

COMPARATIVE ANALYTICAL METHODS FOR THE MEASUREMENT OF CHLORINE DIOXIDE

by

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(ABSTRACT)

Four commercially available methods used for the analysis of low-level Chlorine Dioxide (ClO_2) concentrations in drinking water were evaluated for accuracy and precision and ranked according to cost, efficiency and ease of the methods under several conditions that might be encountered at water treatment plants.

The different analytical methods included:

1. The DPD (N, N-diethyl-p-phenylenediamine) method
2. Lissamine Green B (LGB) wet-chemical method
3. Palintest[®] kit LGB
4. Amperometric titration

All these tests were performed with standard 1.0 mg/L ClO_2 either alone or in the presence of different chlorine species, including chlorite ion (ClO_2^- , 0.5 mg/L), chlorate ion (ClO_3^- , 0.5 mg/L) and chlorine (Cl_2 , 1.0 mg/L). The tests were performed with four different matrices, with different concentrations of 0.1 mg/L ClO_2 , 0.5 mg/L ClO_2 and 1.0 mg/L ClO_2 at a constant temperature of 20°C and at different temperatures of 0°C, 10°C and 20°C at a fixed ClO_2 concentration of 1.0 mg/L.

None of the four methods produced the desired level of either accuracy or precision. For all four methods, interference to the measured ClO_2 concentration from the addition of ClO_2^- , ClO_3^- , and Cl_2 was minimal when the methods were performed according to specifications. The Palintest[®] was the best all-round method because it was easy to perform, performed well at all concentrations tested, and its colored product was stable. The HACH[®] DPD method was also easy to perform and gave the best results when measuring concentrations of 1.0 mg/L ClO_2 . The DPD method was less accurate than the Palintest[®] at lower concentrations. The DPD colored product that formed upon reaction of ClO_2

and DPD was unstable, making it necessary to measure the intensity of the colored product at exactly 1 minute. The amperometric titration and lissamine green methods were more cumbersome and time-consuming to perform than either the DPD or Palintest[®] methods; for this reason they are less desirable for routine use.

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This thesis is dedicated to my Parents.

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CHAPTER I

INTRODUCTION

Chlorine dioxide (ClO_2) is an attractive alternative to chlorine for the treatment of drinking water in that it does not react with organic matter to form trihalomethanes (THM) or haloacetic acids (HAA). In addition, it is effective over a wide pH range for the inactivation of bacteria and viruses and is an effective oxidant for manganese and iron control. The Blacksburg, Christiansburg, VPI (BCVPI) Water Authority plans to substitute ClO_2 for chlorine as a preoxidant and delay the application of chlorine until flocculation is complete.

Though the analytical chemistry for ClO_2 compared to that of chlorine is more complex and less understood, as evidenced by various surveys (Gordon 1996), there have been numerous attempts to evaluate the relative advantages and disadvantages of measuring ClO_2 . A number of methods have been used and proposed for the measurement of ClO_2 . The analytical chemistry of ClO_2 , especially in solution, is complicated by its volatility, its sensitivity to light and instability over time, and interference from related redox species. The interference of the by-product formation when using ClO_2 as a disinfectant is of great concern. Chlorite ion and ClO_3^- are always potential by-products when ClO_2 is used as a disinfectant. Chlorite ion in waters containing free available chlorine or water with $\text{pH} < 4$ will react to form various levels of ClO_2 , Cl^- , and possibly ClO_3^- . Some of the analytical techniques are labor-intensive, use expensive equipments, and require a high degree of technical skill. Comparative studies have been done for different analytical methods to measure the concentration of ClO_2 effectively. Currently several methods are available, but no one method is universal in its ability to accurately and precisely monitor ClO_2 and other chlorine species in drinking water (Dietrich 1992).

The study described in this thesis was designed to measure the ClO_2 concentration using different analytical techniques for future reference of the BCVPI Water Authority's Water Treatment Plant, which provides drinking water at an average rate of seven million gallons per day to the two towns and the University.

The analytical methods were evaluated in solutions of different temperatures that were selected to represent the range of temperatures experienced at the BCVPI Water Authority's WTP. Depending upon the temperature throughout the year, the ClO₂ dosage variation was studied at a laboratory scale. The responses of the different tests at different concentration and different temperatures with varied matrices under consideration were studied. The objectives of the project in the thesis were:

- To evaluate an analytical method that would be ideal for the measurement of ClO₂ concentration in the water treatment plant. Several parameters such as cost, time, interference from other chlorine species, and accuracy and precision; were considered during the evaluation of various methods.
- To evaluate the effects of different matrices including the presence and absence of the oxy-chloro species on the ClO₂ analysis.
- To evaluate the effect of the different temperatures on the measurement of ClO₂.
- To evaluate the effect of the different concentrations on the measurement of ClO₂.

CHAPTER II

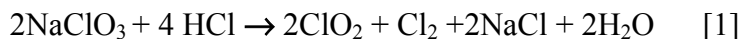
LITERATURE REVIEW

This chapter presents a review of the scholarly work previously completed on the topic of ClO₂ as a water oxidant and disinfectant. Among the subjects here covered include the history and use of ClO₂, its basic properties, how it is generated, its possible applications in water treatment, and methods for its measurement.

HISTORY AND USE OF CHLORINE DIOXIDE

The recent renewal of interest in ClO₂ as an oxidant and disinfectant for public drinking water stems from two related factors. First, it was sparked by the United States Environmental Protection Agency's decision to impose a rule limiting the THM level in all municipal water supplies to 0.10 mg/L. Additionally, ClO₂ was of interest as an alternative to chlorine because it does not react with organic matters to form THMs, provides a more palatable taste, minimizes odor, oxidizes iron and manganese, and reduces oxidant-enhanced coagulation-sedimentation.

Such attention actually is not new. Since its creation in 1811 by English chemist Sir Humphrey Davy, who used H₂SO₄ to synthesize it from the acidification of KClO₃, ClO₂ has been the repeated focus of research. Its versatility and increased importance as an industrial chemical make it a likely subject for study. Over the passage of time, the original H₂SO₄ was replaced by HCl, while KClO₃ was replaced by NaClO₃ for large-scale production (White 1999).



The successful ability of ClO₂ to control phenol-related tastes and odor by oxidizing low-threshold odor compounds led to its first use in the United States in the 1940s, when it was utilized in treatment plants along the Niagara River in New York State (Gates 1998 citing Aston 1947). The clear success of its application in New York quickly led civic leaders and scientists to rely on it for quelling related odor problems in additional municipal potable water treatment facilities (McCarthy 1945; Synan 1945;

Vincent 1946). Regardless of its value in this area, however, during the 1960s-70s, ClO₂ was increasingly abandoned because of a variety of problems related to its implementation. Equipment and installation design problems, as well as the growing cost of chemicals related to its use, provided some of the reasons for ClO₂ to be abandoned. Other factors involved the destruction of facilities due to the corrosive nature of the chemical's highly alkaline precursor solution, the poor conversion rate of earlier chemicals into ClO₂ and inadequate dose control (Gates 1998).

Despite this two decade-long series of setbacks, though, beginning in the 1980s ClO₂ again captured the interest of scientists studying the potential of again using it to treat drinking water. Currently in Northern America, ClO₂ is used full-time in as many as 500 water utilities and on a short-term or seasonal basis in up to 900 plants (Hoehn 1993). Clearly, its popularity has been reclaimed.

BASIC PROPERTIES AND CHEMISTRY OF ClO₂

At room temperature, ClO₂ is an unstable gas, a property that prevents it from being used in high concentration. Usually the chemical can be used effectively only after its compression into a liquid, with a boiling point of 11⁰C and a melting point of -59⁰ C (Sconce 1962). In its pure liquid form, ClO₂ possesses an oily dark amber color and at temperatures above -40⁰F (-40⁰C) is extremely unstable, even to the point of being explosive (Gates 1998; Kirk Othmer 1964). This instability prevents economic shipment and storage of the chemical; generally, it must be generated in situ.

The high solubility of ClO₂ in water, particularly when it is chilled, is one of the most important properties of the chemical. For example, while at 20⁰C and atmospheric pressure the solubility of chlorine is about 7 g/L, that of ClO₂ is about 70 g/L (Gordon *et al* 1972). A solution of ClO₂ is greenish-yellow and smells very similar to chlorine. In air, ClO₂ can be detected at concentrations as low as 0.3 ppm. Several important characteristic and properties of ClO₂ are listed in Table 1.

Table 1: Physical properties of chlorine dioxide. (Don Gates 1998 citing Kaczur and Cawlfeld 1993)

Molecular weight	67.452 g/mol
Melting point	-59 ⁰ C
Boiling point	11 ⁰ C
Vapor pressure, 0 ⁰ C	490 mm Hg
Solubility limit, aqueous, 25 ⁰ C, 34.5 mm Hg	~3 g/L
Solubility limit, aqueous, 0-5 ⁰ C, 70-100 mm Hg	~20 g/L
Solubility limit, aqueous, 20 ⁰ C, 760 mm Hg	~70 g/L
Solubility limit, hexane, 22 ⁰ C	~60g/L
Miscibility limit, liquid –aqueous	~60g/L
Heat of formation at STP	25Kcal/mol
Heat of vaporization STP	6.52Kcal/mol
Heat of solution STP	6.6Kcal/mol
Explosion velocity, pure (non aqueous) ClO ₂	1,250 m/s
Explosion velocity, ClO ₂ in air	50 m/s
Molar absorptivity, E _(360 nm)	1,250 cm ⁻¹ M ⁻¹

Chlorine dioxide requires a number of safeguards to ensure its stability on several levels. Due to its extreme volatility while in solution, ClO₂ is best kept in closed containers (White 1999). Moreover, it photolytically decomposes to ClO₃⁻ when exposed to ultraviolet light, to maintain its strength and avoid such decomposition it should be stored in the dark (Gordon *et al* 1972). Additionally, as the following reaction indicates, in waters with high pH content, the chemical will disproportionate to ClO₂⁻ and ClO₃⁻ (Gordon *et al* 1994 citing Rosenblatt 1978):



To prevent disproportionation from occurring, a pH level between 2 and 10 must be maintained in the solution.

In addition to taking measures meant to prevent decomposition, those who work with ClO₂ must also take care to decrease its volatility. For example, in its gas form,

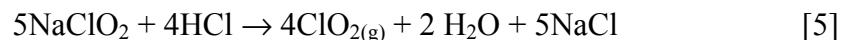
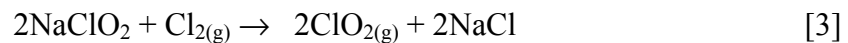
ClO₂ is potentially explosive if in concentrations greater than 10 percent by volume in air or at a pressure greater than 76 mm Hg (1.46 psig). Should it then contact a flammable organic solvent or such oxidized materials as plastic, rubber, cork, or sulfur, denotation will most likely occur. Also, in this condition the chemical is very pressure sensitive and, if compressed for storage or shipping, it can quickly and violently decompose. Even in its aqueous form, ClO₂ possesses some risk. Because ClO₂ does not hydrolyze in water, it remains a highly soluble gas above 11⁰C over a broad range of pH (2-10). Logically, ignition sources such as electric discharges or sparks, heat, and open flame can make such a solution explode or decompose; surprisingly, though, even exposure to bright light—however brief—can bring about detonation flame (Gates 1998 citing Kaczur and Cawfield 1993; Cowley 1993). Ultraviolet light and even fluorescent lights can lead to photolysis (Zika 1985; Griese *et al.*1992).

GENERATING CHLORINE DIOXIDE

Almost universally in the water treatment industry, ClO₂ is produced by reacting NaClO₂ solutions with an oxidizing agent in a mechanical generator. According to Gates (1998) “Depending on generator design, the oxidizing agent is usually:

- (1) gaseous or aqueous chlorine,
- (2) a mineral acid alone or with chlorine, or
- (3) an acid combined with a hypochlorite salt solution.”

For its use in the treatment of drinking water, the most common route to generating ClO₂ involves using the solid or solution form of NaClO₂ in reaction with either chlorine gas (Cl₂), hypochlorous acid (HOCl), or hydrochloric acid (HCl), as shown in the following reactions (Gates 1998 citing Aieta and Berg 1986; Gordon *et al* 1972).



Reactions [3] and [4] indicate that if the reactants are in high enough concentrations, an unstable intermediate— Cl_2O_2 —is formed rather than ClO_2 . On the other hand, under one of the following conditions, ClO_3^- will form: if the concentration of ClO_2^- is low, if the concentration of initial reactants is low, or if there is an excess of chlorine or hypochlorous acid. In the cases of high levels of initial reactants or excessive ClO_2^- concentrations, the intermediate decays to ClO_2 (Ellenberger 1999 citing Gordon and Rosenblatt 1996). Of these potential reactions, the reaction [5] results in an 80 percent conversion of NaClO_2 to ClO_2 , making it far less successful. Because the generator used in this process has become obsolete; the final reaction is no longer used.

Recently, an improved method has been developed for generating a high purity ClO_2 through the reaction of solid NaClO_2 with chlorine gas (Gordon and Rosenblatt 1996). The first step in the process involves mixing the chlorine gas with humidified air. Once this mixture has been achieved, it is passed through a series of cylinders loaded with solid NaClO_2 . Because the resulting ClO_2 occurs as a gas, this method prevents unreacted NaClO_2 from entering the system, and no ClO_3^- is produced.

DISINFECTION BY PRODUCT FORMATION

As the previous discussions suggest, the central byproducts involved with the use of ClO_2 as a disinfectant are ClO_2^- and ClO_3^- . In the case of its use in potable water and wastewater treatment, for example, when normal pH ranges are present, ClO_2 reacts with organic compounds and becomes reduced to ClO_2^- (Masschelein 1979).

When used in treatment facilities, ClO_2 reacts rapidly with any inorganic and naturally occurring biological materials present in the raw water. In the same, the reaction of ClO_2 with any natural organic material produces the byproducts chloride (Cl^-) and ClO_2^- ions, and occasionally ClO_3^- also results (Gordon *et al* 1990). These and other reactions are responsible for the reversion of 70-75 percent of the ClO_2 dose to ClO_2^- . This number varies, of course, depending upon the site, existing pH levels, the amount of light, the pre-existing water quality, and the design of the facility itself, among other factors.

Studies have indicated the amount of reversion is possible among varying sites and conditions. One such project, for example, indicates that when ClO_2 was added to

river water, after 48 hours, 48 percent of the initial dose was recovered as ClO_2^- , 28 percent as Cl^- and 22 percent as ClO_3^- (Miltner 1976). Likewise, in drinking water from other sources, additional studies by Werdehoff and Singer (1987) and Naock and Doer (1981) resulted in 70 percent conversion of ClO_2 to ClO_2^- , with the remaining 30 percent divided equally between ClO_3^- and Cl^- (Gates 1998).

Several other factors can also affect ratios. Bright sunlight, aeration, and recarbonation can result in daily or seasonal variations in the ratios of ClO_2^- to ClO_3^- . In fact, sunlight proves to be one of the most significant factors. For example, the ability of sunlight to decompose ClO_2 —a fact that has been effectively documented—could explain why, following applications of the chemical, affected plants do not recover a ClO_2 residual (Thomson 1993; Zika *et al* 1985). In addition to these factors, the quality of the source water and even the differences in unit processes can dramatically affect results.

Chlorite ion is the main byproduct of reactions involving the introduction of ClO_2 to water. As indicated by the following half-reaction, ClO_2 is reduced by the transfer of a single electron, which results in ClO_2^- (White 1972; Gordon *et al* 1972):



In potable water that has been treated with ClO_2 , the ClO_2^- levels can vary from between 30-70 percent of the initial dose. Of course, the exact variation depends on such factors as temperature, oxidant demand, the presence of other chemicals or processes that can bring about competitive side reactions, and even the efficiency of the generator (Gates citing Hoehn 1993; Lafrance *et al* 1993; Werdehoff and Singer 1987). The level of ClO_2^- can also be affected by the initial dosage of ClO_2 , and the amount of residual ClO_2^- can likewise be reduced by exposure to sunlight (Zika *et al* 1985; Thomson 1993; Shelton 1996). After water passes through treatment plants and into general systems designed for distribution, the ClO_2^- levels generally decrease.

OCCURRENCE OF CHLORITE ION

When ClO_2 is used to disinfect water in treatment facilities, ClO_2^- can be generated from two major sources:

1. Generators: Due to the unreacted NaClO_2 feed stock that passes through it and on into the treated water, any generator using solutions of NaClO_2 can serve as sources of ClO_2^- formation.
2. Reduction of ClO_2 : The greatest amount of ClO_2^- is generated by the inherent reduction of ClO_2 as it acts on target compounds (Gallagher *et al* 1994). Given this fact, it can be assumed that up to 70 percent of the initial ClO_2 dosage becomes ClO_2^- (Werdehoff and Singer 1987).

CHLORITE ION MINIMIZATION

As a contaminant, ClO_2^- is strictly regulated. For example, the maximum contaminant limit (MCL) designated by the proposed D/DBP rule is 1.0 mg/L. This means in turn that in order to ensure compliance with such regulations, the maximum dosage of ClO_2 applied to potable water should be around 1.4 mg/L, except in cases where excess ClO_2^- has been previously decreased or removed altogether. Feed stock control in the generator, the proper “tuning” of the generator, and the use of a ClO_2 generation process that will not produce ClO_2^- are three of the most valuable means of keeping ClO_2^- formation to an absolute minimum.

However, despite efforts to control it, should excess ClO_2^- result, one can turn to two chemical processes proven to be effective in eliminating it:

- Reduced iron: In laboratory experiments, on-site trials, and full-scale treatment conditions, reduced iron (i.e. ferrous; Fe^{+2}) has been used successfully to remove ClO_2^- by reducing it to chloride ion (Cl^-) (Knocke and Iatrou 1993, Griese *et al* 1992).



- Sulfite ion: When the pH range is 5.0-6.5, sulfite ion may be used to reduce the ClO_2^- to chloride ions. As with reduced iron, however, varying pH levels can dramatically alter the effectiveness of this method. The reaction is very effective over pH 5-7 and

it becomes virtually useless when the pH range grows high (Gordon and Bubnis 1995). A comprehensive investigation conducted by Sloommaekers *et al* (1989) indicates that, given the proper pH levels, sulfur dioxide/sulfite ion can in fact be quite effective in removing unwanted ClO_2^- :



CHLORATE ION

The United States Environmental Protection Agency is responsible under the Safe Drinking Water Act for ensuring regulation in water of known or suspected contaminants that could pose health risks to the public. Because it results directly from the process of disinfection—and is thus known as a disinfection byproduct (DBP)— ClO_3^- is among the list of potential candidates for regulation (USEPA 1991).

Like ClO_2^- , ClO_3^- is produced under certain conditions when ClO_2 is added to water. It can derive from several sources. When ClO_2 is generated by NaClO_2 and free chlorine, ClO_3^- can be formed (Aieta *et al* 1986; Lykins *et al* 1990; Gordon *et al* 1990). Likewise, since photodecomposition of ClO_2 produces ClO_2^- and ClO_3^- , water that is treated with ClO_2 and then exposed to forms of light in such facilities as open flocculation-sedimentation basins is likely to contain ClO_3^- . The application of ClO_2 , followed by the addition of free chlorine, can also cause creation of ClO_3^- (Gordon *et al* 1991).

Recent investigations suggest that the use of hypochlorite solutions as disinfectants in drinking water can also generate ClO_3^- (Cotton 1988), and that the same can be produced during the manufacture and storage of such solutions (Bolyard 1992; *Comprehensive Inorganic Chemistry* 1973; Wojtowicz 1979). In basic solution, hypochlorite ions have been proven to disproportionate and produce ClO_3^- as in equation [9]:



Should it occur during storage of hypochlorite solutions, such a reaction could bring about increased ClO_3^- levels. Likewise, when photolysis occurs with hypochlorite

solutions in storage, production of ClO_3^- can occur and concentrations of ClO_3^- can increase (Buxton 1972).

Chlorate ion can occur naturally as a contaminant in source water, or it can be introduced in two essential ways: through the use of ClO_2 during treatments or through the use of hypochlorination as a disinfectant. Studies of EPA DBP samples reveal that similar ClO_3^- concentrations in finished water can result from the use of ClO_2 and hypochlorination, which are ultimately believed to be the major sources of such contamination in drinking water.

Efforts continue discovering an effective method for reducing the formation of ClO_3^- when ClO_2 is used to disinfect drinking water. Since it is known that properly tuned ClO_2 generators can dramatically reduce levels of ClO_3^- in the ClO_2 product stream (Aeita *et al* 1984), current research is focused on creating new, improved generators that will reduce or eliminate ClO_3^- (Griese *et al* 1992; Gordon and Rosenblatt 1996). Additionally, the exposure of treated water to light brings about the photodecomposition of ClO_2 , and in turn leads to ClO_2^- and ClO_3^- formation. Efforts are underway to discover an effective method of shielding water from light (Zika *et al* 1985). Moreover, the value of ferrous ion in the removal of ClO_2 and ClO_2^- also is the focus of much continued research (Griese *et al* 1991; Iatrou and Knocke 1992).

In addition to the better-known ClO_2^- and ClO_3^- , the use of ClO_2 might also result in additional byproducts. It can react with humic and fulvic acids to produce quinones, hydroquinones, aldehydes, and carboxylic acids (Rav-Acha 1984). However, because ClO_2 oxidizes rather than chlorinates organic matter, chlorinated byproducts are formed in only part-per-trillion levels (Richardson 1998).

CHLORINE DIOXIDE APPLICATION IN WATER TREATMENT

In the treatment of drinking water, ClO_2 has two primary functions. It is most commonly used as a primary disinfectant and to reduce formation of trihalomethanes (THMs), as a preoxidant alternative to chlorine (Dietrich *et al* 1992). The use of ClO_2 in the United States traditionally involves an initial application, followed by the introduction of free chlorine or chloramines that are used to maintain distribution system residuals (Aieta and Berg 1986).

While disinfection and preoxidation serve as its major functions, ClO_2 can be used for several other purposes as well. For example, because of its particular chemical characteristic, it has been put to use quite successfully in half a dozen or more water quality control practices involving such diverse purposes as the managing of periodic taste and odor events and the control of THMs and total organic (TOX) levels. It has also proven useful in the control of *Cryptosporidium*, nitrification, and nuisance algae growth in plant basins.

Due to these very unique chemical qualities, ClO_2 can be used to complement the more common disinfectants chlorine and chloramine. A neutral gaseous compound, its solubility increases in cold water, where it can remain longer, thus greatly enhancing its antimicrobial potential.

In addition to possessing these qualities, although some values are close to those for chlorine in waters at neutral pH, the Concentration X Time (C X T) values associated ClO_2 are usually lower than those required for chlorine or chloramines. Generally, in situations where higher pHs and lower temperatures come into play, the use of ClO_2 is much preferred over that of free chlorine because it requires significantly lower C X T values to achieve adequate disinfection. By controlling residual loss through volatilization, water with a cooler temperature promotes extended ClO_2 retention.

The benefits of ClO_2 are many. First and foremost, it has been proven an effective agent against the bacteria, viruses, protozoan cysts, and *Cryptosporidium* often found in untreated public water sources (Sobsey *et al* 1989; USEPA 1990; Peeters *et al* 1989; Korich *et al* 1990; Finch, Liyanage, and Belosevic 1995). It acts primarily by directly oxidizing the tyrosine-, methionyl-, or cystein- portions of the proteins in

microorganisms, thus interfering with central structural regions of metabolic enzymes or membrane components. In essence, through this process ClO₂ deactivates the microorganisms (Alvarez 1982). As an added bonus, due to the broad-spectrum antimicrobial capabilities of ClO₂, many of the most prevalent microbial species are prevented from developing resistance to the chemical, thus ensuring its continued success.

Research has long established the positive properties of ClO₂. For example, in 1947, Ridenour and Ingols reported that the chemical's ability to destroy spores on an equal residual basis far surpassed that of chlorine (Ridenour *et al* 1947). Two years later, another test—this time by Ridenour and Armbruster—determined that in concentrations of less than 0.1 mg/L, in water with a temperature of between 5⁰C and 20⁰C and pH values of about 7, ClO₂ took just five minutes of contact to destroy such common water pathogens as *Eberthella typhosa*, *Shigella dysenteriae* and *Salmonella paratyphi B* (Ridenour and Armbruster 1949). Increased pH levels only made the chemical more effective.

Such research proving the superiority of ClO₂ to chlorine continued unabated into the 1950s and beyond. In 1953, for example, Hettische and Ehlbeck (1953) proved that ClO₂ proved superior to chlorine and ozone in its action on the poliomyelitis virus. A later study by Ridenour and Ingols (1957) not only validated that ClO₂ was as effective in its disinfecting properties as chlorine but also established that, unlike that of chlorine, the bactericidal efficiency of ClO₂ remained unaffected by pH values from 6-10.

Research conducted by Malpas in 1973 resulted in the knowledge that against *E. coli*, *Salmonella Typhosa* and *Salmonella paratyphi*, ClO₂ proved as effective as chlorine in its bactericidal efficiency (Malpas 1973). In addition, subsequent studies have shown it to be effective in the fight against mollusks, such as the zebra mussel (*Dreissena polymorpha*), which have in the past been known to impair the effectiveness of water treatment plants by clogging intake pipes (Griese and Rosenblatt 1996).

ADVANTAGES AND DISADVANTAGES OF CHLORINE DIOXIDE

The use of ClO_2 as a disinfectant in water treatment facilities has both disadvantages and advantages that can be summarized:

Disadvantages

Chlorine dioxide possesses several disadvantages:

- The cost of ClO_2 is far greater than that of chlorine, that could make its use prohibitive in certain applications, particularly in economically deprived Third World regions where even chlorine is not readily affordable.
- Aggressive regulatory monitoring requirements exist related to health issues.
- Its use requires a far more complicated method of analysis, as well as more highly skilled operators.
- Specialized mechanical equipment to generate ClO_2 may still be required.
- The need exists to store two or three chemicals, not just one as is the case with chlorination.
- It cannot be transported as a compressed gas; it must be generated on-site.
- As prepared by some processes, it may contain significant amounts of free chlorine, which could defeat the objective of using ClO_2 to avoid the formation of THMs.

Advantages

On the other hand, ClO_2 also has distinct advantages:

- It acts as an effective, fast-acting, broad-spectrum bactericide.
- As a viricide, it is superior to chlorine, which makes it a promising candidate for water reuse disinfection.
- It kills chlorine-resistant pathogens such as encysted parasites *Giardia* and *Cryptosporidium*.
- It does not react with ammonia nitrogen or primary amines.
- It does not react with oxidizable organic material to form trihalomethanes.
- It destroys THM precursors and enhances coagulation.

- It is excellent for the destruction of phenols, which cause taste and odor problems in potable water supplies.
- It has a long track record in the removal of iron and manganese. It is superior to chlorine, particularly when the iron and manganese occur in complexed compounds.
- It involves decreased formation of halogenated DBPs (THMs, TOX, and HAAs), assuming well-maintained generators.
- It provides improved taste-and-odor control for algal-related compounds, as well as reduced color problems.
- It promises improved C X T credits over a broader pH range.
- It allows for better *Giardia* and *Cryptosporidium* control than do chlorine and chloramines.

NON-DISINFECTION USES OF CHLORINE DIOXIDE

In addition to its value as a disinfectant, ClO₂ is used for a variety of other purposes, such as to control water taste and odor, reduce manganese levels, and remove iron.

Control of Taste and Odor

Chlorine dioxide has often been used to ensure that the taste and odor of municipal water supplies remains palatable. As previously stated, the first concentrated use of ClO₂ in a water treatment plant in the United States occurred in the No. 2 Niagara Falls Plant beginning in January 1944. There, it served the valuable purpose of controlling phenolic tastes and odor, as well as those that arise naturally in water, particularly during summer, due to algae and vegetation decomposition (Synan *et al* 1945; Aston 1947). Similarly, a treatment facility in Alberta, Canada, used the chemical as a disinfectant to remove chlorophenolic and other tastes and odors from its municipal water supply, thereby establishing another valuable use (Walker *et al* 1986).

For three basic reasons, ClO₂ is the most effective and efficient chemical to use in controlling tastes and odors that arise from phenolic compounds:

1. Chlorine dioxide reacts more completely and many times more quickly than free available chlorine in eliminating the phenolic compounds that can alter the taste of water.
2. It has been proven by repeated tests to destroy the chlorophenol taste caused by petrochemicals.
3. Its efficiency is increased by a higher pH environment, rather than decreased (as is the case with HOCl).

In addition, ClO₂ has been used effectively to oxidize other compounds that can cause odors and inhibit the taste of water supplies, including mercaptans and disubstituted organic sulfides.

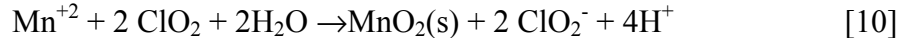
While ClO₂ has proven useful in the oxidation of many taste- and odor-producing compounds, a few remain resistant to its effects. For example, in 1986, Lalezary *et al* reported that even after greater dosages and longer contact times than those generally expected of most water treatments, ClO₂ was capable of decreasing existent geosmin and 2-methylisoboreneol (MIB) concentrations by a mere 30 percent (Lalezary *et al* 1986).

Interestingly, ClO₂ can create its own particular brand of odor. As reported by Hoehn *et al* (1990) and Dietrich *et al* (1992), consumers of ClO₂⁻ treated water report experiencing two types of odor as a result of treatment: first, a strong chlorinous (bleachy) odor, a result of ClO₂ regeneration in the system from ClO₂⁻ in the presence of free chlorine; second, an odor that has been variously described as “oily,” “kerosene-like,” and akin to that of cat litter or even cat urine, which most likely results from a reaction between the gas phase of the water as it runs from the tap and any number of organic substances already present in the atmosphere of homes with new carpet.

Manganese Minimization

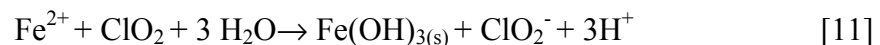
Most impounded water and even a large amount of well-drawn water contains manganese, which even in small quantities can result in offensive “black” water regardless of the distribution system. When manganese is present, it can result in irreparably stained laundry, encrustation of water mains and plumbing fixtures, and ultimately a goodly amount of debris flowing from the water taps them. As an oxidant against manganese, ClO_2 has proven to be a much more effective and faster-acting solution than chlorine (White 1972). Treatment begins with the oxidation of Mn^{+2} to MnO_2 and the subsequent precipitation of manganese dioxide (MnO_2)_(s). Sedimentation or filtration then completes the process of removing the resulting MnO_2 (s), (Knocke *et al* 1987).

The oxidation-reduction reaction that occurs between Mn^{+2} and ClO_2 produces ClO_2^- , which depends upon the transfer of one electron between ClO_2 and ClO_2^- . As Knocke *et al* (1990) have proven, ClO_2^- cannot be used to oxidize Mn (II). The same experimentation notes that the reaction between ClO_2 and Mn^{+2} occurs at a neutral pH:



Iron Removal

Effects similar to those created by manganese—staining of laundry, encrustation of fixtures—can occur as a result of the presence of iron in water. Moreover, iron can also prompt the growth of bacteria in the distribution system (White 1972). To reduce iron, ClO_2 can be used quite effectively. It oxidizes various states of iron, from the moderately soluble ferrous state to the ferric ion resulting in the formation of ferric hydroxide as a heavy gelatinous brown floc, which can be removed by sedimentation followed by filtration. As noted by Knocke *et al* (1990), in water treatment situations, ClO_2 can result in iron oxidation as follows:



ANALYTICAL TECHNIQUES FOR MEASURING CHLORINE DIOXIDE

A recommendation by the US EPA designates that in “finished” water, the combined residuals of ClO_2 , ClO_2^- and ClO_3^- should not exceed 1.0 mg/L. This prohibition means that in cases where the oxidant demand exceeds 1.5 mg/L, ClO_2 cannot be used for the simple reason that the resulting residual ClO_2^- already would be at its maximum level. As a result of this and other regulations limiting the amount of residual disinfectants and DBPs permissible in treated water, the water industry has had to reconsider the methods it uses to measure and analyze ClO_2 , ClO_2^- , and ClO_3^- residuals. Although it was initially believed that simple “test kit” procedures could be used to help the industry meet the new regulations, subsequent review suggests that more sophisticated methods of measurement are demanded: the existent procedures were developed only as general oxidation methods and were subject to varying levels of interference (Gordon *et al* 1987, 1992).

As recorded in the *Standard Methods for the Examination of Water and Wastewater* (1989), several alternative analytical methods have long been available. However, many of these methods present their own peculiar sets of problems. The non-specific nature of the existing methods covering ClO_2 , ClO_2^- and ClO_3^- , for example, have created confusion when attempts have been made to apply them to oxyhalogens. In turn, many of the methods currently used to measure oxyhalogens were developed primarily for chlorine; attempts to modify them for use in measuring ClO_2 , ClO_2^- , and ClO_3^- can be problematical because of potential levels of interference (Gates 1998).

Any successful analytical method should consider such factors as

1. the number of measures available for analysis,
2. the specific details of the methodology;
3. the potential costs,
4. possible detection limits,
5. possible interferences,
6. the technique used for sample preservation,
7. the time and skill required for implementation of the method,
8. the training of personnel that must be undertaken, and

9. calculations for quantitative analysis. (Dietrich 1992)

Obviously, the most desirable analytical method will also be accurate, precise, robust, and sensitive.

Several methods for quantifying ClO_2 , ClO_2^- and ClO_3^- are presently available, including amperometric titration, the DPD method (N,N-diethyl- para phenylene diamine), and the lissamine green B method. These methods, along with the chemistry involved, will be briefly described in the following sections.

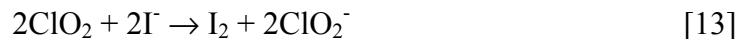
Amperometric Titration

To determine the levels of ClO_2 , chlorine, ClO_2^- and ClO_3^- that exist in any aqueous solution, amperometric titration is the preferred method. Phenyl arsine oxide (PAO) is the titrant used for such determination, and the sample pretreatment required to differentiate between the various chlorine species present can be accomplished by two basic methods: purging (Chen 1967) and pH adjustment (Prince 1964; Tang 1980). This procedure in no way attempts to distinguish between free and combined chlorine.

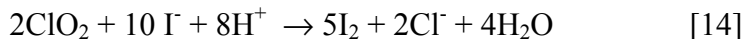
The reactions of chlorine species with iodide pertinent to analysis, along with the pH value at which the reactions become useful for analysis, are shown in Equations 12-16:



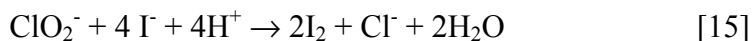
pH: 7.2<0.1



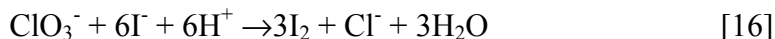
pH: 7



pH: 2<0.1



pH: 2 <0.1



pH<0.1

In order to reduce the existing ClO_2 to chloride, the transfer of five electrons is required (Gordon 1982). The reaction consists of two steps:

- **Step 1:** In order to form ClO_2^- , one electron is transferred to the ClO_2 molecule. The reduction of ClO_2 stops at this point if the reaction pH is at or above 7. This first step is represented by Equation 13, which represents a mere one-fifth of the ClO_2 reduction. Should the reaction pH be lowered to 2, the second step occurs.
- **Step 2:** In Step 2, four more electrons are transferred to the ClO_2^- to complete the reduction of ClO_2 to chloride, as shown in Equation 15.

Equation 13 represents the overall reduction of ClO_2 to chloride. Any ClO_2^- present in the sample generated for Step 2 will likewise be reduced to chloride through the transfer of four electrons. The following represents the reaction of the titrant PAO with iodine:



Precision is key to successful completion of this process. For ClO_2 , the method detection limit is 0.05 mg/L, an exact number that demands of the titration process a precise level of analysis. In addition, because titration relies so completely on calculating the differences between two large numbers, even the smallest of differences in titrant volumes could result in cumulative and potentially destructive errors in measurement. Likewise, at the low pH conditions demanded for proper ClO_2^- and ClO_3^- analysis, the method can be affected by such common place interferences as the presence of dissolved oxygen, manganese, copper, or nitrate (Aieta *et al* 1984). Because they interfere with the amperometric method for free available chlorine, chloramines, too, can potentially interfere with the success of ClO_2 measurements (Jensen and Johnson 1990; Dietrich *et al*, 1992).

The DPD Method

An extension of the popular N,N-diethyl-p-phenylenediamine method of measuring free chlorine and chloramines levels in waters, the DPD method utilizes a methods-by-difference approach (Palin 1960, 1967, 1975). In this process, the success of which depends on a pH measurement of 6.2 to 6.5, glycine is added to the water to eliminate the presence of chlorine. Once introduced, the glycine reacts quickly with any chlorine present to become chloraminoacetic acid, thus halting further reactions.

Due to the rapid and ready oxidation of DPD, numerous adaptations of this method have been used to great success with other oxidant species, particularly ClO_2 and ozone. Under this method, measuring ClO_2 levels requires the implementation of multiple steps to correct for the presence of ClO_2^- , free available chlorine, monochloramine, dichloramine, and total available chlorine.

The DPD colorimetric methods are based on the fact that the amount of colored reactive product produced during the process is in direct proportion to the level of oxidants in the water samples. As a result, several factors can potentially affect the accuracy of the analysis: the addition of I^- vs. the direct oxidation of DPD, the use of appropriate agents for chemical masking, the reproducible addition of reagents, and the presence of interfering species.

For determining the level of free available chlorine and inorganic chloramines, the most widely used and accepted colorimetric method uses DPD as an indicator (*Standard Methods* 1989; Palin 1986). Since DPD is a component of both acid-based and oxidation reactions, it is the oxidation reaction that forms the basis for the colorimetric method here mentioned (Moore 1982). When an oxidant is present, DPD oxidizes to create a highly colored semiquinoid free radical. Using the DPD HACH[®] Kit to measure ClO_2 indicates possible ClO_2^- interference as a result of the continued and irreversible DPD reaction (Gordon 2000).

The Lissamine Green B Method

In 1991, Chiswell and O'Halloran developed yet another method for measuring ClO_2 levels: the Lissamine Green B (LGB) Method, a spectrophotometric procedure which relies on decolorization to indicate levels or the presence of ClO_2 . This test is

based on the oxidation of LGB dye, which results in reduced levels of color absorption. Since LGB is a triphenylmethane dye and since the standard redox potential in LGB is about +1.0 V, this method proves exceptionally useful in determining chlorine species, particularly since most of them have a standard redox potential that equals or is greater than +1.0 V. The use of this reagent with an equal redox potential dramatically reduces the possibility that combined chlorine and ClO_2^- will interfere with the final measurement.

Despite its potential, LGB still remains little used (Chiswell and O'Halloran 1991). Nonetheless, LGB continues to be a promising and interesting reagent primarily because it is not impacted by chlorine interference, a problem common to other ClO_2 reagents, such as DPD. When free available chlorine is present, LGB responds readily to ClO_2 . Moreover, because it is also resistant to combined forms of chlorine, an ammonium buffer system is implemented to provide chlorine inactivation.

The LGB method involves first the addition of an ammonia buffer with a pH level of 9.0 and a reagent solution to a water sample. The sample absorption is then analyzed spectrophotometrically at 614 nm, typically in a 1 cm quartz cuvette. The use of a buffer with a pH level of 9.0 ensures that any free chlorine in the form of hypochlorite, which is a weaker oxidant than hypochlorous acid and less likely to react with the LGB reagent solution. Given higher pH levels, the disproportionation of ClO_2 become increasingly significant.

Hofman *et al* (1998) confirmed initial suppositions that the LGB method was indeed superior to the more common and traditional analytical methods for measuring ClO_2 , which suffer variously from high detection limits, lack of precision, and skewed responses due to interference from oxidants other than ClO_2 . For the LGB method, the method detection limit in reagent water was at 20⁰C calculated to be as low as 0.05 mg/L. In addition to revealing marked levels of precision, when analyzing samples within 20 minutes, this method also proves itself impressively immune to interference by chlorine, ClO_2^- , or ClO_3^- , even at concentration levels as high as 5 mg/L. Finally, chlorine is reacted with ammonia prior to the beginning of the LGB analysis, which suggests that chloramines also do not interfere with measurements. Finally, the LGB method is

potentially more immune to the sorts of color interferences that can occur as the result of organic matter present in the sample.

CHAPTER III

MATERIALS AND METHODS

This chapter discusses the materials and methods utilized in the preparation of this thesis.

REAGENTS

The following ACS certified reagents were purchased from Fisher Scientific: Potassium iodide (CAS 7681-11-0), Phenyl Arsine Oxide (CAS 637-03-6), Ammonium Chloride (CAS 12125-02-9), 4percent Chlorine gas (CAS 7782-50-5) and (CAS 1336-21-6). Three other reagents—sodium chlorite (80 percent) (CAS 7758-19-2), sodium chlorate (99+ percent) (CAS 7775-09-9) and Lissamine Green B (CAS 3087-16-9)—were purchased from Aldrich (Milwaukee, WI).

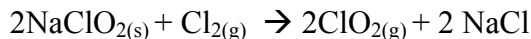
GLASSWARE AND PLASTICWARE

The analytical methods used for this research relied on glassware purchased from Fisher Scientific in Atlanta. Prior to the beginning of the procedure, this glassware was carefully prepared according to a multi-stage process, which began with its overnight soaking in a 1:1 nitric acid bath. The glassware was then rinsed five to six times in deionized water, rinsed the same number of times in distilled water, and then allowed to air dry. All pipettes, beakers, and volumetric flasks were prepared in a like manner, beginning with overnight soaking in a 1:1 acid bath, followed by a soaking in laboratory detergent. These instruments were then washed and cleaned three to four times with distilled, deionized water, and then air-dried.

Except in procedures involving ClO_2 , where it was avoided because of its high ClO_2 demand, plasticware was also utilized. These implements were first cleaned in a bath of water and the detergent Sparkleen[®]. Following this procedure, the plastics were then rinsed with Nanopure[®] water before being allowed to air dry.

CHLORINE DIOXIDE GENERATION

Chlorine dioxide was generated with a CDG laboratory-scale ClO₂ generator. By injecting 4 percent chlorine gas through a proprietary solid NaClO₂ reactor cartridge, a ClO₂ stock solution was produced. A reaction between the chlorine and the NaClO₂, represented by the following equation, generated the ClO₂:



At this point, the ClO₂ created as a result of this procedure was trapped inside standard glass bottles containing chilled distilled water. The bottles containing the ClO₂ were then immersed in an ice bath and, in order to prevent photolytic decomposition of the materials, covered tightly with aluminum foil. When the distilled water in the bottle trap turned a bright yellow-green color, which indicates the presence of ClO₂, the creation of ClO₂ was stopped. When measured, the solution indicated ClO₂ levels of 500 mg/L to 1200 mg/L.

The next step in the process involved the transferring of the stock solution to a brown glass container, which was then refrigerated in a cooler at a temperature of 4°C. After this occurred, and prior to each use, a working ClO₂ solution was created by diluting approximately 50 mg/L of the concentrated stock solution with distilled, deionized Nanopure[®] water. Relying on the Beer-Lambert Law, and using a Beckman (Fuller, California) spectrophotometer (DU[®] 640) set at 360 nm, the exact concentration of the ClO₂ was measured. The following equation applies to this part of the process:

$$\text{Absorbance} = \log(I / I_0) = \epsilon l C$$

Where

I = Intensity of light transmitted through the sample

I₀ = Intensity of light transmitted through the reference blank

ε = Molar absorption of ClO₂ in m⁻¹cm⁻¹

l = cuvette path length, cm

C = concentration of the species of interest in mol/L

By multiplying the molar concentration by 67,450 mg/L/mole, the ClO₂ concentration then could be expressed in mg/L.

EXPERIMENTAL PROCEDURES

The experimental procedure studied several factors, such as the temperature of the raw water and the setup of the water distribution system. The temperature range of the water being treated at the WTP ranges from 0°C to 20°C throughout the year. To account for this fluctuation, the different analytical methods were tested at three different temperatures: 0°C, 10°C and 20°C. Depending upon the temperatures throughout the year, the concentration of ClO₂ to be dozed varies greatly. The same analytical methods were used at different concentrations of 0.1 mg/L ClO₂, 0.5 mg/L ClO₂ and 1.0 mg/L ClO₂ at the temperature of 20°C. Further tests were carried out to study the effect of ClO₂⁻ on the stability of ClO₂ over a period of time.

When a data set was to be examined, a two-liter of the reagent water was made, kept overnight, and then subjected to all four tests using the same 2L reagent water. Roughly two replicates were generated for each of the four tests using the same 2L reagent water. These tests then were performed for four different matrices using a concentration of 1 mg/L ClO₂ as the base, with five replicates for each matrix. To study the effect of different concentrations on the measurement of ClO₂, two concentrations—0.1 mg/L ClO₂ and 0.5 mg/L ClO₂—also were studied. The data generated was tabulated in the same manner as it was with the case of 1.0 mg/L ClO₂, using four different tests for four different matrices.

The necessity for varying doses of ClO₂ in the water treatment plant in relation to the temperature prompted further study of how different temperatures affected the measurement of ClO₂. The tests were carried out at temperatures of 0°C, 10°C and 20°C, the only difference being that the reagent water used in the test was maintained at the above-mentioned temperatures while all the other reagents used in the tests were at room temperature.

The 2L ClO₂ solution was used to perform the four tests and the same solution was used to generate two more replicates of the same tests. The first method to be performed using the reagent water was amperometric titration, which consisted of four

steps and involved two 5-minute periods during which the solution was kept in utter darkness. The first step of titration was generally completed within 8 minutes, then the solution was shielded from light for approximately 5 minutes. During this period of darkness, the DPD HACH[®] Kit Test was performed and the results recorded. The second step of the titration, which took roughly 3 minutes, was then undertaken. Step 3, which took 5 minutes, was then performed, followed by another 5-minute period of darkness. During this five-minute interval, the Palintest[®] Kit was performed. The final step of the Amperometric titration was then completed. Finally, the LGB wet method was performed. This involved preparing the standards and measuring the ClO₂ under consideration, a procedure that took roughly 25 minutes for completion. The cumulative time for all tests performed would be about 50 minutes.

PREPARATION OF STANDARDS

All the standards vital to the experimentation were prepared, stored in volumetric flasks, and covered with aluminum foil to prevent light-catalyzed reactions. The different standards, which are described in this section, were prepared using Nanopure[®] water.

Reagent Water

Prior to each experiment, Nanopure[®] reagent water was treated overnight with 1 ppm ClO₂ to eliminate any ClO₂ demand. The treated Nanopure[®] water was then purged with nitrogen for at least 30 minutes or until the Palintest[®] kit measured a result of 0.00 mg/L ClO₂. Although the Palintest[®] kit gave these results, there was some ClO₂⁻ left in the reagent water. This amount of ClO₂⁻ was very negligible, however, and accounted only to about 0.12 mg/L.

Ion Chromatography Method

A Dionex 300 ion chromatograph equipped with a conductivity detector and an AS40 Automated Sampler was used to analyze the ClO₂⁻. Two basic columns were utilized in the process: a DionexAG9-HC, 4 mm anion guard and a Dionex AS9-HC, 4 mm anion separator. Also purchased from Dionex was an ASRS-I, 4 mm anion suppressor. In order to purge from the reagent water as much ClO₂⁻ as possible, the fluid

was filtered through powdered, activated carbon and then analyzed using ion chromatography. Although the resulting measurement indicated some ClO_2^- decrease, at about 0.015 mg/L the actual reduction was insignificant. This procedure indicated that ClO_2^- could not be removed completely from the sample; hence, it should be noted that all ClO_2 demand free water used for this research contained as background 0.12-mg/L of ClO_2^- .

To determine the measurement of ClO_2^- , this research utilized the ion chromatography procedure prescribed by the Environmental Protection Agency Method 300.1 (USEPA 2000). This method calls for a sample loop volume of 100 mL and a 9.0 mM sodium carbonate eluent dispensed at a flow rate of 1.0 mL/minute. Using an anion self-generating suppressor, suppression was achieved. The resulting recycle mode and detector output range was 3 microsiemens, while the background conductivity measured approximately 27 microsiemens. The ClO_2^- had a retention time of roughly 5.2 minutes, and the concentrations were quantified by the integrated peak areas.

Chlorite Ion Standard (0.5 mg/L)

The procedure involved the placement of 0.1341 mg. of highly-purified NaClO_2 into a 250 mL volumetric flask containing 50 mL of Nanopure[®] water. The solution was mixed properly until dissolved. To this, 150 mL Nanopure[®] water was added to produce 200 mL. of standard ClO_2^- solution at 0.5 mg/L.

Chlorate Ion Standard Solution (0.5 mg/L)

Into a 250 mL volumetric flask containing 50 mL of Nanopure[®] water, 0.1275 gm of sodium chlorate (NaClO_3) was placed and mixed until dissolved. To this, 150 mL of Nanopure[®] water was added to get the desired standard ClO_3^- solution of 0.5-mg/L.

Chlorine Solution (1 mg/L)

Approximately 30-40 μl . of Clorox[®] were added to one liter of Nanopure[®] water and mixed thoroughly. The concentration of chlorine in mg/L was then determined using the DPD chlorine kit.

Lissamine Green B Solutions

A stock solution of Lissamine Green B was prepared by dissolving 961 mg of dye in 100 mL of Nanopure[®] water. When needed, a reagent solution was prepared from this stock by diluting the 100 mL stock solution to 500 mL Nanopure[®] water. Such a prepared LGB stock solution would remain stable for at least several months.

Ammonia Buffer Solution (pH 9)

A 2M NH_3 solution was prepared by diluting 10mL of a 30 percent NH_4OH solution, with one liter with reagent water, and a 2M NH_4Cl was prepared by dissolving 107 g NH_4Cl in 1 liter of Nanopure[®] water.

The working ammonia buffer was prepared by pipetting 2 mL of 2M NH_3 and 8 mL of 2M NH_4Cl solution into a 100 mL volumetric flask and diluted to volume with Nanopure[®] water.

Care was taken to keep the ammonia buffer solution and the LGB dye solution separate. As LGB is unstable in the solution at pH 9, each had to be added individually to the sample for analysis.

AMPEROMETRIC TITRATIONS

This section of the chapter will focus on the use of amperometric titrations, beginning with a description of the procedure.

General Description of Amperometric Titration

For all titrations undertaken by this research, the implement of choice was the Fisher Scientific Titrator series 17T2000 Amperometrix which, to generate a current as a function of the halogen concentration, utilizes platinum measuring and copper counter electrodes. For titration, the procedure required immersion of these electrodes into a

solution of ClO₂ sample that was being continuously agitated. As a result of this agitation, a small DC potential across the electrodes can be observed. The instrument's milliammeter displays the current flow, and when ClO₂ is present in the sample, this fact is indicated by the movement of the milliammeter pointer to the upper portion of the scale. To neutralize the halogen and decrease the current, phenyl arsine oxide (PAO) is gradually added to the sample. The halogen decreases in proportion to the amount of PAO added, so as more titrant is added, the current diminishes. When enough PAO is added to the sample to react with all the halogen, the milliammeter pointer stops moving, signaling the end of titration.

Specific Procedure for Amperometric Titration

Amperometric titration involves titrating a sample with a pH measurement of 7 with PAO. To a 200 mL sample, 1 mL pH 7 buffer and 1 g KI crystals were added and titrated against 0.00564 N PAO. The reading, which is the mL of PAO when the response of the milliammeter is stagnant, is noted (A mL). To this same solution, 2.5 mL 2.5 N HCl was added, and the sample was placed in total darkness for 5 minutes, after which it was again titrated and the readings recorded (B mL).

To a second 200 mL sample, 1 mL of a buffer with a pH measurement of 7 was added, and the solution was then purged with nitrogen for 10 minutes to remove ClO₂. Following this, KI crystals were added. This solution was then titrated, and the readings were noted (C mL). To this solution, 2.5 mL 2.5 N HCl was added. The sample was then shielded from light for 5 minutes and then again titrated, after which the readings noted (D mL). The calculations were as follows:

$$\text{Chlorine Dioxide (ClO}_2\text{) mg/L} = [(B\text{mL}-D\text{mL}) \times 0.00564 \text{ N} \times 16863] / 200 \text{ mL.}$$

As there were technical problems associated with the delivery of the titrant using the pump assembly of the amperometric titrator, the addition of the titrant PAO was accomplished using the digital titrator, which featured a window showing the numeric count. A count of 805 was taken as 1 mL. The calibration of the digital titrator was performed using the weight of 1 gm of Nanopure[®] water. When exactly one gram of

water was weighed on the highly precise mechanical balance, the numeric count in the window of the digital titrator read 805.

DPD HACH[®] KIT

This research method used the DPD HACH[®] kit and its powder pillows. The main instrument—the Pocket Colorimeter[™]—is factory-calibrated, which saves time, as well as the expense of constructing a calibration curve.

In this procedure, twenty percent of the chlorine in ClO_2 is reduced to ClO_2^- , and the ClO_2 then reacts with a DPD (N,N-diethyl-p-phenylenediamine) indicator to form a pink color. The color intensity is proportional to the ClO_2 in the sample. Chlorine interferences are eliminated by adding glycine reagent[®], which converts free chlorine to chloroaminoascorbic acid, but has no effect on ClO_2 at the test pH. Thus the measurement was carried out using each sample.

Such tests were performed using the powder pillows. The sample was filled in the cell (provided with the kit) to the 10-mL line and then capped. The cell was then placed into the appropriate holder and covered with the light shield. At this point, the colorimeter was then “zeroed” by pressing of the *zero* button. Four drops of glycine reagent were added to the same sample and swirled to mix; to this mixture, the contents of one DPD Powder Pillow were then immediately added. The cell was capped and swirled gently for 20 seconds, and then the undissolved powder was allowed to settle for 30 seconds. Within one minute after the addition of the DPD to the sample, the sample was placed into the cell holder and covered with the light shield. The reading was obtained by pressing the *read* button and the results were obtained in mg/L ClO_2 .

Care was taken not to use plastic containers; moreover, the sample’s cells and collection containers were thoroughly cleaned after each use. To minimize ClO_2 loss, the samples were tested immediately after preparation, and the instrument was re-zeroed for every sample reading.

LISSAMINE GREEN B METHOD (WET METHOD)

A spectrophotometric procedure, the Lissamine Green B (LGB) Method or “wet” method is based on the depolarization of lissamine green B dye in the presence of ClO₂ (Chisewell and O’Halloran 1991). The fading of the solution when ClO₂ reacts with LGB proportionally, indicates the amount of ClO₂ in sample water. For those components of the research that utilized this method, individualized standard curves were devised for both each matrix and the data set as a whole. The standards for the experiment were six different concentrations of the ClO₂ stock solution prepared in the volumetric flask. The standard curves were prepared prior to every new batch by adding varying amounts of standardized ClO₂ solution. The six standard concentrations were 0.6 mg/L ClO₂, 0.8 mg/L ClO₂, 1.2-mg/L ClO₂, 1.4 mg/L ClO₂ and 1.6 mg/L ClO₂. The LGB solution (2.5 mL) and pH 9 buffer (5 mL) were added to each of the seven 50 mL volumetric flasks and were filled to the mark with Nanopure[®] water. The ClO₂ standards were placed in a 1 cm cuvette, and the absorption of each was then determined spectrophotometrically at 614 nm. Each time new reagent water was made, the standard curve was refigured.

PALINTEST[®] KIT

The portable Palintest[®] kit is developed on the same principles as is the LGB test, but does not require preparation of the standard curve. The Palintest[®] colorimeter was first zeroed using Nanopure[®] water, and then the sample solution to be analyzed was filled in the cell provided by the kit. A tablet of the LGB dye and a tablet of low range chlor diox buffer were crushed together with a small portion of the sample water, the tablet-water solution was then mixed thoroughly, and the contents of the first containing the sample water was mixed up to the mark and swirled to ensure proper mixing. After a period of 50-60 seconds, the sample was placed into the colorimeter—which had been previously zeroed—and the reading directly noted down on the LCD panel in the form of mg/L ClO₂.

CHLORINE DIOXIDE DEMAND

Using the DPD HACH[®] and Palintest[®] kits, tests were performed to study the initial stability of the ClO₂, as well as the effects of ClO₂⁻ might have on this stability. To determine the potential for DPD to undergo continued oxidation following its initial reaction with ClO₂, a series of ClO₂ measurements were made over a period of 300 seconds using both kits. To study the effect of ClO₂⁻ on both kits, a matrix of 1 mg/L of ClO₂ and 0.5 mg/L ClO₂⁻ were analyzed at 20°C over a period of 300 seconds.

STATISTICAL CALCULATIONS

Statistical analysis was conducted using the SAS. The data generated during this project had multiple variables; used different matrices, concentrations, and techniques; and was governed by four analytical techniques. Due to significant interaction among the data obtained, a Multiple ANOVA test was performed on the data set for different temperatures and different concentrations. Univariate analysis tests were also performed on the data set in two ways: with three-way analysis considering no factor interaction and with three-way analysis considering interactions of all factors. The results of such tests—i.e., the ClO₂ concentration—were affected by more than one factor; hence, they were designed so that the analysis of variance can be used to test the effects of different factors on the concentration of the ClO₂.

To determine their effects on the analysis, the different parameters established for this project were studied individually. The bias and the precision were analyzed for different parameters and then plotted in the form of a graph using the xy scatter graph, as well as box plots using the software Minitab.

Results were then tabulated in the form of bar graphs with the means of the test response for different matrices indicating the variance from the actual standard concentration. The results were also graphically represented for the bias values from the different tests at different temperatures and at different concentrations with different matrices. An alpha value (α) value of 0.05 was selected for all analyses.

CHAPTER IV

RESULTS

Data analysis was completed through the use of the SAS. Similar results can be achieved through both the Univariate and Multiple Analysis of Variance (MANOVA) tests; however, when given the choice, MANOVA would be preferred. Such a decision is prompted by the fact that homogeneity of variance across the trials (equal variance on all five test scores) as well as homogeneity of covariance (equal covariances across all pairs of trials) are assumed by univariate results, while the MANOVA tests derive from a more realistic—if slightly more complicated—assumption about these same measurements. When the MANOVA tests are used, each trial involves the modeling of a separate variance for each of the five replicates and of a separate covariance for each data set. Such a technique might estimate more measurements than are really necessary; however, in the end, the test series provides more realistic results.

Test results alone support the fact that the MANOVA tests provide more significant measurements. Likewise, Roy's test can be chosen because it produces the most significant value. As indicated by the output, Wilks' Lambda is quite exact; therefore, its results too can be reported. In addition to the Wilks' Lambda, the Hotelling Lawley trace values should be considered in judging the hypothesis of this research.

In order to successfully test the comparison of the analytical tests used in this research and to discover the potential for data parameter interaction, the project demands the complex structuring of data relating temperatures and concentration with the tests and the resulting matrices. In this case, the use of MANOVA permits linear combination of the different tests and matrices at differing temperatures, a measurement that result in an independent variable. A new variable is then created combining all dependent variables, including tests and matrices, so that the mean differences are maximized. At this point, the test considers the data generated by the dependent variables as a single dependent variable; differences are then measured among them, and the effect of interaction between the dependent variables is also noted.

This project also compiled the statistical results for individual parameters. These results were presented in the form of acceptance or rejection of the null hypothesis, which states that there is no difference in the parameters for any single test.

CHLORINE DIOXIDE AT DIFFERENT TEMPERATURES

MANOVA and univariate tests were carried out on the data for the different temperatures. The test involved a null hypothesis, as well as an alternate one. The Null Hypothesis for the test was

*There is **no** difference among the different methods and different matrices used for the experimentation to compare the analytical techniques used to measure the concentration of ClO₂.*

The Alternate Hypothesis for the test was

There is a difference among the different methods and different matrices used for the experimentation to compare the analytical techniques used to measure the concentration of ClO₂.

MANOVA tests were applied to the data obtained at the different temperatures, and the results were presented in the form of several statistics tests:

Statistic	Value	F Value	Num DF	Den DF	Pr>F
Wilks' Lambda	0.52476428	6.69	18	470	<0.0001
Pillai's Trace	0.55149731	6.31	18	504	<0.0001
Hotelling-Lawley Trace	0.76348484	7.00	18	326.05	<0.0001
Roy's Greatest Root	0.49669998	13.91	6	168	<0.0001

Of all these statistical tests, the Hotelling Lawley Trace value is particularly vital: it indicates that the Pr > F is <0.0001, which rejects the Null Hypothesis that the methods under study are the same and proves instead that there is a difference. The P-value being <0.0001 indicates that we can be 99.99percent sure of the difference among the methods used for the comparison study.

The three-way Univariate analysis with all interactions confirmed the rejection of the null hypothesis when the source of interaction for matrix*test*temperature gave the value of Pr>F as <0.0001:

<u>Source</u>	<u>DF</u>	<u>Type III SS</u>	<u>Mean Square</u>	<u>F Value</u>	<u>Pr > F</u>
matrix*test*temp	18	0.34645528	0.01924752	6.07	<0.0001

The Univariate analysis indicates that for a given test the concentration of ClO₂ varied with the change in matrix, as evidenced by the results obtained for three- way Univariate analysis with no three-factor interaction:

<u>Source</u>	<u>DF</u>	<u>Type III SS</u>	<u>Mean Square</u>	<u>F Value</u>	<u>Pr > F</u>
matrix*test	9	1.06031389	0.11781265	32.79	<0.0001

The ClO₂ concentration for a given test also showed structure with the different temperature, as in these results:

<u>Source</u>	<u>DF</u>	<u>Type III SS</u>	<u>Mean Square</u>	<u>F Value</u>	<u>Pr > F</u>
test*temperature	6	0.38555139	0.06425856	17.89	<0.0001

The ClO₂ concentration also showed structure for different temperatures for a given test, which can be confirmed by the P value of 0.0001 obtained by the univariate analysis with no three-factor interaction:

<u>Source</u>	<u>DF</u>	<u>Type III SS</u>	<u>Mean Square</u>	<u>F Value</u>	<u>Pr > F</u>
matrix*temperature	6	0.09889583	0.01648264	4.59	0.0001

For the different tests performed at a constant concentration of 1 ppm, with varying temperatures of 0°C, 10°C and 20°C, the results were:

<u>Source</u>	<u>DF</u>	<u>Type III SS</u>	<u>Mean Square</u>	<u>F Value</u>	<u>Pr > F</u>
Test	3	1.02563611	0.34187870	107.73	<0.0001
Matrix	3	0.64241833	0.21413944	67.48	<0.0001
Temperature	2	7.39537750	3.69768875	1165.22	<0.0001

These tests demonstrate that the different parameters—analytical methods, matrices, and temperatures—were significantly different for a given analysis.

Consideration of the high positive bias results was possibly attributed to the consistent human error that might have occurred through out the measurement of the actual concentration of ClO_2 . Possible reasons held responsible for the consistent high values of the measured concentration of ClO_2 than the actual desired concentration of ClO_2 for the project would be due to some of the ClO_2 demand present in the laboratory water treated overnight, the presence of the ClO_2^- as a background interference and the errors in making up the working solution of the desired concentration of ClO_2 from the stored stock solution of ClO_2 .

Test responses for the experiment carried out at the temperatures of 0°C , 10°C and 20°C , with different matrices and different analytical techniques, are plotted graphically in Figure 4-1. The values on the y-axis are the different matrices, which were used during the experimentation:

1. 1 mg/L ClO_2
2. 1 mg/L ClO_2 + 0.5 mg/L ClO_2^-
3. 1 mg/L ClO_2 + 0.5 mg/L ClO_2^- + 0.5 mg/L ClO_3^-
4. 1 mg/L ClO_2 + 1.0 mg/L Cl_2

Values on the x-axis represent the test responses of ClO_2 in mg/L for the particular matrix and analytical method:

1. Amperometric Titrations,
2. DPD HACH[®] Kit,
3. The LGB Wet Method, and
4. The Palintest[®] kit

As the standard solution of ClO_2 was prepared as 1 mg/L, the horizontal line at 1.00 mg/L ClO_2 on the y-axis is the standard set for all the analytical techniques. To be proven

more accurate, the methods test responses should be nearer to the horizontal line of 1 mg/L ClO₂.

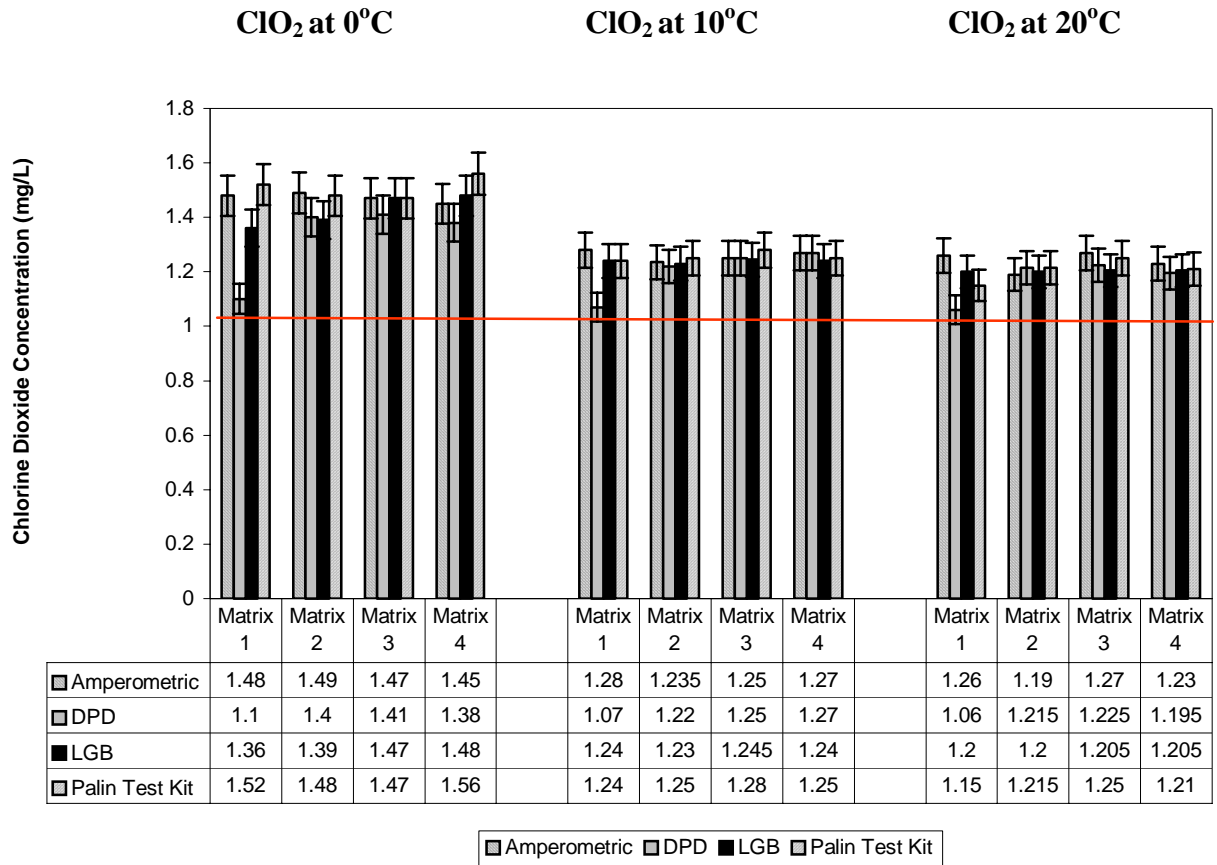


Figure 4-1: Chlorine dioxide concentrations at different temperatures measured for different matrices with the various analytical techniques used for the ClO₂ concentration measurements.

In Figure 4-1, error bars above and below the boxes represent the 5th and 95th percentiles of the response. The solid line corresponds to the standard concentration of 1.0 mg/L ClO₂ that should be achieved for a test to adequately measure ClO₂. The measured concentration of ClO₂ using the different test for a specific matrix showed variance.

In the case of matrix 1, the DPD test proved to be better than the others at all temperatures, although for almost all tests the measured concentration of ClO₂ increased than the standard concentration with the decrease in temperature. For matrix 2, the DPD test showed an increase in the measured concentration, while the other tests remained almost unaffected by the change in matrix. The same case was observed with the other two matrices, which contained ClO₂⁻, ClO₃⁻ and chlorine species in addition to ClO₂.

The LGB and the amperometric titration methods remained unaffected for a particular matrix within the given temperature but gave lower concentration results for the increased temperature, again as shown in Figure 4-1. In general, the DPD test showed more variation than other analysis tests with different matrices. The Palintest[®] kit showed a consistent response at different matrices, thus proving it was unaffected by the chlorine species present in the matrices under consideration. The LGB (wet) method gave almost the same result as that obtained by the Palintest[®] kit. The amperometric titration results were reproducible but gave higher ClO₂ concentrations than the standard.

CHLORINE DIOXIDE AT DIFFERENT CONCENTRATIONS

As stated earlier, because the MANOVA test has been proven more accurate and reliable, it was chosen over the Univariate test for this research project. The ensuing experiments resulted in data that proved to be completely interrelated; hence, it was necessary to perform a multiple variance test, the Null Hypothesis for which was

There is no difference among the different methods and different matrices used for the experimentation to compare the analytical techniques used to measure the concentration of ClO₂.

For the same test, the Alternate Hypothesis was

There is a difference among the different methods and different matrices used for the experimentation to compare the analytical techniques used to measure the concentration of ClO₂.

MANOVA tests were performed on the data obtained at different concentrations, with the following statistical results:

Statistic	Value	F Value	Num DF	Den DF	Pr>F
Wilks' Lambda	0.50917445	5.34	18	356.87	<0.0001
Pillai's Trace	0.56511476	4.95	18	384	<0.0001
Hotelling-Lawley Trace	0.82321549	5.72	18	246.06	<0.0001
Roy's Greatest Root	0.61698249	13.16	6	128	<0.0001

Of these tests, the Hotelling Lawley Trace value proves to be the most important, as its Pr > F measurement of <0.0001 rejects the Null Hypothesis and proves instead that there is a difference among the methods under study. The P-value of <0.0001 further indicates that we can be 99.99 percent sure of the difference among the methods used for the comparison study.

For the different tests performed at constant temperature of 20°C, with varying concentrations of 0.1 ppm, 0.5 ppm and 1.0 ppm, the results were

<u>Source</u>	<u>DF</u>	<u>Type III SS</u>	<u>Mean Square</u>	<u>F Value</u>	<u>Pr > F</u>
Test	3	0.5687191	0.1895730	134.02	<0.0001
Matrix	3	0.2038163	0.0679388	48.03	<0.0001
ppm	2	101.7672315	50.8836157	35973.70	<0.0001

The P value of the individual test parameters tentatively rejects the Null Hypothesis that they are equal; thus, it accepts the alternative hypothesis that at a constant temperature there is a significant difference among the parameters under experimentation.

Test responses for the experiment carried out at the temperatures of 0.1 ppm, 0.5 ppm and 1.0 ppm, with differing matrices and analytical techniques, are plotted in Figure 4-2. The values on the y-axis indicate the different matrices:

- X mg/L ClO₂
- X mg/L ClO₂ + 0.5 mg/L ClO₂⁻
- X mg/L ClO₂ + 0.5 mg/L ClO₂⁻ + 0.5 mg/L ClO₃⁻
- X mg/L ClO₂ + 1.0 mg/L Cl₂

Values on the x-axis represent the test responses of ClO₂ in mg/L for the particular matrix and a given analytical method:

- Amperometric Titrations,
- DPD HACH[®] Kit,
- LGB Wet Method, and
- Palintest[®] Kit.

Figure 4-2 represents the tests that were used to measure the ClO₂ at different concentrations. The first group of bar graphs represents the experiments carried out for the ClO₂ concentrations at 0.1 ppm, while the second and third groups symbolize those carried out for the ClO₂ concentrations at 0.5 and 1.0 ppm, respectively.

For the first group of different matrices for 0.1 ppm, the solid line at 0.1 ppm corresponds to a standard ClO₂ concentration. Similarly, the solid lines at 0.5 ppm and 1.0 ppm correspond to the groups of different matrices for 0.5 ppm and 1.0 ppm, respectively. For the matrices of group one for 0.1 ppm, the Palintest[®] Kit proved to be the most accurate method. The DPD and the Amperometric methods produced results that were too high for almost all the matrices. The LGB wet method also gave significantly better results for nearly all of the different matrices. For the matrices of group two for 0.5 ppm, the Palintest[®] again superior, along with the LGB (wet) method, which was significantly better than the other two. For the results of the third group, the amperometric titrations proved to be problematical, while the other three tests did considerably better and gave significant results. The data at 1 ppm showed that, when tested with different matrices containing chlorine species, the DPD test revealed interferences.

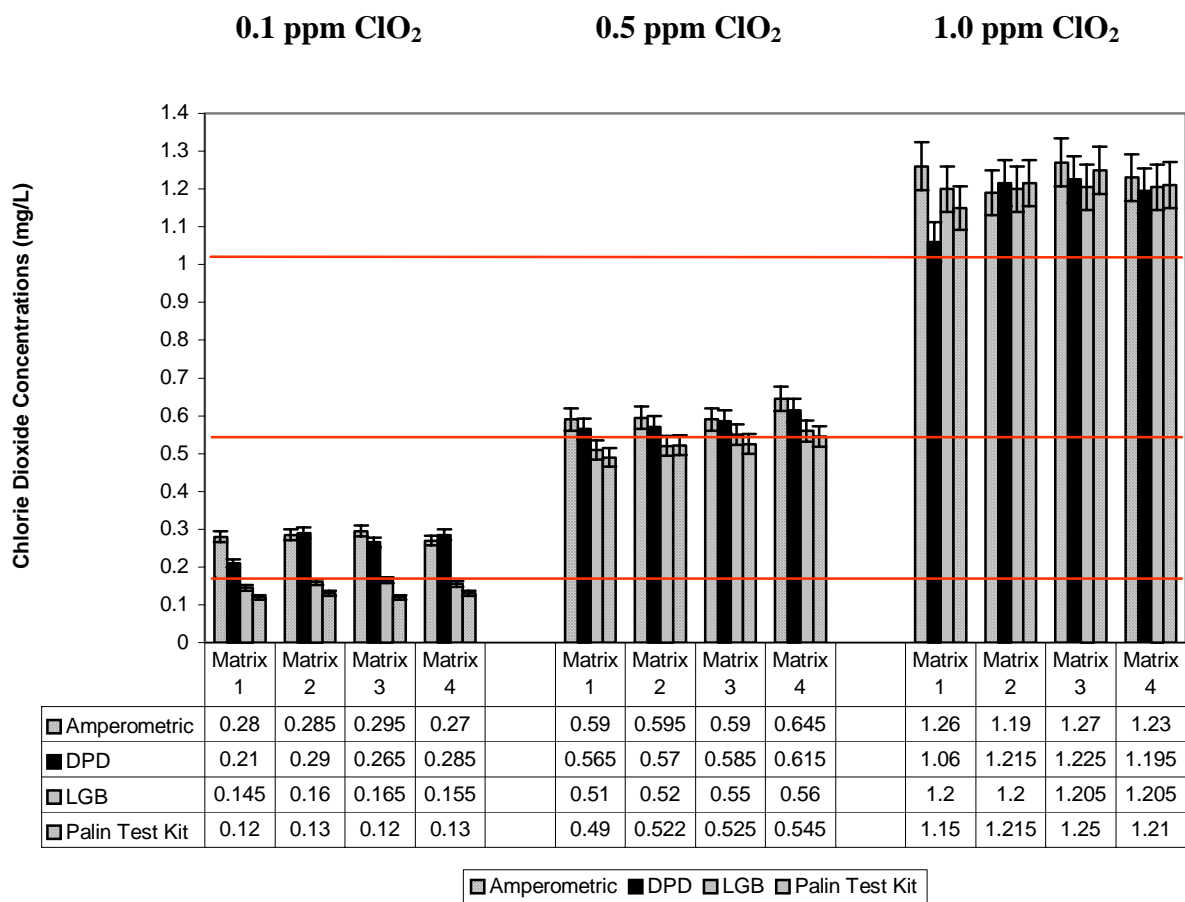


Figure 4-2: Chlorine dioxide concentrations at different actual concentrations measured for different matrices with the various analytical techniques used for the Chlorine Dioxide Concentration Measurements

The Palintest[®] kit produced consistent results at almost all concentrations and with different matrices, with the LGB (wet) test results proving nearly identical. When compared to the other analytical methods, it is easy to discern that the amperometric titrations results were off.

To better understand the different combinations of the methods at different temperatures and different concentrations with different matrices, an interaction study was done for all temperatures and all concentrations being normalized. The result was tabulated in the form of P values for the different combinations of the test performed, where less P values indicate the significant difference between the tests for a particular matrix, as shown in Table 4.1

Table 4.1: Interactions (normalized) among the methods at different temperatures and concentrations used for the test analysis of the ClO₂ concentration.

Interaction Among Methods at All Temperatures							
Matrix	All Tests	Palin LGB	Palin DPD	Palin Ampero	LGB DPD	LGB Ampero	DPD Ampero
1	<0.0001	0.1794	0.0342	<0.0001	0.4965	<0.0001	<0.0001
2	<0.0001	0.5049	<0.0001	<0.0001	<0.0001	<0.0001	0.7141
3	<0.0001	0.2280	<0.0001	<0.0001	<0.0001	<0.0001	0.0013
4	<0.0001	0.4282	<0.0001	<0.0001	<0.0001	<0.0001	0.0150
<u>Interaction among methods at all concentrations</u>							
Matrix	All Tests	Palin LGB	Palin DPD	Palin Ampero	LGB DPD	LGB Ampero	DPD Ampero
1	<0.0001	<0.0001	<0.0001	0.0016	<0.0001	<0.0001	<0.0001
2	<0.0001	<0.0001	<0.0001	0.2829	0.6016	0.0177	0.0059
3	0.0012	0.0106	0.0015	0.7979	0.3072	0.0472	0.005
4	<0.0001	0.001	<0.0001	0.1099	0.0247	0.2693	0.0025

Likewise, to obtain a clearer perspective on the statistical differences of the various parameters of the different tests used to measure ClO₂ concentrations, an interaction study was performed to measure those individual temperatures and concentrations. The resulting P-values for the different combination of the test further indicated whether there was any significant differences in a given test combination at a specific temperature with a given form of matrix. The higher the values of P obtained, the more identical the results for that pair of test methods. The results are as shown in Table 4.2.

Table 4-2: Interactions among the methods at individual temperatures and concentration used for the test analysis of the ClO₂ concentration.

	All Tests	Palin LGB	Palin DPD	Palin Ampero	LGB DPD	LGB Ampero	DPD Ampero
Matrix	0°C						
1	<0.0001	<0.0001	<0.0001	0.0991	<0.0001	<0.0001	<0.0001
2	<0.0001	<0.0001	<0.0001	0.7227	0.5979	<0.0001	<0.0001
3	0.0034	0.9693	0.0033	1	0.0014	0.9727	0.0043
4	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.3052	0.0005
Matrix	10°C						
1	<0.0001	1	<0.0001	0.019	<0.0001	0.0068	<0.0001
2	0.2429	0.1443	0.0486	0.3298	0.4513	0.8641	0.4064
3	0.255	0.0463	0.1835	0.1844	0.6243	0.8106	0.8419
4	0.3129	0.317	0.5612	0.5744	0.1064	0.1248	0.947
Matrix	20°C						
1	<0.0001	0.6165	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
2	0.577	0.8472	0.432	0.2153	0.4978	0.2064	0.5278
3	0.0041	0.0161	0.2069	0.3755	0.3278	0.0017	0.027
4	0.2994	0.4881	0.3221	0.4967	0.6785	0.1617	0.0852
	All Tests	Palin LGB	Palin DPD	Palin Ampero	LGB DPD	LGB Ampero	DPD Ampero
Matrix	0.1 ppm						
1	<0.0001	0.2424	<0.0001	<0.0001	0.0006	<0.0001	<0.0001
2	<0.0001	0.1105	<0.0001	<0.0001	<0.0001	<0.0001	0.7486
3	<0.0001	0.0125	<0.0001	<0.0001	<0.0001	<0.0001	0.0263
4	<0.0001	0.1576	<0.0001	<0.0001	<0.0001	<0.0001	0.5218
	All Tests	Palin LGB	Palin DPD	Palin Ampero	LGB DPD	LGB Ampero	DPD Ampero
Matrix	0.5 ppm						
1	<0.0001	0.6218	<0.0001	<0.0001	0.0004	<0.0001	0.1256
2	<0.0001	0.5049	0.0049	<0.0001	0.0029	<0.0001	0.0853
3	<0.0001	0.2280	<0.0001	<0.0001	0.0088	<0.0001	0.7976
4	<0.0001	0.5376	0.0003	<0.0001	0.0043	<0.0001	0.0160
	All Tests	Palin LGB	Palin DPD	Palin Ampero	LGB DPD	LGB Ampero	DPD Ampero
Matrix	1.0 ppm						
1	<0.0001	0.5130	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
2	0.1213	0.8012	0.2236	0.0540	0.3649	0.0288	0.3209
3	<0.0001	0.0019	0.0513	0.1672	0.1914	<0.0001	0.0006
4	0.0142	0.3654	0.1255	0.2889	0.5794	0.0157	0.0073

The responses of the different tests with regard to the percent of bias at different temperatures and different concentrations were studied for different matrices and presented graphically as shown in Figures 4.3 and 4.4.

The xy scatter graph represented by Figure 4.3, which indicates the percent of bias at different temperatures, shows that as the temperature increases, the percent of bias decreases. The percent of bias concept was considered for the tests because the concentration used for the experiments were different; hence, the difference between the measured concentration and the known concentration could lead to errors with the increasing concentrations.

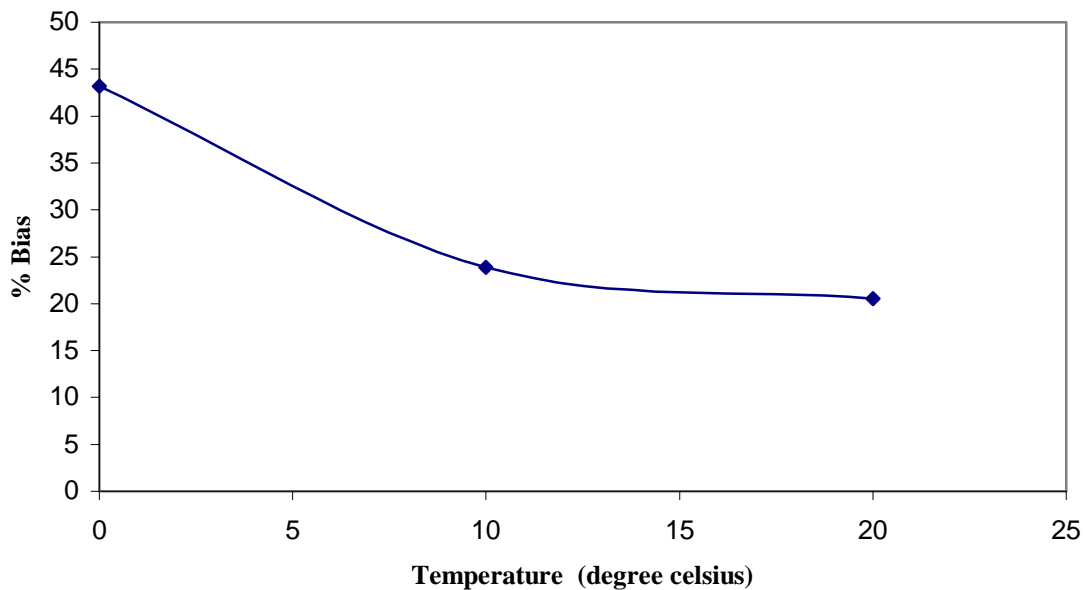


Figure 4-3: Percent bias for the different analytical techniques and matrices at the different temperatures.

Likewise, the xy scatter graph shown as Figure 4.4, which indicates the average percent of bias at different concentrations, reveals a range where the different methods give the minimum bias from the actual concentration. That measurement lies between the concentration ranges of 0.4 to 0.8 ppm.

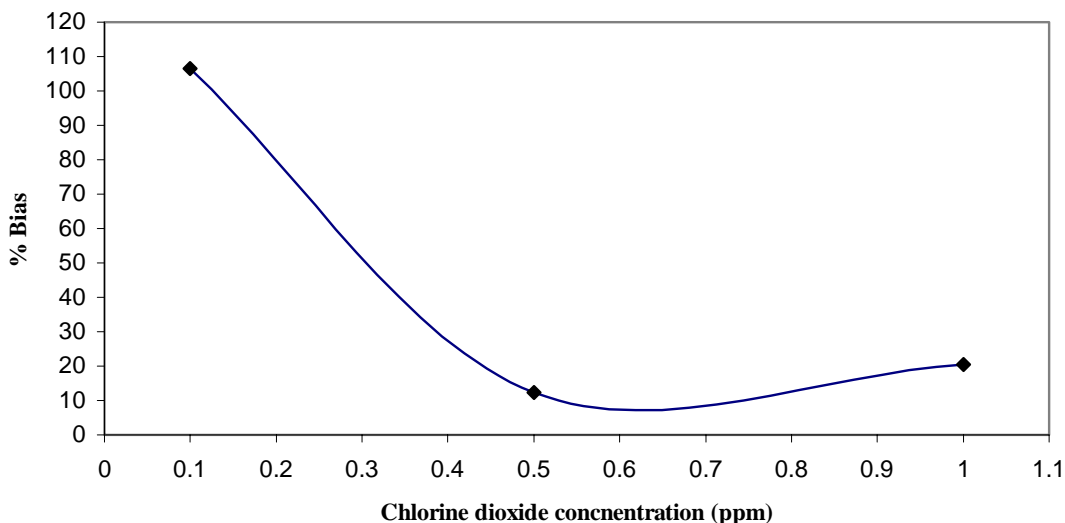


Figure 4-4: Percent bias for the different analytical techniques and matrices at the different concentrations.

The box plots in Figure 4-5 and Figure 4-6 show the percent of bias response for the different tests used in the project at different temperatures and different concentrations, respectively. The following figures—4-7 and 4-8—indicate the percent of bias response for different matrices at different temperatures and different concentrations, respectively. Box plots were chosen for displaying the bias data because they provide information regarding its range and variability. The interpretation of these plots, according to Gallagher *et al* (1994), is as follows:

“ Eighty percent of the concentrations fall in the range between the upper and lower tails that appear outside the boxes. Thus, 10 percent of the data fall below the lower tail (Q_{10}) and 90 percent fall below the upper tail (Q_{90}). The asterisks below or above each of the tails correspond to individual data points called outliers. The lower and upper lines composing the box are respectively, the upper limits of the first and third quartiles of the data (Q_{25} and Q_{75} , respectively), and the line inside the box shows the upper limit of the second quartile (Q_{50}) and denotes the median value.”

To further prove statistically that there were differences among the temperatures and concentrations, as well as the methods and matrices, a t-test was performed on the

data that constructed the graphs and the box plots. The t-calculated value for the different tests was compared to the t-critical value of each test at the given value of the alpha level of 0.05 and the appropriate degree of freedom from the t-distribution value charts (Walpole 1998). The null hypothesis of there being no difference among the estimated means. When the different parameters were compared individually, it was discovered that the t-calculated was almost higher than the t-critical value, thus indicating rejection of the null hypothesis and tentative acceptance of the alternative hypothesis that differences existed between the tested means.

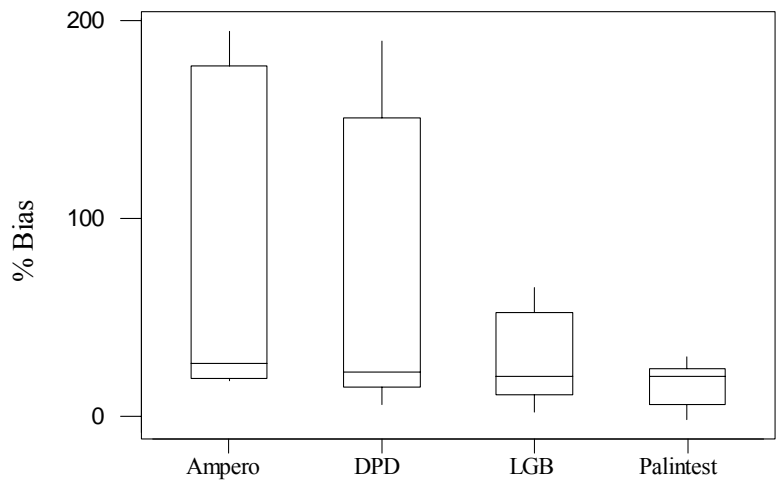


Figure 4-5: Percent bias in the ClO₂ concentration for the different analytical techniques measuring ClO₂ concentration at different temperatures.

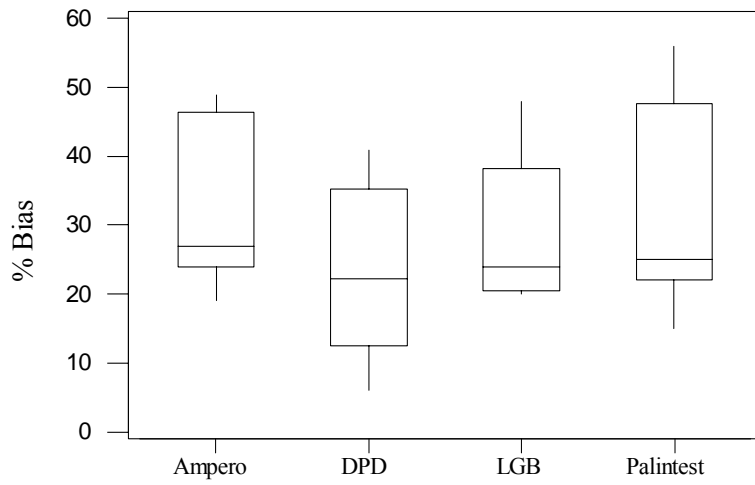


Figure 4-6: Percent of bias in the ClO_2 concentration for the different analytical techniques measuring ClO_2 concentration at different concentrations.

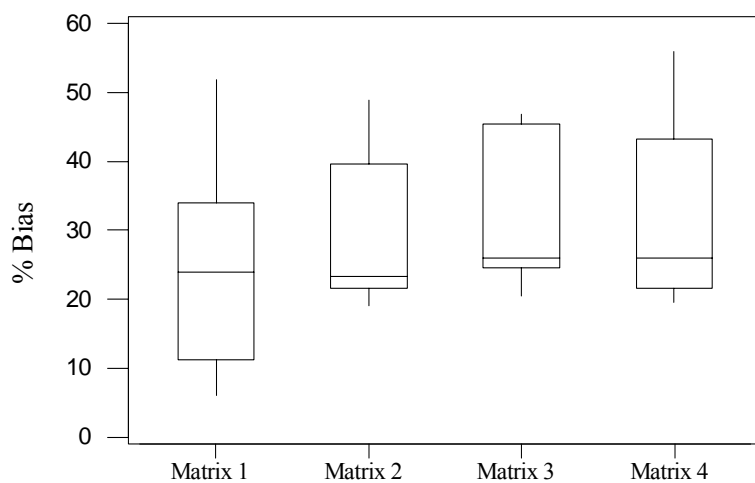


Figure 4.7: Percent of bias in the ClO_2 concentration for the different analytical techniques measuring ClO_2 concentration for different matrices with and without added oxy-chlorine species at different temperatures.

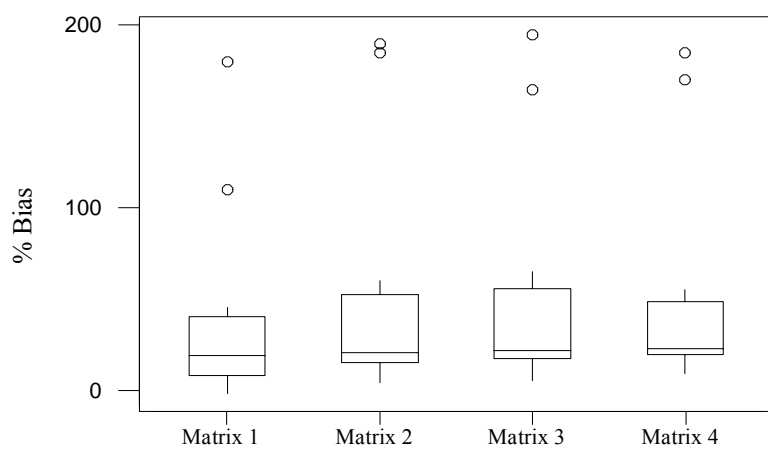


Figure 4-8: Percent of bias in the ClO_2 concentration for the different analytical techniques measuring ClO_2 concentration for different matrices with and without added oxy-chlorine species at different concentrations.

OXIDANT DEMAND CURVE

As a general oxidation method, DPD reacts with a number of oxidants. In the DPD method, ClO_2 oxidizes DPD, and as a by-product ClO_2^- is formed. The potential for DPD to undergo oxidation was studied and, on the basis of the readings noted in Table 4.3 a graph was plotted. The data showed that over a period of 300 seconds, the apparent ClO_2 concentration decreased, as seen in Figure 4-9.

Table 4-3: Chlorine dioxide demand curve using the DPD HACH® Kit over a five-minute period of time.

Time (sec)	Known Chlorine Dioxide (mg/L)	Measured Chlorine Dioxide (mg/L)
0	1.00	1.2
10	1.00	1.1
30	1.00	1.04
60	1.00	0.95
90	1.00	0.83
120	1.00	0.75
240	1.00	0.63
300	1.00	0.59

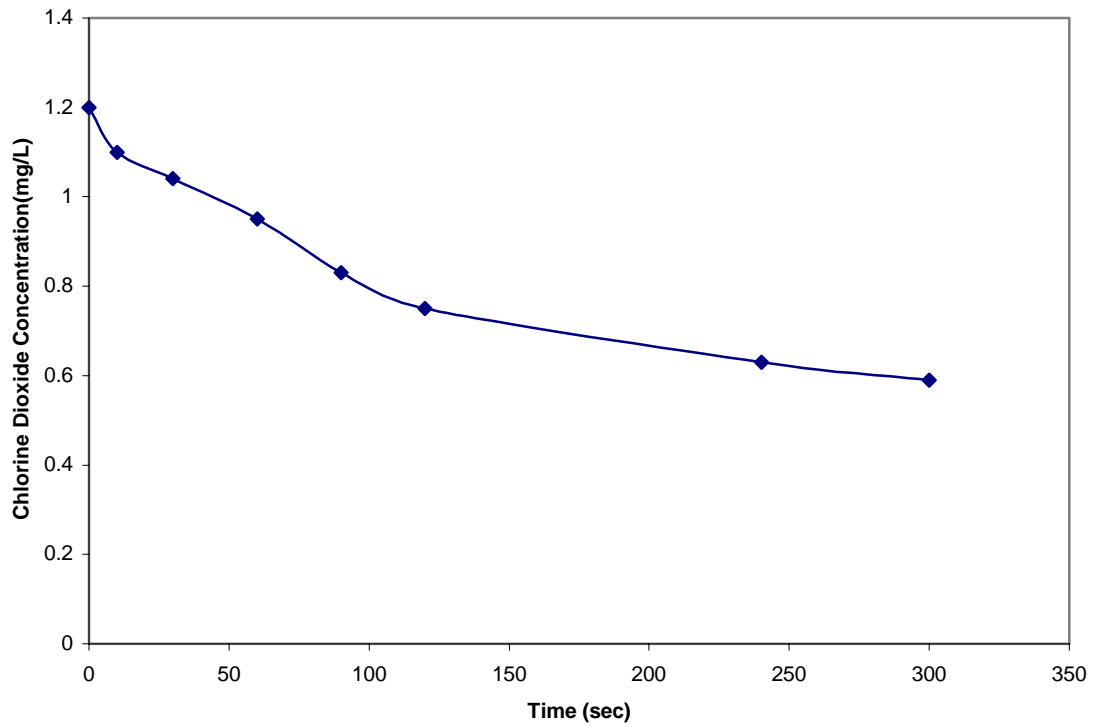


Figure 4-9: Chlorine dioxide demand curve using the DPD HACH[®] Kit over a five-minute period of time at 20°C.

CHLORINE DIOXIDE AND CHLORITE ION STUDY

The effect of excess ClO_2^- (0.5 mg/L) on the stability of ClO_2 was also studied, and over a period of 300 seconds, the standards were analyzed by the DPD HACH[®] and the reference Palintest[®] kits. The results of this analysis are shown in Table 4-4. The graph was plotted as shown Figure 4-10. The data showed results similar to those indicated by Figure 4-9, while the Palintest[®] Kit data remained unaffected and nearly the same, which indicates that the reference LGB method was not affected by the presence of 0.5 mg/L ClO_2^- .

Table 4-4: Chlorine dioxide measurement in the presence of 0.5 mg/L ClO_2^- using the DPD and the reference Palintest[®] for a time period of 5 minutes.

Time	Known Chlorine Dioxide Concentration (mg/L)	DPD : ClO_2 Concentration (mg/L)	Palin : ClO_2 Concentration (mg/L)
0	1.00	1.29	1.19
10	1.00	1.20	1.17
30	1.00	1.09	1.16
60	1.00	0.96	1.16
90	1.00	0.87	1.15
120	1.00	0.74	1.12
240	1.00	0.67	1.11
300	1.00	0.61	1.09

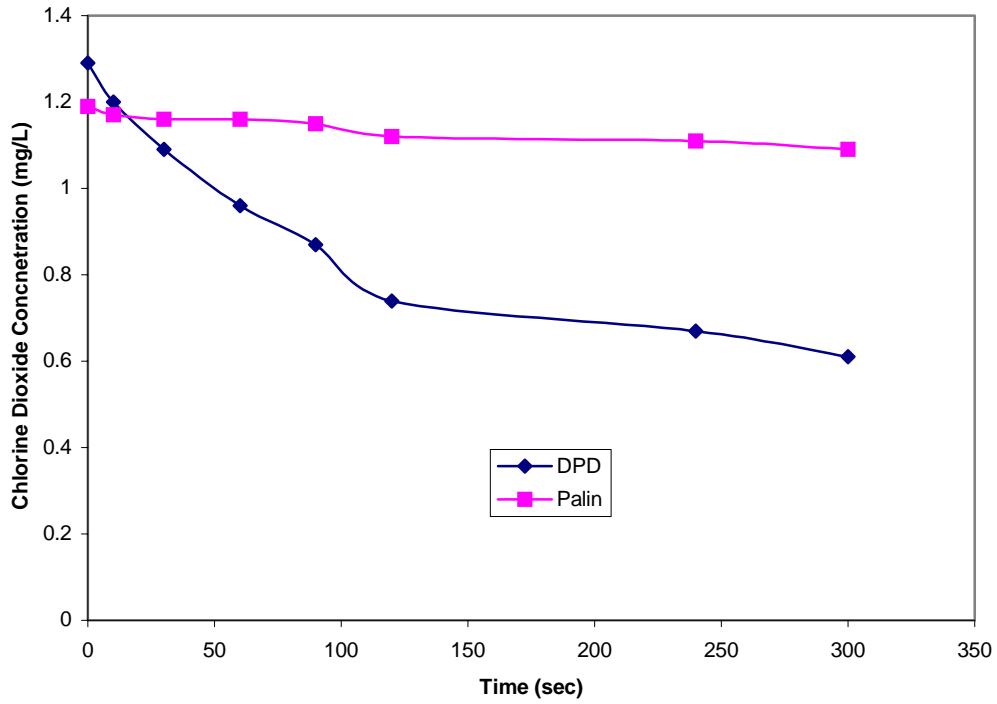


Figure 4-10: Chlorine dioxide measurement in the presence of 0.5 mg/L ClO_2^- using the DPD and the reference Palintest[®] for a time period of 5 minutes.

COST AND TIME ANALYSIS

In an effort both to better understand the different analytical techniques and to help judge which analytical method ultimately proved superior, the cost and time taken for completion of the method analysis were determined with the sample size of 1 and 20. It is important to note that the cost analysis excludes the price of instruments; in other words, the expenditure required for the glassware was not taken into consideration. The results of this analysis are shown in Table 4-5.

Table 4-5 : Time and cost analysis for ClO₂.

	Analytical Techniques			
	DPD HACH [®] Kit	Palintest [®] Kit	LGB (wet) Method	Amperometric Titration
Cost of the Instrument	\$ 320.00	\$ 500.00	\$ 12,000.00	\$ 2600.00
Analysis cost				
1 sample	\$ 0.15	\$ 0.40	\$ 0.35	\$ 0.35
20 samples	\$ 3.00	\$ 8.00	\$ 2.50	\$ 6.00
Analysis Time				
1 sample	1 min	90 sec	30 min	20 min
20 samples	20 min	30 min	45 min	6 hours

When using the DPD HACH[®] Kit, different results were produced by the matrices depending upon the presence or absence of ClO₂⁻. Results obtained from the DPD HACH[®] Kit Method for the different matrices are represented graphically in Figure 4-11, which shows differences in the measured responses as a result of the presence or absence of ClO₂⁻.

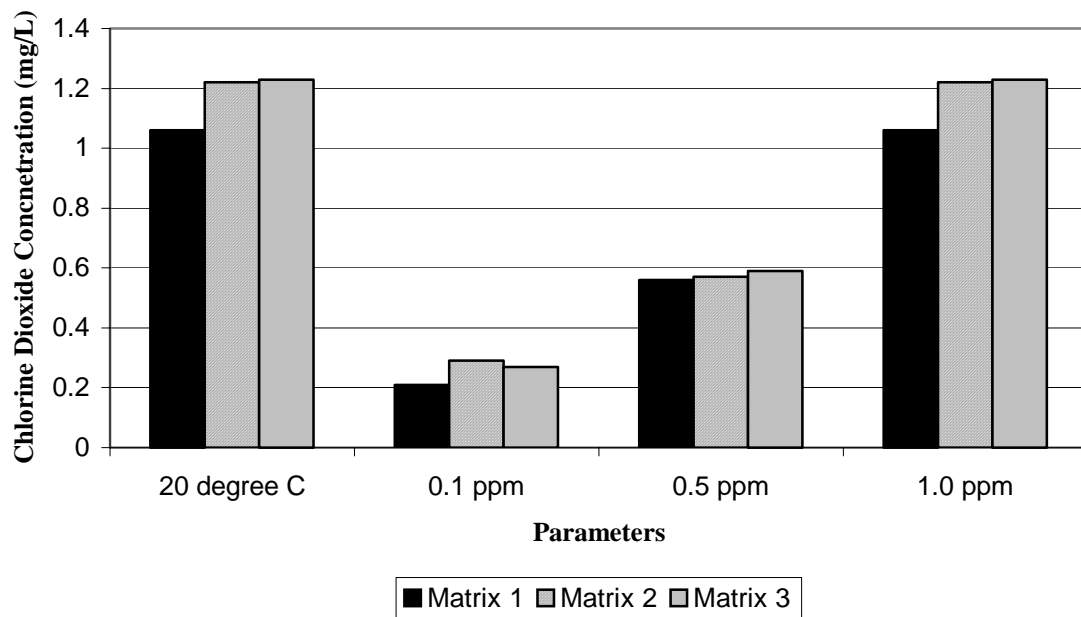


Figure 4-11: DPD fading at different temperatures and concentrations using the DPD HACH[®] Kit for the matrices with and without added oxy-chlorine species.

CHAPTER V

DISCUSSION

Research has long been conducted—and will continue to be performed—on the topic of methods comparison. This research has established certain parameters. One of the most important considerations for any method, for example, is accuracy, as in the ability of a method to determine the correct concentration of a disinfectant in a solution.. An equally important consideration is precision, such as how well the particular analytical method can reproduce the same measurement of the concentration (Gordon 2002).

All the tests performed in this project except the DPD HACH[®] Kit with 1 mg/L ClO₂ only, gave high results for measured concentration of ClO₂, with 20 percent higher being consistently observed for 1 mg/L samples. Possible reasons may include the operator error for the different tests performed. The reason for the amperometric titrations to give high results may be attributed to the calculations which are done by the difference method in which a small error may lead to a large error when the small error is encountered in the experiment. The possible reason for the DPD method to give high results may be possible due to the calibration inconsistency of the kit. The possible reason for the Palintest[®] to give higher results may be attributed to the dye tablets used for the experiment. Two tablets were available for the experiments which were LR (Low Range) and HR (High Range) tablets, the low range tablets were used for all the experiments carried out for the project and that might be the possible reason that the tests performed well when the LR tablets were used for the tests and thus gave good results when used with lower concentrations. Though the LR tablets could be used for the 1 mg/L ClO₂ concentration, but this might be a possible consideration as a potential reason for the higher values of ClO₂ concentration at 1 mg/L concentrations.

In this research, the results obtained from the studies of ClO₂ measurements at different temperatures show that there is indeed an observable temperature effect. The data proves that with a decrease in temperature from 10°C to 0°C, the concentration changes by as much as 20 percent. As the temperature decreases the test response conversely increases (Figure 4-3). One possible reason for such behavior could be those

relationships between the absorbance and concentration that are typically temperature dependent. In addition, the lower volatility of ClO₂ in cold water could possibly result in lower gas losses.

Quite possibly, these variations in measurement could be best explained by considering the dependency of the Henry's Law constant, a strong function of temperature, which deems that the higher the temperature, the lower the solubility of the compound in water, and the easier the contaminant can be stripped. In other words, as temperature increases, Henry's Law constant, H, also rises (Chidgopkar 1996).

According to Sander (1999), the simplest way to describe Henry's Law as a function of temperature can be given as:

$$k_H = k_H^\square \times \exp \left\{ - \frac{\Delta_{\text{soln}} H}{R} \left(\frac{1}{T} - \frac{1}{T^\square} \right) \right\}$$

where, k_H^\square = Henry's Law constant at 298° K

$\Delta_{\text{soln}} H$ = Heat of the solution, cal/mol

T^\square = Temperature (298° K)

T = Temperature at which the Henry's Law constant is to be found

Based on the constants and the values of Henry's constants at known temperatures, the values of the Henry's constants were calculated at different temperatures and are as noted:

Henry's constant at 0°C is 0.3627 (M/atm)⁻¹

Henry's constant at 10°C is 0.556 (M/atm)⁻¹

Henry's constant at 20°C is 0.828 (M/atm)⁻¹

These calculations indicate that at lower temperatures the ClO₂ gas was trapped in the water and thus was responsible for higher values of concentration than those obtained at higher temperatures.

Also, according to the Van't Hoff Equation

$$K = C' \exp (- \Delta H^{\circ}/RT),$$

it can be concluded that the rate of reaction is inversely proportional to the temperature, which indicates that for an endothermic reaction like that of the dissolution of ClO₂ in water (with ΔH being positive), an increase in temperature will shift the equilibrium towards the direction of more complete reaction. At lower temperatures, there would have been an accompanying initial slow reaction rate that would have been the possible source of more ClO₂ in the solution, thus resulting in higher readings. On the basis of this fact, it can be inferred that at lower temperatures more ClO₂ is retained in the cold water and less lost to volatilization.

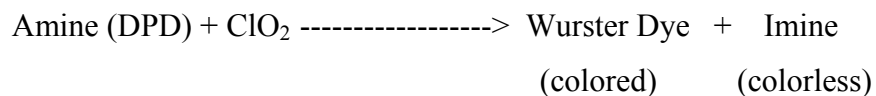
The unexpectedly high results that accompanied the use of amperometric titrations could be attributed to the method itself, as it determines the concentrations by differences—a technique subject to large cumulative errors in terms of both accuracy and precision. The subtractions of two large numbers to produce a small one means that the error associated with those large numbers is then propagated to small numbers (Themilius 1989). Also, under this method, clean and regularly conditioned electrodes are necessary for sharp amperometric titration end points, but as the electrodes contact the sample, certain species in the sample may plate out or coat the metallic surface, possibly resulting in higher responses (Harp 1995). Also, the alternative use of a digital titrator with the PAO contributes to some error percentage, as the pump assembly of the amperometric titrator abruptly responds to the titrant addition. Finally, the reagent quantity that was used for 1 ppm was also used for the lower concentration of 0.1 ppm and 0.5 ppm, thus making the amperometric titration method more susceptible to interferences.

The high results that accompanied use of the DPD HACH[®] Kit could be attributed to the performance of the kit. For example, because the kit is initially calibrated when manufactured, repeated usage over an extended period of time could result in altered calibration and, in turn, unexpected errors. In fact, sometimes the DPD HACH[®] Kit has been discovered to possess an error rate of 25-30 percent (Gordon 2002). Also, the masking step, which involves the addition of glycine, necessitates additional manipulation of the analyte solution, potentially resulting in loss of the highly volatile

ClO₂. The relatively low oxidation potential of the DPD reagent compared to other chlorine species makes this kit disadvantageous, although it produces very good results when the matrix does not involve any other chlorine species other than ClO₂.

It is also important to consider that many manufacturers of test kits sometimes modify their procedure in order to make the kit function properly, which could possibly result in unexpected errors (Gordon 2002).

The ClO₂ measurements obtained in this project were observed to be almost 20 percent higher than the value always prepared for the experimentation. This could be attributed to the chemistry of the DPD. The chemical basis of the DPD-ClO₂ reaction is depicted by the following equation:



The DPD amine is oxidized by ClO₂ into two oxidative products. At a near neutral pH, the DPD reacts with small amounts of ClO₂ to produce the primary oxidation product, a semi-quinoid cationic compound known as wurster dye. This relatively stable free radical species accounts for the magenta color in the DPD test. At higher oxidant levels, DPD can be further oxidized to form the relatively unstable, colorless imine compound, which results in the apparent fading of the colored solution (Harp 1995). Also in the DPD tests for ClO₂, the DPD indicator itself undergoes oxidation and produces the same colored wurster dye product as the reaction of the DPD with ClO₂. Hence, when the DPD reagent is added to the sample containing ClO₂, the amount of color measured will be the sum of the reaction product of DPD-ClO₂ and the added oxidized DPD. Dissolved oxygen in the sample can also promote the additional oxidation of the DPD colored product (*Standard Methods*, 18th Edition). Thus the generally high measurements of ClO₂ can be attributed to the abovementioned causes and would be responsible for the 20 percent higher values obtained when the DPD HACH[®] Kit is used as one of the analytical methods.

Results obtained from the studies of measurements for different concentrations of ClO_2 showed that at lower concentrations amperometric titration and the DPD HACH[®] Kit gave high results. Also, below 1 mg/L, Amperometric Titration is highly dependent on the skill of the technician and is subject to interference at lower levels of concentrations (Gordon 1996).

Although the LGB wet method produces significantly good results, it is a lengthy process and requires very precise laboratory analytical techniques. The Palintest[®] kit which provides for ClO_2 measurements at lower concentrations possesses the following advantages over the other analytical methods used for the project under consideration:

- Other chlorine species do not interfere with it,
- Only two reagents are necessary;
- The resulting color produced after the addition of the sample is stable, making the method an excellent prospect for analysis in the field, and
- No manipulation of the analyte solution is necessary.

Observed over a five-minute period, the DPD data showed a decrease in ClO_2 concentration, which produces a “fading” phenomenon as a result of ClO_2^- oxidizing the highly colored semiquinoid product to a colorless quinoid product. The same occurs when the ClO_2 was spiked with 0.5 mg/L ClO_2^- , which indicates that DPD HACH[®] Kit tests are time-dependent and thus, when time is an issue, become unreliable.

Results obtained from the ion chromatography suggested that the ClO_2 demand for water had 0.12 mg/L ClO_2^- , which may be responsible for the 20 percent higher results obtained when matrix one, which contains only ClO_2 , is being considered. The preparation of standards and the working solution of 1 mg/L might likewise be affected by human and instrument errors to an extent of 10 percent.

Matrix interference was also observed during the experimentation, as can be seen from the box plots. In Figure 4-7, Matrix 1—which contained only 1 ppm ClO_2 —is shown to have produced consistent results at different temperatures when compared to other matrices containing oxy-chlorine species in addition to the ClO_2 . These high results may be due to the interferences of the oxy-chlorine species present in the solution: it can react with the reagents used for the different experiments and thus led to an increased concentration of ClO_2 . As evidenced by matrix 4, there is a possibility that chlorine will

react with the background ClO_2^- present in the reagent water and form ClO_2 , which would logically lead to higher concentrations of the latter.

All of these methods were performed using laboratory water; hence, there could be a possible deterioration of the method performance should natural waters be utilized. It is possible that unknown matrix effects in natural water could affect the calibration curves obtained in the reagent water do not apply accurately in the natural water.

CHAPTER VI

SUMMARY AND CONCLUSIONS

SUMMARY

The results of this project can be summarized as follows:

1. The temperature effect observed in the measurement of ClO_2 might be attributed to the lower volatility of the ClO_2 in cold water, rendering high values of ClO_2 concentration at decreased temperatures. The standard DPD and Plain Test kits base calibrations on temperatures of roughly 20-25°C. Hence the same calibration curves when used at lower temperature could contribute to inaccurate ClO_2 concentration measurements. Also, for the LGB wet method, the standard curves were prepared at 20°C and only the matrices were studied at 0°C and 10°C, which could be a possible cause of inaccurate results. Thus, the effect is observed when there is a temperature difference between the standard curve and the sample is more than 10°C. Almost to an extent of about a 20 percent decrease in the measured concentration of the ClO_2 with the increase in temperature of about 10°C was observed.
2. The measured concentration of ClO_2 increases as the actual concentration of the solution decreases. When expressed in the percent of bias, this results in a higher percent at lower concentrations rather than at higher concentrations. The difference measured between the actual and measured values remains the same, but at higher concentrations the difference in the percent of bias is less.
3. Matrices containing only ClO_2 showed minimum variation at different temperatures, but at different concentrations a consistent variation of about 25-30 percent is observed. This is caused by the inaccuracy of the methods at very low concentrations. The matrices containing oxychlorine species, along with ClO_2 , showed about 30-40 percent variance for different tests at lower concentration but with an increase in actual concentration, the variance was about 15-20 percent.
4. The Palintest[®] showed a minimum variation of about 5 percent for the different concentrations, indicating that it is not concentration-dependent. However, with a change in temperature it revealed a significant variance of about 15-20 percent, a

measurement that makes it temperature-dependent. The test works more effectively at a normal temperature of 20°C.

5. Chlorine dioxide measurements exhibit a ClO_2^- interference due to the continued oxidation of the DPD reaction product, which is a non-reversible reaction. This presents a major problem because when ClO_2 oxidizes DPD, ClO_2^- is the reaction product, which interferes with the spectrophotometer reading. As a result, in the experiments carried out to study the oxidant demand curve, a higher value than the actual is produced.
6. The amperometric titration method is discovered to be more precise than the DPD test, with a variance of about 10 percent with all the matrices. However, it possesses several disadvantages: higher detection limits, greater consumption of time, and increased reliance on the technical expertise of the operator.
7. Similar to the amperometric titration method, the LGB wet method has shortcomings that involve analytes manipulation, a great consumption of time, and a dependence on operator skills.

For measuring ClO_2 , the Palintest[®] Kit and the LGB wet method possess improvements over the most common analytical techniques, namely the amperometric titration and the DPD HACH[®] Kit, which have been reported to suffer from high detection limits, poor precision, and interferences from oxidants other than ClO_2 .

So which of these four methods proves the best for this work? The comparison indicates that while none of the methods came close to ideal standards, the Palintest[®] kit can be determined to possess several distinct advantages: it is more sensitive, precise, and convenient. Cost and time analyses likewise signify that the Palintest[®] kit is more economical. Finally, with this kit chlorine is reacted with ammonia by adding chloridiox buffer tablets, so it can be concluded that chloramines do not interfere with it.

In order to better understand the various methods and come to a determination of which proves superior to the rest, one must consider the conceptual qualities of an ideal analytical method for ClO_2 analysis. Based on the knowledge gained by the author as a result of this study, an arbitrary rating of the ClO_2 analytical methods was produced, as indicated in Table 6-1. Four analytical techniques and different parameters were

considered. A ranking of “1” indicates that a method does not meet the ideal standards, while “5” indicates superior performance.

Table 6-1: Ratings of analytical techniques for ClO₂ vs. the ideal method.

Parameters	Amperometric Titrations	DPD HACH[®] Kit	LGB (wet)	Palintest[®] Kit
Precision	4	3	4	4
Accuracy	3	3	3	4
Performance with different matrices	3	2	4	4
Temperature variation	3	3	3	4
Concentration variation	2	3	4	4
No special Skills	2	4	3	4
Reagent stability	3	3	4	3
Procedure time	2	4	3	4
Cost effective	2	4	3	4
TOTAL SCORE	24	29	31	35

Although amperometric titration long has been considered the standard method in North America, findings indicate that unless precautions are taken, several sources of error can occur with this technique. Amperometric titration requires much greater levels of operator skill, as well as a more thorough understanding of the nature of the sample under analysis. Moreover, as amperometric titrations are not easily adapted to the field, some trade-off in precision and accuracy can be expected due to analyte loss or changes in the sample during the holding period. Thus, as subjectively indicated by Table 6.1, the maximum total score of the Palintest[®] Kit method proves it is closer than any other technique to the ideal method.

CONCLUSIONS

- The Palintest[®] was the best method for the measurement of the concentration of the ClO₂ at the given parameters of different temperatures, concentrations and with different matrices
- Matrix 1, which contains only ClO₂ was judged to be the best matrix for the measurement of ClO₂ as it was free from the other oxychlorine species and thus gave better results than the other matrices used during the project.
- The measured concentration of ClO₂ increased with decreasing temperature. The temperature range from 10°C to 20°C was judged to be the best temperature range where the different methods gave positive bias from 18 percent to 24 percent.
- The measured concentration of ClO₂ increased with the decrease in the actual concentration of ClO₂. The concentration range from 0.4 mg/L to 1.0 mg/L was judged to be the best concentration range for the measurement of ClO₂ giving a positive bias ranging from 15 percent to 20 percent.

RECOMMENDATIONS

- Studies of different matrices at different concentrations and temperatures would provide additional means of comparison. As the tests in this project were carried out just with different temperatures at the same concentrations, additional tests at the concentrations of 0.1 ppm and 0.5 ppm should be carried out at different temperatures.
- The preparation of a standard curve for the LGB wet method for the appropriate test at the desired temperature may further lead to more accurate readings. As the standard curve prepared for all the temperature experiments were carried out at the ambient temperatures while the samples were at different temperatures of 0°C and 10°C. Thus the standard curves if prepared at the same temperatures as of the samples would give different results.
- The experiments should be carried out with the measurement of ClO_2^- using ion chromatography prior to preparation of the laboratory reagent water every time.

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APPENDIX A

RAW ANALYTICAL DATA
FOR
CHLORINE DIOXIDE MEASUREMENT AT VARYING
CONCENTRATIONS AND TEMPERATURE

Table A-1: Determination of Chlorine Dioxide in solutions containing 0.1 mg/L ClO₂ and maintained at 20°C.

Experiment Date: 10/12/01-11/21/01

Matrices	Test	Chlorine Dioxide (mg/L)			
		Palintest [®] Kit	LGB (wet)	DPD HACH [®] Kit	Amperometric Titrations
0.1 mg/L Chlorine Dioxide	1	0.11	0.15	0.18	0.23
	2	0.13	0.13	0.23	0.31
	3	0.12	0.12	0.22	0.30
	4	0.12	0.17	0.21	0.24
	5	0.14	0.15	0.19	0.29
x ± sd		0.12±0.01	0.14±0.02	0.21±0.02	0.27±0.04
0.1 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite	1	0.12	0.16	0.32	0.31
	2	0.13	0.18	0.31	0.29
	3	0.12	0.12	0.24	0.26
	4	0.13	0.15	0.25	0.24
	5	0.13	0.18	0.29	0.38
x ± sd		0.13±0.01	0.16±0.02	0.28±0.04	0.30±0.05
0.1 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite + 0.5 mg/L Chlorate	1	0.12	0.16	0.31	0.31
	2	0.13	0.15	0.29	0.30
	3	0.11	0.18	0.27	0.30
	4	0.12	0.19	0.21	0.28
	5	0.13	0.15	0.28	0.29
x ± sd		0.12±0.01	0.17±0.02	0.27±0.04	0.30±0.01
0.1 mg/L Chlorine Dioxide + 1 mg/L Chlorine	1	0.12	0.13	0.30	0.31
	2	0.13	0.14	0.38	0.28
	3	0.11	0.15	0.23	0.23
	4	0.12	0.16	0.29	0.24
	5	0.13	0.18	0.26	0.28
x ± sd		0.12±0.01	0.15±0.02	0.29±0.06	0.27±0.03

Table A-2: Determination of Chlorine Dioxide in solutions containing 0.1 mg/L ClO₂ and maintained at 20 °C.

Experiment Date: 10/21/01-11/02/01

Matrices	Test	Chlorine Dioxide (mg/L)			
		Palintest [®] Kit	LGB (wet)	DPD HACH [®] Kit	Amperometric Titrations
0.1 mg/L Chlorine Dioxide	1	0.13	0.12	0.15	0.26
	2	0.13	0.15	0.22	0.33
	3	0.15	0.16	0.21	0.27
	4	0.12	0.16	0.24	0.25
	5	0.11	0.14	0.17	0.28
x ± sd		0.13±0.01	0.15±0.02	0.20±0.04	0.28±0.03
0.1 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite	1	0.13	0.16	0.33	0.33
	2	0.14	0.15	0.34	0.25
	3	0.12	0.17	0.32	0.28
	4	0.13	0.15	0.27	0.25
	5	0.17	0.16	0.24	0.27
x ± sd		0.14±0.02	0.16±0.01	0.30±0.04	0.28±0.03
0.1 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite + 0.5 mg/L Chlorate	1	0.12	0.18	0.31	0.27
	2	0.13	0.18	0.23	0.33
	3	0.12	0.17	0.21	0.34
	4	0.15	0.19	0.25	0.27
	5	0.14	0.13	0.23	0.25
x ± sd		0.13±0.01	0.17±0.02	0.25±0.04	0.29±0.04
0.1 mg/L Chlorine Dioxide + 1 mg/L Chlorine	1	0.14	0.14	0.32	0.29
	2	0.13	0.16	0.31	0.25
	3	0.12	0.14	0.24	0.27
	4	0.14	0.16	0.26	0.28
	5	0.19	0.20	0.23	0.29
x ± sd		0.14±0.03	0.16±0.02	0.27±0.04	0.28±0.02

Table A-3: Determination of Chlorine Dioxide in solutions containing 0.5 mg/L ClO₂ and maintained at 20 °C.

Experiment Date:11/02/01-11/09/01

Matrices	Test	Chlorine Dioxide (mg/L)			
		Palintest [®] Kit	LGB (wet)	DPD HACH [®] Kit	Amperometric Titrations
0.5 mg/L Chlorine Dioxide	1	0.49	0.46	0.57	0.56
	2	0.52	0.48	0.54	0.54
	3	0.54	0.51	0.59	0.59
	4	0.47	0.50	0.61	0.61
	5	0.51	0.54	0.59	0.58
X ± sd		0.51±0.03	0.50±0.03	0.58±0.03	0.58±0.03
0.5 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite	1	0.51	0.53	0.58	0.59
	2	0.53	0.53	0.59	0.55
	3	0.45	0.51	0.55	0.60
	4	0.49	0.48	0.61	0.53
	5	0.48	0.45	0.57	0.60
X ± sd		0.49±0.03	0.50±0.03	0.58±0.02	0.57±0.03
0.5 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite + 0.5 mg/L Chlorate	1	0.48	0.54	0.61	0.59
	2	0.43	0.53	0.57	0.54
	3	0.47	0.57	0.58	0.63
	4	0.51	0.51	0.54	0.59
	5	0.53	0.58	0.59	0.60
X ± sd		0.48±0.04	0.55±0.03	0.58±0.03	0.59±0.03
0.5 mg/L Chlorine Dioxide + 1 mg/L Chlorine	1	0.49	0.58	0.61	0.64
	2	0.52	0.54	0.57	0.63
	3	0.54	0.53	0.59	0.59
	4	0.55	0.56	0.68	0.66
	5	0.52	0.57	0.60	0.61
X ± sd		0.52±0.02	0.56±0.02	0.61±0.04	0.63±0.03

Table A-4: Determination of Chlorine Dioxide in solutions containing 0.5 mg/L ClO₂ and maintained at 20 °C.

Experiment Date: 11/09/01-11/14/02

Matrices	Test	Chlorine Dioxide (mg/L)			
		Palintest [®] Kit	LGB (wet)	DPD HACH [®] Kit	Amperometric Titrations
0.5 mg/L Chlorine Dioxide	1	0.47	0.52	0.52	0.59
	2	0.52	0.49	0.56	0.55
	3	0.56	0.51	0.53	0.59
	4	0.43	0.50	0.57	0.58
	5	0.45	0.53	0.55	0.68
x ± sd		0.49±0.05	0.51±0.02	0.55±0.02	0.60±0.05
0.5 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite	1	0.57	0.57	0.54	0.63
	2	0.54	0.54	0.57	0.62
	3	0.53	0.58	0.53	0.65
	4	0.59	0.56	0.59	0.58
	5	0.57	0.46	0.57	0.62
x ± sd		0.56±0.02	0.54±0.05	0.56±0.02	0.62±0.03
0.5 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite + 0.5 mg/L Chlorate	1	0.58	0.55	0.61	0.59
	2	0.54	0.55	0.67	0.58
	3	0.44	0.58	0.52	0.65
	4	0.58	0.54	0.58	0.58
	5	0.59	0.53	0.64	0.60
x ± sd		0.55±0.06	0.55±0.02	0.60±0.02	0.60±0.03
0.5 mg/L Chlorine Dioxide + 1 mg/L Chlorine	1	0.57	0.55	0.54	0.65
	2	0.57	0.57	0.58	0.64
	3	0.55	0.58	0.67	0.68
	4	0.56	0.55	0.57	0.67
	5	0.60	0.54	0.63	0.65
x ± sd		0.57±0.02	0.56±0.02	0.60±0.05	0.66±0.02

Table A-5: Determination of Chlorine Dioxide in solutions containing 1.0 mg/L ClO₂ and maintained at 20 °C.

Experiment Date: 12/14/01-12/19/01

Matrices	Test	Chlorine Dioxide (mg/L)			
		Palintest [®] Kit	LGB (wet)	DPD HACH [®] Kit	Amperometric Titrations
1.0 mg/L Chlorine Dioxide	1	1.11	1.13	1.05	1.23
	2	1.12	1.14	1.04	1.24
	3	1.15	1.15	1.06	1.21
	4	1.14	1.18	1.07	1.23
	5	1.17	1.16	1.13	1.26
x ± sd		1.14±0.02	1.15±0.02	1.07±0.04	1.23±0.02
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite	1	1.19	1.21	1.23	1.23
	2	1.23	1.25	1.21	1.19
	3	1.16	1.13	1.15	1.15
	4	1.21	1.24	1.19	1.15
	5	1.19	1.27	1.25	1.27
x ± sd		1.20±0.02	1.22±0.05	1.21±0.04	1.20±0.05
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite + 0.5 mg/L Chlorate	1	1.23	1.20	1.24	1.26
	2	1.21	1.23	1.22	1.29
	3	1.25	1.19	1.25	1.31
	4	1.23	1.25	1.21	1.21
	5	1.28	1.21	1.20	1.34
x ± sd		1.24±0.03	1.22±0.02	1.22±0.02	1.28±0.05
1.0 mg/L Chlorine Dioxide + 1 mg/L Chlorine	1	1.12	1.22	1.16	1.22
	2	1.14	1.25	1.17	1.28
	3	1.26	1.22	1.26	1.24
	4	1.22	1.12	1.22	1.20
	5	1.25	1.16	1.19	1.27
x ± sd		1.20±0.06	1.19±0.05	1.20±0.04	1.24±0.03

Table A-6: Determination of Chlorine Dioxide in solutions containing 1.0 mg/L ClO₂ and maintained at 20 °C.

Experiment Date: 12/09/01-12/14/01

Matrices	Test	Chlorine Dioxide (mg/L)			
		Palintest [®] Kit	LGB (wet)	DPD HACH [®] Kit	Amperometric Titrations
1.0 mg/L Chlorine Dioxide	1	1.12	1.15	1.07	1.28
	2	1.15	1.16	0.94	1.24
	3	1.16	1.12	1.09	1.27
	4	1.15	1.16	1.07	1.25
	5	1.12	1.15	1.12	1.27
x ± sd		1.14±0.02	1.15±0.02	1.06±0.07	1.26±0.02
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite	1	1.21	1.29	1.21	1.24
	2	1.25	1.25	1.16	1.15
	3	1.16	1.04	1.17	1.13
	4	1.25	1.25	1.27	1.19
	5	1.18	1.21	1.19	1.24
x ± sd		1.21±0.04	1.21±0.10	1.20±0.04	1.19±0.05
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite + 0.5 mg/L Chlorate	1	1.23	1.23	1.23	1.28
	2	1.21	1.22	1.24	1.25
	3	1.31	1.16	1.21	1.24
	4	1.24	1.21	1.23	1.24
	5	1.21	1.21	1.19	1.31
x ± sd		1.24±0.04	1.21±0.03	1.22±0.02	1.26±0.03
1.0 mg/L Chlorine Dioxide + 1 mg/L Chlorine	1	1.14	1.27	1.16	1.24
	2	1.18	1.23	1.18	1.26
	3	1.23	1.22	1.24	1.29
	4	1.28	1.15	1.20	1.16
	5	1.27	1.19	1.21	1.20
x ± sd		1.22±0.06	1.21±0.04	1.20±0.03	1.23±0.05

Table A-7: Determination of Chlorine Dioxide in solutions containing 1.0 mg/L ClO₂ and maintained at 20 °C.

Experiment Date: 12/01/01-12/07/01

Matrices	Test	Chlorine Dioxide (mg/L)			
		Palintest [®] Kit	LGB (wet)	DPD HACH [®] Kit	Amperometric Titrations
1.0 mg/L Chlorine Dioxide	1	1.19	1.19	1.09	1.30
	2	1.14	1.21	1.04	1.28
	3	1.23	1.17	1.11	1.34
	4	1.16	1.10	1.06	1.27
	5	1.12	1.19	0.95	1.20
x ± sd		1.17±0.04	1.17±0.04	1.05±0.06	1.28±0.05
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite	1	1.23	1.25	1.23	1.25
	2	1.24	1.21	1.15	1.19
	3	1.19	1.11	1.13	1.09
	4	1.24	1.24	1.24	1.14
	5	1.29	1.22	1.21	1.19
x ± sd		1.24±0.04	1.21±0.06	1.19±0.05	1.17±0.06
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite + 0.5 mg/L Chlorate	1	1.24	1.21	1.25	1.25
	2	1.29	1.21	1.21	1.21
	3	1.31	1.16	1.20	1.16
	4	1.28	1.19	1.18	1.31
	5	1.19	1.20	1.28	1.35
x ± sd		1.26±0.05	1.19±0.02	1.22±0.04	1.26±0.08
1.0 mg/L Chlorine Dioxide + 1 mg/L Chlorine	1	1.19	1.24	1.15	1.19
	2	1.18	1.25	1.16	1.25
	3	1.25	1.20	1.21	1.15
	4	1.28	1.18	1.19	1.21
	5	1.24	1.15	1.24	1.30
x ± sd		1.23±0.04	1.20±0.04	1.19±0.04	1.22±0.06

Table A-8: Determination of Chlorine Dioxide in solutions containing 1.0 mg/L ClO₂ and maintained at 0 °C.

Experiment Date: 11/14/01-11/20/01

Matrices	Test	Chlorine Dioxide (mg/L)			
		Palintest [®] Kit	LGB (wet)	DPD HACH [®] Kit	Amperometric Titrations
1.0 mg/L Chlorine Dioxide	1	1.56	1.33	1.03	1.30
	2	1.52	1.32	0.96	1.42
	3	1.45	1.35	1.12	1.52
	4	1.57	1.35	1.13	1.63
	5	1.46	1.39	1.05	1.46
x ± sd		1.51±0.06	1.35±0.03	1.06±0.07	1.47±0.12
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite	1	1.42	1.38	1.37	1.52
	2	1.32	1.44	1.40	1.52
	3	1.49	1.33	1.35	1.49
	4	1.43	1.46	1.30	1.36
	5	1.54	1.39	1.43	1.52
x ± sd		1.44±0.08	1.40±0.05	1.37±0.05	1.48±0.07
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite + 0.5 mg/L Chlorate	1	1.59	1.38	1.27	1.37
	2	1.52	1.51	1.32	1.47
	3	1.49	1.52	1.36	1.49
	4	1.34	1.57	1.42	1.44
	5	1.46	1.52	1.30	1.36
x ± sd		1.48±0.09	1.50±0.07	1.33±0.06	1.43±0.06
1.0 mg/L Chlorine Dioxide + 1 mg/L Chlorine	1	1.59	1.46	1.25	1.38
	2	1.53	1.39	1.29	1.40
	3	1.49	1.44	1.38	1.35
	4	1.39	1.42	1.32	1.43
	5	1.52	1.48	1.41	1.53
x ± sd		1.50±0.07	1.44±0.03	1.33±0.07	1.42±0.07

Table A-9: Determination of Chlorine Dioxide in solutions containing 1.0 mg/L ClO₂ and maintained at 0 °C.

Experiment Date: 11/20/01-11/24/01

Matrices	Test	Chlorine Dioxide (mg/L)			
		Palintest [®] Kit	LGB (wet)	DPD HACH [®] Kit	Amperometric Titrations
1.0 mg/L Chlorine Dioxide	1	1.51	1.31	1.08	1.29
	2	1.49	1.34	1.10	1.42
	3	1.56	1.39	1.14	1.53
	4	1.58	1.41	1.15	1.61
	5	1.49	1.34	1.12	1.42
x ± sd		1.53±0.04	1.36±0.04	1.12±0.03	1.45±0.12
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite	1	1.49	1.31	1.37	1.38
	2	1.56	1.40	1.48	1.62
	3	1.59	1.38	1.40	1.60
	4	1.46	1.42	1.38	1.49
	5	1.55	1.38	1.46	1.51
x ± sd		1.53±0.05	1.38±0.04	1.42±0.05	1.52±0.04
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite + 0.5 mg/L Chlorate	1	1.61	1.46	1.39	1.41
	2	1.59	1.51	1.48	1.52
	3	1.61	1.60	1.41	1.46
	4	1.39	1.49	1.56	1.49
	5	1.49	1.54	1.47	1.23
x ± sd		1.54±0.10	1.52±0.05	1.46±0.07	1.42±0.11
1.0 mg/L Chlorine Dioxide + 1 mg/L Chlorine	1	1.61	1.44	1.32	1.41
	2	1.62	1.56	1.39	1.42
	3	1.63	1.47	1.42	1.32
	4	1.56	1.49	1.57	1.41
	5	1.51	1.58	1.46	1.59
x ± sd		1.59±0.05	1.51±0.06	1.43±0.09	1.43±0.10

Table A-10: Determination of Chlorine Dioxide in solutions containing 1.0 mg/L ClO₂ and maintained at 0 °C.

Experiment Date: 11/25/01-11/30/01

Matrices	Test	Chlorine Dioxide (mg/L)			
		Palintest [®] Kit	LGB (wet)	DPD HACH [®] Kit	Amperometric Titrations
1.0 mg/L Chlorine Dioxide	1	1.51	1.34	1.05	1.43
	2	1.50	1.37	1.12	1.52
	3	1.52	1.38	1.13	1.51
	4	1.44	1.47	1.09	1.49
	5	1.56	1.33	1.13	1.61
x ± sd		1.51±0.04	1.38±0.06	1.10±0.03	1.51±0.06
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite	1	1.51	1.41	1.36	1.39
	2	1.52	1.42	1.39	1.53
	3	1.51	1.38	1.47	1.52
	4	1.42	1.37	1.40	1.47
	5	1.41	1.34	1.39	1.42
x ± sd		1.47±0.05	1.38±0.03	1.40±0.04	1.47±0.06
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite + 0.5 mg/L Chlorate	1	1.51	1.41	1.39	1.47
	2	1.46	1.42	1.46	1.53
	3	1.36	1.38	1.51	1.57
	4	1.28	1.36	1.48	1.62
	5	1.31	1.33	1.32	1.58
x ± sd		1.38±0.10	1.38±0.04	1.43±0.08	1.55±0.06
1.0 mg/L Chlorine Dioxide + 1 mg/L Chlorine	1	1.61	1.56	1.34	1.59
	2	1.49	1.51	1.39	1.63
	3	1.62	1.47	1.43	1.41
	4	1.59	1.49	1.56	1.49
	5	1.58	1.52	1.39	1.62
x ± sd		1.58±0.05	1.51±0.03	1.42±0.08	1.55±0.09

Table A-11: Determination of Chlorine Dioxide in solutions containing 1.0 mg/L ClO₂ and maintained at 10 °C.

Experiment Date: 12/19/01-12/24/01

Matrices	Test	Chlorine Dioxide (mg/L)			
		Palintest [®] Kit	LGB (wet)	DPD HACH [®] Kit	Amperometric Titrations
1.0 mg/L Chlorine Dioxide	1	1.21	1.19	1.07	1.26
	2	1.17	1.21	0.95	1.31
	3	1.23	1.23	0.98	1.26
	4	1.24	1.24	1.06	1.28
	5	1.19	1.19	1.13	1.32
x ± sd		1.21±0.03	1.21±0.02	1.04±0.07	1.29±0.03
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite	1	1.25	1.25	1.29	1.23
	2	1.23	1.18	1.19	1.19
	3	1.19	1.12	1.21	1.18
	4	1.24	1.29	1.26	1.24
	5	1.31	1.19	1.17	1.26
x ± sd		1.24±0.04	1.21±0.07	1.22±0.05	1.22±0.03
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite + 0.5 mg/L Chlorate	1	1.29	1.22	1.27	1.25
	2	1.26	1.27	1.24	1.27
	3	1.30	1.19	1.29	1.26
	4	1.28	1.25	1.28	1.28
	5	1.25	1.23	1.25	1.26
x ± sd		1.28±0.02	1.23±0.03	1.27±0.02	1.26±0.01
1.0 mg/L Chlorine Dioxide + 1 mg/L Chlorine	1	1.18	1.28	1.31	1.29
	2	1.24	1.21	1.19	1.35
	3	1.28	1.28	1.29	1.31
	4	1.24	1.18	1.27	1.19
	5	1.25	1.31	1.28	1.27
x ± sd		1.24±0.04	1.25±0.05	1.27±0.05	1.28±0.06

Table A-12: Determination of Chlorine Dioxide in solutions containing 1.0 mg/L ClO₂ and maintained at 10 °C.

Experiment Date: 12/24/01-12/29/01

Matrices	Test	Chlorine Dioxide (mg/L)			
		Palintest [®] Kit	LGB (wet)	DPD HACH [®] Kit	Amperometric Titrations
1.0 mg/L Chlorine Dioxide	1	1.25	1.21	1.07	1.24
	2	1.23	1.25	0.94	1.36
	3	1.29	1.24	1.20	1.22
	4	1.27	1.29	1.08	1.31
	5	1.28	1.25	1.15	1.35
x ± sd		1.26±0.02	1.25±0.03	1.09±0.10	1.30±0.06
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite	1	1.29	1.23	1.16	1.31
	2	1.22	1.24	1.20	1.16
	3	1.18	1.21	1.21	1.18
	4	1.29	1.25	1.27	1.23
	5	1.28	1.21	1.11	1.29
x ± sd		1.25±0.05	1.23±0.02	1.19±0.06	1.230±.07
1.0 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite + 0.5 mg/L Chlorate	1	1.28	1.26	1.28	1.22
	2	1.29	1.28	1.24	1.23
	3	1.31	1.21	1.24	1.26
	4	1.32	1.26	1.26	1.22
	5	1.29	1.23	1.22	1.28
x ± sd		1.30±0.02	1.25±0.03	1.25±0.02	1.24±0.03
1.0 mg/L Chlorine Dioxide + 1 mg/L Chlorine	1	1.21	1.22	1.26	1.21
	2	1.28	1.21	1.29	1.32
	3	1.29	1.22	1.26	1.21
	4	1.26	1.26	1.23	1.26
	5	1.27	1.24	1.29	1.21
x ± sd		1.26±0.03	1.23±0.02	1.27±0.03	1.240±.05

Table A-13: Determination of Chlorine Dioxide in solutions containing 1.0 mg/L ClO₂ and maintained at 10 °C.

Experiment Date: 12/29/01-01/03/02

Matrices	Test	Chlorine Dioxide (mg/L)			
		Palintest [®] Kit	LGB (wet)	DPD HACH [®] Kit	Amperometric Titrations
0.1 mg/L Chlorine Dioxide	1	1.24	1.27	0.96	1.34
	2	1.22	1.24	0.97	1.29
	3	1.24	1.25	1.12	1.23
	4	1.23	1.27	1.07	1.26
	5	1.26	1.22	1.20	1.32
x ± sd		1.24±0.01	1.25±0.02	1.06±0.10	1.29±0.04
0.1 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite	1	1.31	1.24	1.12	1.33
	2	1.30	1.22	1.27	1.25
	3	1.26	1.24	1.23	1.21
	4	1.23	1.29	1.29	1.21
	5	1.19	1.23	1.21	1.17
x ± sd		1.26±0.05	1.24±0.03	1.22±0.07	1.23±0.06
0.1 mg/L Chlorine Dioxide + 0.5 mg/L Chlorite + 0.5 mg/L Chlorate	1	1.22	1.26	1.23	1.23
	2	1.26	1.27	1.22	1.25
	3	1.25	1.23	1.24	1.22
	4	1.30	1.28	1.26	1.27
	5	1.27	1.21	1.26	1.22
x ± sd		1.26±0.03	1.25±0.03	1.24±0.02	1.24±0.02
0.1 mg/L Chlorine Dioxide + 1 mg/L Chlorine	1	1.22	1.27	1.22	1.23
	2	1.26	1.22	1.24	1.29
	3	1.31	1.22	1.28	1.25
	4	1.26	1.20	1.28	1.29
	5	1.28	1.25	1.31	1.34
x ± sd		1.27±0.03	1.23±0.03	1.27±0.04	1.28±.04

VITA

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