agency, 2009).

Year	Method Identification	Organization	Active Reagent(s)	Detector	Reference
Chlorine Dioxide					
2005	327 Rev 1.1	EPA	Horseradish peroxidase (enzymatic)	Spectrophotometer	EPA Publication 815-R-05-008
2005	4500-ClO2 E	Standard Methods	Phenyl arsine oxide or Sodium thiosulphate	Amperometry	Standard Methods 21st Edition
2000	4500-ClO2-00	Standard Methods Online	Iodine	Amperometry	http://www.standardmethods.org
1998	4500-ClO2 D	Standard Methods	DPD and glycine (for masking free chlorine)	Colourimeter	Standard Methods 20th Edition
1998	4500-ClO2 E	Standard Methods	Phenyl arsine oxide or Sodium thiosulphate	Amperometry	Standard Methods 20th Edition
1995	4500-ClO2 D	Standard Methods	DPD and glycine (for masking free chlorine)	Colourimeter	Standard Methods 19th Edition
1995	4500-ClO2 E	Standard Methods	Phenyl arsine oxide or Sodium thiosulphate	Amperometry	Standard Methods 19th Edition

Appendix A (Continued)

Year	Method Identification	Organization	Active Reagent(s)	Detector	Reference
Chlorite (Daily Monitoring)					
2008	D6581-00R05	ASTM International	Calibration Standards	Ion Chromatography	ASTM Volume 11.01, April 2008
2005	327 Rev 1.1	EPA	Horseradish peroxidase (enzymatic)	Spectrophotometer	EPA Publication 815-R-05-008
2005	4500-ClO2 E	Standard Methods	Phenyl arsine oxide or Sodium thiosulphate	Amperometry	Standard Methods 21st Edition
2002	326 Rev 1.0	EPA	Calibration Standards	Ion Chromatography	EPA Publication 815-R-03-007
2001	317 Rev 2.0	EPA	Calibration Standards	Ion Chromatography	EPA Publication EPA 815-B-01-001
2000	4500-ClO2 E-00	Standard Methods Online	Iodine	Amperometry	http://www.standardmethods.org
1998	4500-ClO2 E	Standard Methods	Phenyl arsine oxide or Sodium thiosulphate	Amperometry	Standard Methods 20th Edition
1995	4500-ClO2 E	Standard Methods	Phenyl arsine oxide or Sodium thiosulphate	Amperometry	Standard Methods 19th Edition
1993	300.0 Rev 2.1	EPA	Calibration Standards	Ion Chromatography	EPA Publication EPA/600/R-93/100
Chlorite (Distribution Monitoring)					
2008	D6581-00R05	ASTM International	Calibration Standards	Ion Chromatography	ASTM Volume 11.01, April 2008
2002	326 Rev 1.0	EPA	Calibration Standards	Ion Chromatography	EPA Publication 815-R-03-007
2001	317 Rev 2.0	EPA	Calibration Standards	Ion Chromatography	EPA Publication EPA 815-B-01-001
2000	300.1 Rev 1.0	EPA	Calibration Standards	Ion Chromatography	EPA Publication 815-R-00-014
1993	300.0 Rev 2.1	EPA	Calibration Standards	Ion Chromatography	EPA Publication EPA/600/R-93/100

Appendix B:

Raw Experimental Data from the Investigation of Using DEA and TEA as a FAC Suppressant

Oxidant Volume (ppm Cl_2)	**% ClO_2**	**% OCl^-**	**A (ppm Cl_2)**	**B (ppm Cl_2)**	**C (ppm Cl_2)**	**D (ppm Cl_2)**	**G (ppm Cl2)**	***FAC (ppm Cl_2)***	***Chlorine Dioxide (ppm Cl_2)***	***Total Available Cl_2 (ppm)***	***Chlorite (ppm Cl_2)***
0	0	0	0.003153	0.003204	0.003306	0.003459	0.003051	0.0001	0.0153	0.0155	0
0.25	0	100	0.003765	0.003918	0.003918	0.004071	0.003867	-0.0001	0.0193	0.0194	0
0.5	0	100	0.004683	0.004683	0.004683	0.004683	0.003306	0.0014	0.0165	0.0179	0
0.75	0	100	0.005346	0.005346	0.005244	0.005244	0.005193	0.0002	0.0260	0.0260	0
1	0	100	0.006009	0.00606	0.006009	0.005805	0.003867	0.0021	0.0193	0.0215	0
0.25	25	75	0.00402	0.00402	0.00402	0.00402	0.00402	0.0000	0.0201	0.0201	0
0.5	25	75	0.005142	0.005142	0.005142	0.005091	0.004122	0.0010	0.0206	0.0216	0
0.75	25	75	0.00611	0.006162	0.00606	0.00606	0.005091	0.0010	0.0255	0.0264	0
1	25	75	0.006978	0.007029	0.006927	0.006774	0.00504	0.0019	0.0252	0.0271	0
0.25	50	50	0.004377	0.004428	0.004377	0.004377	0.00402	0.0004	0.0201	0.0205	0
0.5	50	50	0.005652	0.005703	0.005652	0.005805	0.004938	0.0007	0.0247	0.0254	0
0.75	50	50	0.006927	0.00708	0.006978	0.008202	0.005958	0.0010	0.0298	0.0308	0
1	50	50	0.007641	0.007743	0.00759	0.015036	0.00657	0.0011	0.0329	0.0339	0
0.25	75	25	0.004683	0.004734	0.00453	0.00912	0.00453	0.0002	0.0227	0.0227	0
0.5	75	25	0.005958	0.005958	0.005907	0.013098	0.005601	0.0004	0.0280	0.0283	0
0.75	75	25	0.007488	0.007284	0.007233	0.018912	0.006876	0.0006	0.0344	0.0347	0
1	75	25	0.008661	0.00861	0.008559	0.023043	0.008202	0.0005	0.0410	0.0414	0
0.25	100	0	0.004938	0.004938	0.004938	0.010854	0.005091	-0.0002	0.0255	0.0253	0

Appendix B (Continued)

0.5	100	0	0.006774	0.006774	0.006723	0.017892	0.006519	0.0003	0.0326	0.0328	0	
0.75	100	0	0.008406	0.008355	0.008304	0.023706	0.007998	0.0004	0.0400	0.0403	0	
1	100	0	0.009783	0.009783	0.009681	0.028347	0.009732	0.0001	0.0487	0.0486	0	

Oxidant Volume (ppm Cl_2)	**% DEA**	**% TEA**	**% ClO_2**	**% OCl^-**	**A (ppm Cl_2)**	**B (ppm Cl_2)**	**C (ppm Cl_2)**	**D (ppm Cl_2)**	**G (ppm Cl_2)**	***FAC (ppm Cl_2)***	***Chlorine Dioxide (ppm Cl_2)***	***Total Available Cl_2 (ppm)***	***Chlorite (ppm Cl_2)***
0	0	100	0	0	0.003102	0.003204	0.003357	0.003459	0.003357	0.0000	0.0168	0.0168	0.0000
0.25	0	100	0	100	0.003969	0.003969	0.00402	0.004122	0.003255	0.0007	0.0163	0.0170	0.0000
0.5	0	100	0	100	0.00453	0.004632	0.004632	0.004683	0.003255	0.0013	0.0163	0.0177	0.0000
0.75	0	100	0	100	0.005295	0.005448	0.005397	0.005397	0.003306	0.0020	0.0165	0.0186	0.0000
1	0	100	0	100	0.005907	0.00606	0.00606	0.005907	0.003306	0.0026	0.0165	0.0193	0.0000
0.25	0	100	25	75	0.004122	0.004173	0.004173	0.005652	0.003306	0.0008	0.0165	0.0174	0.0000
0.5	0	100	25	75	0.004836	0.004989	0.00504	0.007998	0.003306	0.0015	0.0165	0.0183	0.0000
0.75	0	100	25	75	0.005958	0.006009	0.00606	0.010242	0.003306	0.0027	0.0165	0.0193	0.0000
1	0	100	25	75	0.006723	0.006876	0.006876	0.012435	0.003255	0.0035	0.0163	0.0199	0.0000
0.25	0	100	50	50	0.004377	0.004428	0.004479	0.007692	0.003357	0.0010	0.0168	0.0179	0.0000
0.5	0	100	50	50	0.005499	0.005652	0.005703	0.011211	0.003459	0.0020	0.0173	0.0195	0.0000
0.75	0	100	50	50	0.006774	0.006723	0.006672	0.014475	0.00351	0.0033	0.0176	0.0207	0.0000
1	0	100	50	50	0.007896	0.007947	0.007845	0.018249	0.00351	0.0044	0.0176	0.0219	0.0000
0.25	0	100	75	25	0.004683	0.004581	0.004683	0.008916	0.003663	0.0010	0.0183	0.0193	0.0000
0.5	0	100	75	25	0.00555	0.00555	0.005652	0.014118	0.003102	0.0024	0.0155	0.0181	0.0000
0.75	0	100	75	25	0.006723	0.006672	0.006621	0.0183	0.003153	0.0036	0.0158	0.0192	0.0000

Appendix B (Continued)

1	0	100	75	25	0.008508	0.008508	0.008457	0.022686	0.003102	0.0054	0.0155	0.0227	0.0018
0.25	0	100	100	0	0.004785	0.004785	0.004836	0.011262	0.003153	0.0016	0.0158	0.0174	0.0000
0.5	0	100	100	0	0.006417	0.006417	0.006315	0.017535	0.003051	0.0034	0.0153	0.0185	0.0000
0.75	0	100	100	0	0.008151	0.0081	0.007998	0.022992	0.003153	0.0050	0.0158	0.0230	0.0024
1	0	100	100	0	0.009528	0.009528	0.009477	0.02748	0.003204	0.0063	0.0160	0.0275	0.0052

Oxidant Volume (ppm Cl_2)	**% DEA**	**% TEA**	**% ClO_2**	**% OCl^-**	**A (ppm Cl_2)**	**B (ppm Cl_2)**	**C (ppm Cl_2)**	**D (ppm Cl_2)**	**G (ppm Cl_2)**	***FAC (ppm Cl_2)***	***Chlorine Dioxide (ppm Cl_2)***	***Total Available Cl_2 (ppm)***	***Chlorite (ppm Cl_2)***
0	25	75	0	0	0.003051	0.003051	0.003102	0.003306	0.003106	0.0000	0.0155	0.0155	0.0000
0.25	25	75	0	100	0.003867	0.003867	0.003867	0.00402	0.003051	0.0008	0.0153	0.0161	0.0000
0.5	25	75	0	100	0.004581	0.004581	0.004581	0.004734	0.003153	0.0014	0.0158	0.0172	0.0000
0.75	25	75	0	100	0.005244	0.005397	0.005395	0.005346	0.003153	0.0021	0.0158	0.0180	0.0000
1	25	75	0	100	0.006162	0.006111	0.00606	0.006009	0.003153	0.0030	0.0158	0.0187	0.0000
0.25	25	75	25	75	0.00402	0.004071	0.004071	0.007539	0.003051	0.0010	0.0153	0.0163	0.0000
0.5	25	75	25	75	0.00504	0.004989	0.00504	0.007998	0.003102	0.0019	0.0155	0.0174	0.0000
0.75	25	75	25	75	0.006162	0.00606	0.006009	0.01065	0.003153	0.0030	0.0158	0.0186	0.0000
1	25	75	25	75	0.00708	0.007131	0.00708	0.013098	0.003204	0.0039	0.0160	0.0199	0.0000
0.25	25	75	50	50	0.004377	0.004377	0.004428	0.007488	0.003204	0.0012	0.0160	0.0172	0.0000
0.5	25	75	50	50	0.005652	0.005652	0.00555	0.010956	0.003306	0.0023	0.0165	0.0188	0.0000
0.75	25	75	50	50	0.006723	0.006672	0.006672	0.014475	0.003459	0.0033	0.0173	0.0205	0.0000
1	25	75	50	50	0.007896	0.007947	0.007845	0.017841	0.003357	0.0045	0.0168	0.0213	0.0000
0.25	25	75	75	25	0.004887	0.004938	0.004938	0.009681	0.003357	0.0015	0.0168	0.0184	0.0000
0.5	25	75	75	25	0.00657	0.006264	0.006213	0.014373	0.003612	0.0030	0.0181	0.0207	0.0000

Appendix B (Continued)

0.75	25	75	75	25	0.007743	0.007641	0.007284	0.018402	0.003561	0.0042	0.0178	0.0215	0.0000
1	25	75	75	25	0.008916	0.008865	0.008559	0.022584	0.003612	0.0053	0.0181	0.0230	0.0000
0.25	25	75	100	0	0.004836	0.004836	0.004785	0.011211	0.003051	0.0018	0.0153	0.0170	0.0000
0.5	25	75	100	0	0.006264	0.006315	0.0062213	0.016872	0.003102	0.0032	0.0155	0.0186	0.0000
0.75	25	75	100	0	0.0081	0.008049	0.007998	0.023043	0.003102	0.0050	0.0155	0.0230	0.0026
1	25	75	100	0	0.009579	0.009579	0.009579	0.28041	0.003102	0.0065	0.0155	0.2804	0.2584

Oxidant Volume (ppm Cl_2)	**% DEA**	**% TEA**	**% ClO_2**	**% OCl^-**	**A (ppm Cl_2)**	**B (ppm Cl_2)**	**C (ppm Cl_2)**	**D (ppm Cl_2)**	**G (ppm Cl_2)**	***FAC (ppm Cl_2)***	***Chlorine Dioxide (ppm Cl_2)***	***Total Available Cl_2 (ppm)***	***Chlorite (ppm Cl_2)***
0	50	50	0	0	0.003051	0.003051	0.003051	0.003204	0.003051	0.0000	0.0153	0.0153	0.0000
0.25	50	50	0	100	0.003867	0.003816	0.003918	0.004071	0.003153	0.0007	0.0158	0.0165	0.0000
0.5	50	50	0	100	0.00453	0.004581	0.004581	0.004836	0.003153	0.0014	0.0158	0.0172	0.0000
0.75	50	50	0	100	0.005346	0.005346	0.005346	0.005652	0.003204	0.0021	0.0160	0.0182	0.0000
1	50	50	0	100	0.006111	0.06162	0.006111	0.006315	0.003204	0.0029	0.0160	0.0189	0.0000
0.25	50	50	25	75	0.004122	0.004071	0.004122	0.005958	0.003051	0.0011	0.0153	0.0163	0.0000
0.5	50	50	25	75	0.004989	0.005091	0.00504	0.008202	0.003153	0.0018	0.0158	0.0177	0.0000
0.75	50	50	25	75	0.005958	0.00606	0.006009	0.01497	0.003102	0.0029	0.0155	0.0184	0.0000
1	50	50	25	75	0.00708	0.007131	0.00708	0.013047	0.003153	0.0039	0.0158	0.0197	0.0000
0.25	50	50	50	50	0.004428	0.004479	0.004479	0.007845	0.003204	0.0012	0.0160	0.0173	0.0000
0.5	50	50	50	50	0.005703	0.005754	0.005754	0.012282	0.003204	0.0025	0.0160	0.0186	0.0000

Appendix B (Continued)

0.75	50	50	50	50	0.006876	0.006876	0.006876	0.021666	0.003153	0.0037	0.0158	0.0217	0.0022
1	50	50	50	50	0.008049	0.0081	0.008049	0.019422	0.003255	0.0048	0.0163	0.0211	0.0000
0.25	50	50	75	25	0.00453	0.00453	0.004479	0.009222	0.003153	0.0014	0.0158	0.0171	0.0000
0.5	50	50	75	25	0.006111	0.00606	0.006111	0.015189	0.003051	0.0031	0.0153	0.0183	0.0000
0.75	50	50	75	25	0.003102	0.003102	0.003102	0.018708	0.003102	0.0000	0.0155	0.0187	0.0032
1	50	50	75	25	0.008559	0.008559	0.008457	0.023196	0.003102	0.0055	0.0155	0.0232	0.0023
0.25	50	50	100	0	0.004734	0.004785	0.004683	0.010752	0.003102	0.0016	0.0155	0.0171	0.0000
0.5	50	50	100	0	0.006417	0.006621	0.006468	0.017586	0.003102	0.0033	0.0155	0.0189	0.0000
0.75	50	50	100	0	0.007896	0.007947	0.007845	0.022584	0.003255	0.0046	0.0163	0.0226	0.0017
1	50	50	100	0	0.009171	0.00912	0.00912	0.026154	0.003255	0.0059	0.0163	0.0262	0.0040

Oxidant Volume (ppm Cl_2)	**% DEA**	**% TEA**	**% ClO_2**	**% OCl^-**	**A (ppm Cl_2)**	**B (ppm Cl_2)**	**C (ppm Cl_2)**	**D (ppm Cl_2)**	**G (ppm Cl_2)**	***FAC (ppm Cl_2)***	***Chlorine Dioxide (ppm Cl_2)***	***Total Available Cl_2 (ppm)***	***Chlorite (ppm Cl_2)***
0	25	75	0	0	0.003102	0.003051	0.003051	0.003255	0.003153	0.0000	0.0158	0.0157	0.0000
0.25	25	75	0	100	0.003816	0.003714	0.003714	0.005805	0.003	0.0008	0.0150	0.0157	0.0000
0.5	25	75	0	100	0.004479	0.004479	0.00453	0.006468	0.003051	0.0014	0.0153	0.0167	0.0000
0.75	25	75	0	100	0.005346	0.005244	0.005244	0.007437	0.003102	0.0022	0.0155	0.0177	0.0000
1	25	75	0	100	0.005958	0.005907	0.005958	0.007641	0.003051	0.0029	0.0153	0.0182	0.0000

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