

**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

in partial fulfilment of the requirements of the degree of

Master of Science

Department of Civil Engineering

University of Manitoba

Winnipeg, Manitoba, Canada

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Abstract

The objectives of this work were 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 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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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.

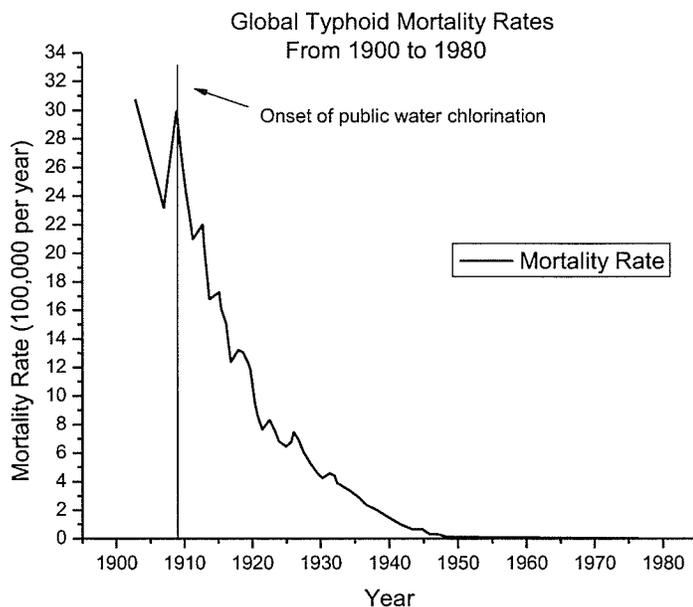
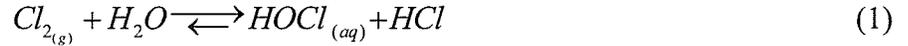


Figure 1: Global typhoid mortality rates exemplifying the effects of large scale chlorination, figure adapted from American Water Works Association, 2006.

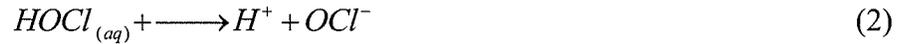
One of the greatest advantages gained from the use of chlorine is the ability to effectively achieve a broad-spectrum germicidal potency, while simultaneously allowing for residual disinfection throughout drinking water distribution systems. Furthermore, chlorine also permits the control of various taste 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).



Equation (1) is then followed by the partial dissociation of the weak acid, hypochlorous acid, to the hypochlorite anion, presented in equation (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 ($pK_{a_{HOCl}} = 7.5$). 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)).

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

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.

$$K_{ocl^-} = \frac{[H^+][OCI^-]}{[HOCl]} = 3 \times 10^{-8} \text{ M at } 25^\circ\text{C} \quad (4)$$

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

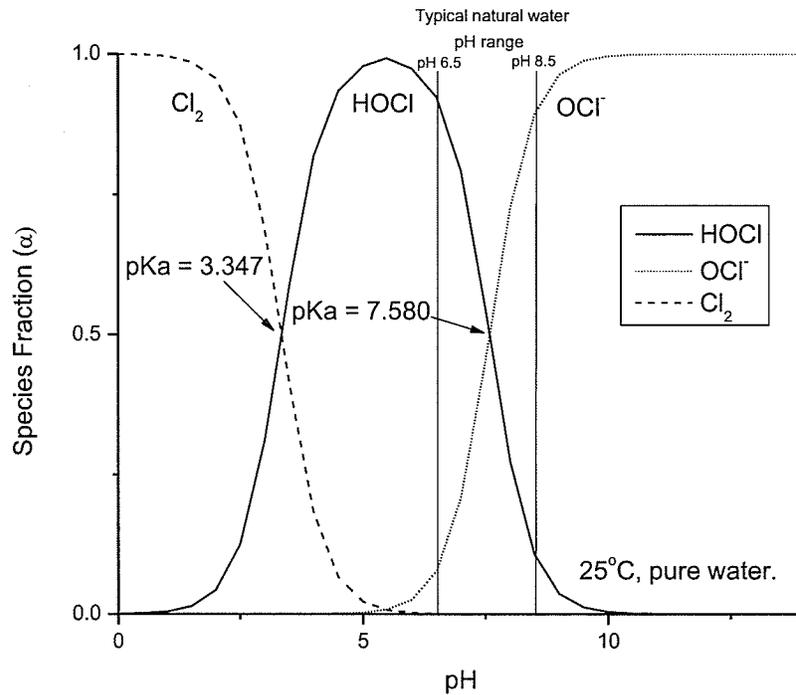


Figure 2: Distribution of Cl_2 , $HOCl$, and OCI^- as a function of pH in pure water.

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.