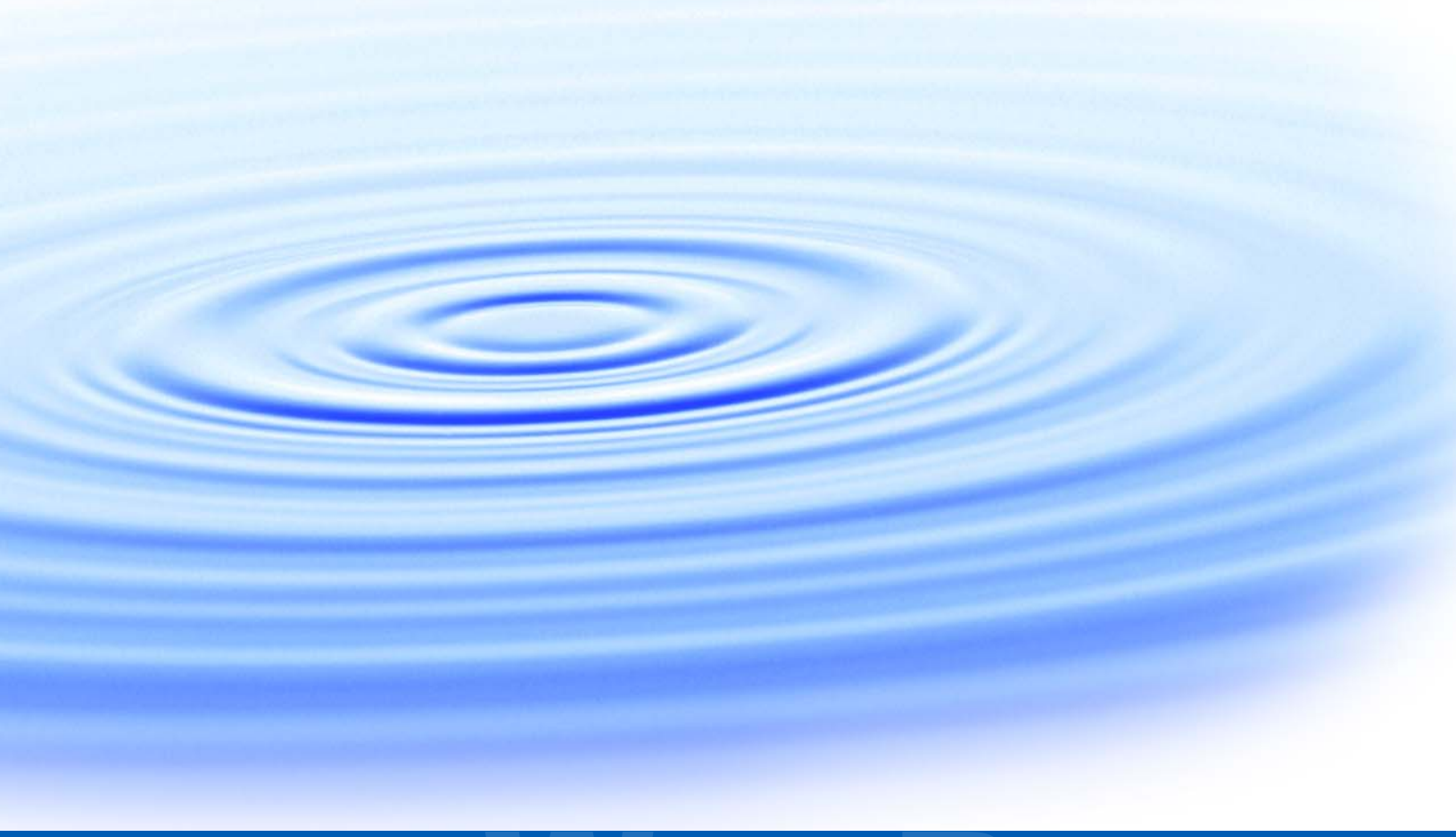
WATEREUSE FOUNDATION

Methods for the Detection of Residual Concentrations of Hydrogen Peroxide in Advanced Oxidation Processes



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About the WateReuse Foundation

The mission of the WateReuse Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, salinity management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of increasing reliability and quality.

The Foundation's funding partners include the Bureau of Reclamation, the California State Water Resources Control Board, the Southwest Florida Water Management District, the California Department of Water Resources, and the California Energy Commission. Funding is also provided by the Foundation's Subscribers, water and wastewater agencies, and other interested organizations.

Methods for the Detection of Residual Concentrations of Hydrogen Peroxide in Advanced Oxidation Processes

Philip J. Brandhuber, Ph.D.
HDR Engineering Inc.

Gregory Korshin, Ph.D.
University of Washington

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For more information, contact:
WateReuse Foundation
1199 North Fairfax Street, Suite 410
Alexandria, VA 22314
703-548-0880
703-548-5085 (fax)
www.WateReuse.org/Foundation

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FOREWORD

The WateReuse Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide high-quality water, protect public health, and improve the environment.

A Research Plan guides the Foundation's research program. Under the plan, a research agenda of high-priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities, including water professionals, academics, and Foundation Subscribers. The Foundation's research focuses on a broad range of water reuse research topics, including the following:

- Defining and addressing emerging contaminants
- Public perceptions of the benefits and risks of water reuse
- Management practices related to indirect potable reuse
- Groundwater recharge and aquifer storage and recovery
- Evaluating methods for managing salinity and desalination
- Economics and marketing of water reuse

The Research Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project and provide technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's Project Managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

The Foundation's funding partners include the Bureau of Reclamation, the California State Water Resources Control Board, the California Department of Water Resources, the Southwest Florida Water Management District, the California Energy Commission, Foundation Subscribers, water and wastewater agencies, and other interested organizations. The Foundation leverages its financial and intellectual capital through these partnerships and funding relationships. The Foundation is also a member of the Global Water Research Coalition.

This publication is the result of a Foundation study and is intended to communicate the results of the research project. The purpose of this project was to develop a laboratory method for reliable quantification of hydrogen peroxide in the 0.5- to 5-mg/L concentration range that is effective in a natural water matrix as well as in the presence of combined chlorine (chloramine).

David L. Moore
President
WateReuse Foundation

G. Wade Miller
Executive Director
WateReuse Foundation

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The project team recognizes the efforts of Gregg Oelker (United Water) and Steve Fitzsimmons (Orange County Water District) in completing the interlaboratory study. Special thanks are due to Uzi Daniel (West Basin) for her support of the project.

Principal Investigator and Project Manager
Philip Brandhuber, Ph.D., *HDR Engineering Inc.*

Co-Principal Investigator
Greorgy Korshin, Ph.D., *University of Washington*

Project Advisory Committee
Marco Aieta, *Carollo Engineers*
Robert Cheng, *Long Beach Water Department*
Andrew Murphy, *Bureau of Reclamation*
Rhodes Trussell, *Trussell Technologies*

Technical Advisory Committee
Andrew Eaton, *MWH Labs*
Gil Gordan, *University of Miami*
Rick Sakaji, *East Bay Municipal Utility District*

EXECUTIVE SUMMARY

PROJECT BACKGROUND AND OBJECTIVES

Advanced oxidation processes (AOPs), coupling either ultraviolet (UV) irradiation or ozonation in the presence of hydrogen peroxide, are advanced treatment techniques that have been installed by several utilities to meet California Department of Public Health regulations. Of prime importance in monitoring the performance of AOPs is the ability to accurately measure residual hydrogen peroxide concentrations. In addition to monitoring performance, accurate measurement of hydrogen peroxide residuals may also provide an economic benefit, since systems could be operated on the basis of residual concentration rather than of applied dose, permitting the ability to "fine tune" the process. Yet, at present, it is not clear that a simple laboratory method for the detection of hydrogen peroxide exists that is free of interference from other oxidants such as chloramines.

The purpose of this project was to develop a laboratory method for reliable quantification of hydrogen peroxide in the 0.5- to 5-mg/L concentration range that is effective in a natural water matrix as well as in the presence of combined chlorine (chloramine).

PROJECT APPROACH

A step-by-step process was used to select and test peroxide detection methods. First, the performance requirements for the detection method were defined, and a literature review of existing methods was completed. In conjunction with the Project Advisory Committee (PAC), the methods were prioritized for their likelihood of meeting the performance requirements. Two methods then underwent preliminary bench-level evaluation by the University of Washington. Based on this evaluation, the titanium oxalate detection method was determined to be both simple and accurate with little interference from chloramine. Additional evaluations of the method were performed by the University of Washington in which the method detection level (MDL), bias, and precision were determined. Lastly, an interlaboratory evaluation of the titanium oxalate method was performed by the West Basin and Orange County Water District (OCWD) laboratories, using both Orange County and West Basin water. Method bias and precision for peroxide quantification using the titanium oxalate method were calculated for the analyses performed by these laboratories.

Definition of Performance Requirements

In consultation with the OCWD, West Basin and the PAC, the following performance requirements for the peroxide detection method were defined:

- The method should be a laboratory method. An online or real-time measurement is not required. A rapid method is desirable but not imperative. It was anticipated that the method will be used at a frequency ranging from daily to weekly.

- The method should be able to reliably quantify hydrogen peroxide in the 0.5- to 5.0-mg/L concentration range.

- The method should be effective in a natural water matrix. However, the specific focus of the project should be on the Orange County and West Basin water matrices.
- The method should be effective in the presence of combined chlorine (chloramine).
- The method should be relatively simple and not require highly specialized equipment or instrumentation.
- If possible, a spectrophotometric method is preferred over a fluorescence method.

Identification of Existing Methods

The literature review identified 13 different published methods for hydrogen peroxide detection. These methods can be broken down into four basic categories. These include titration, spectrophotometry, fluorescence, and chemiluminescence. A summary of published methods identified by the literature review is included in Table ES-1.

Prioritization of Methods to Be Evaluated

Based on the literature review (see Chapter 2), and in consultation with the PAC, it was concluded that the spectrophotometric copper–2,9-diemethyl-1,10-phenanthroline (DMP) and titanium oxalate methods were most likely to be free of interference by chloramine. Hence, in prioritizing the methods to be evaluated, these methods were considered first. If either of these methods was determined not to be effective, the peroxidase leuco crystal violet, peroxidase–*N*,*N*-diethyl-*p*-phenylenediamine (DPD), peroxovanadium, and cobalt carbonate methods would be considered in descending order of priority.

Selection of Method for Additional Evaluation

The copper–DMP and titanium oxalate methods were initially compared on the basis of their sensitivity to the presence of peroxide in a sample and the degree to which chloramine interferes with the measurement of known peroxide concentrations. Sensitivity was inferred from the slope of H_2O_2-absorbance correlation, whereas interference was inferred by a change in absorbance caused by varying chloramine concentration at a constant peroxide concentration.

When compared, the slope of H_2O_2-absorbance correlation for the copper–DMP method was found to be greater than the titanium oxalate method, indicating that the copper–DMP method is inherently more sensitive to the presence of peroxide than is the titanium oxalate method. However, the titanium oxalate method was found to be practically unaffected by the presence of chloramine and/or organic matter in water, while the copper–DMP method was found to be sensitive to its presence. The insensitivity of the titanium oxalate method to the presence of peroxide is shown in Figure ES-1. This figure illustrates that OCWD water, spiked with two constant concentrations of hydrogen peroxide at various chloramine concentrations, showed no effects from chloramine when the absorbance of titanium–hydrogen peroxide complex formed by the titanium oxalate method was being measured.

Table ES-1. Summary of Analytical Methods from Literature Review

Type	Method	H_2O_2 Range	Reaction Mechanism and Detection Conditions	Performance Assessment/Interference
Titration	Iodometric	0.1– 6 wt %	Oxidize iodide to iodine, titrated with thiosulfate and starch.	Not accurate at low concentration; subject to interference.
	Permanganate	0.25–70 wt %	Reduce permanganate to manganous ion.	Not accurate at low concentration.
	Ceric sulfate	1–13 wt %	With ferroin indicator, titrate to pale blue.	Not accurate at low concentration.
Spectrophotometry	Cobalt carbonate	≤0.1 mg/L	Formation of a UV-absorbing complex between Co^{3+} and carbonate, detection at 260 nm.	Reducing and complexing agents; combined and free chlorine effects not known.
	Iodometric	0.05–10 mg/L	Oxidize iodide to iodine with molybdate catalyst at pH = 5; detection at 351 nm.	Evidence of interference from oxidants.
	Titanium oxalate	0.1–50 mg/L	Formation of colored peroxotitanium complex; detection at 400 nm.	Some UV-absorbing species, turbidity, color; combined and free chlorine effects not known.
	Peroxidase enzyme-leuco crystal	0.1–10 mg/L	Oxidation of leuco crystal violet dye by H_2O_2 in presence of peroxidase enzyme catalyst; detection at 596 nm.	Usually interference free, slow color development, sensitive to sunlight; combined and free chlorine effects not known.
	Peroxidase enzyme –DPD	0.02–10 mg/L	Oxidation of DPD by H_2O_2 in presence of peroxidase enzyme catalyst; detection at 551 nm.	Likely interference from combined and free chlorine; color unstable.
	Copper–DMP	0.03–10 mg/L	Reduction of Cu(II) and formation of copper–DMP complex; detection at 454 nm.	Reported to be effective in presence of chlorine; stable color.
	Peroxovanadium	4–10 mg/L	Reduction of V(V) and formation of peroxovanadium cation; detection at 450 nm.	High detection limit; interference not known.
Fluorescence	Peroxidase enzyme–POHPAA	>0.001 mg/L	Peroxidase catalyzed oxidation of POHPAA by H_2O_2; fluoresces at 400 nm.	Known positive interference with chlorine.
	Peroxidase enzyme–scopoletin	>0.00005 mg/L	Peroxidase catalyzed oxidation of scopoletin by H_2O_2; measure decay of fluorescence at 395 nm.	Possible positive interference with chlorine.
Chemi-luminescence	Luminol	>0.0002 mg/L	Catalyzed decomposition of luminol by H_2O_2 in presence of cobalt or copper; detect luminescence of decomposition product.	Positive interference from natural water (possibly organic matter); interference from combined and free chlorine unknown.

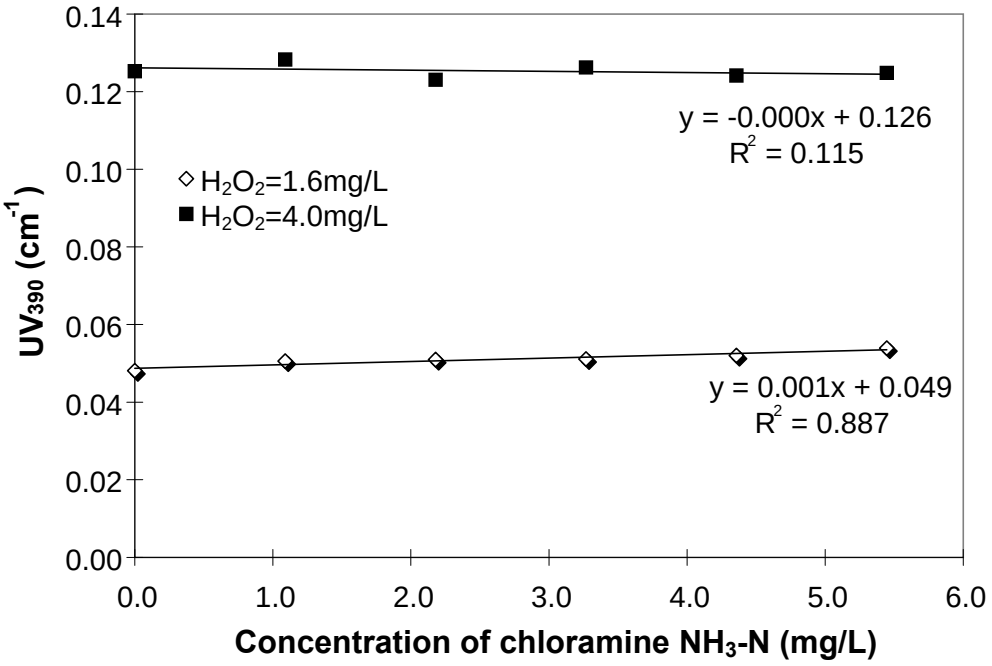

Figure ES-1. Lack of effect from varying chloramine concentrations in Orange County water on the absorbance at 390 nm.

Based on this information, it was concluded that the titanium oxalate method is considerably more robust and interference free than the other methods under consideration. It also affords acceptable levels of precision and sensitivity as well as simplicity in meeting the requirements defined above.

ASSESSMENT OF TITANIUM OXALATE METHOD PERFORMANCE

Description of the Titanium Oxalate Method

The basis of the method is the formation of a titanium(IV)–peroxide complex in the presence of sulfuric acid. Potassium titanium oxalate ($K_2TiO[C_2O_4]_2 \cdot H_2O$; CAS 14481-26-6), a commercially available titanium(IV) salt, is used as the source of titanium(IV). The titanium(IV)–peroxide complex is yellowish orange, and its concentration can be quantified by spectrophotometric analysis with a maximum response at 390 nm.

The titanium oxalate method is divided into five steps. The first step involves the preparation of reagents needed for the analysis. The second step is the standardization of a peroxide solution for use in developing the calibration curve. The standardization is performed by potassium permanganate titration. The third step consists of developing a calibration curve, relating measured optical density to the known concentration of peroxide standards at 390 nm. Step 4 is the preparation of the sample for analysis by pipetting the unknown peroxide sample into deionized water, titanium oxalate, and sulfuric acid, forming the titanium(IV)–peroxide complex.

Step 5 completes the analysis by determining the optical density of the unknown sample and determining its peroxide concentration from the calibration curve developed in step 3. Figure ES-2 provides a graphic illustration of the method. The detailed steps for performing the method are included in Appendix A.

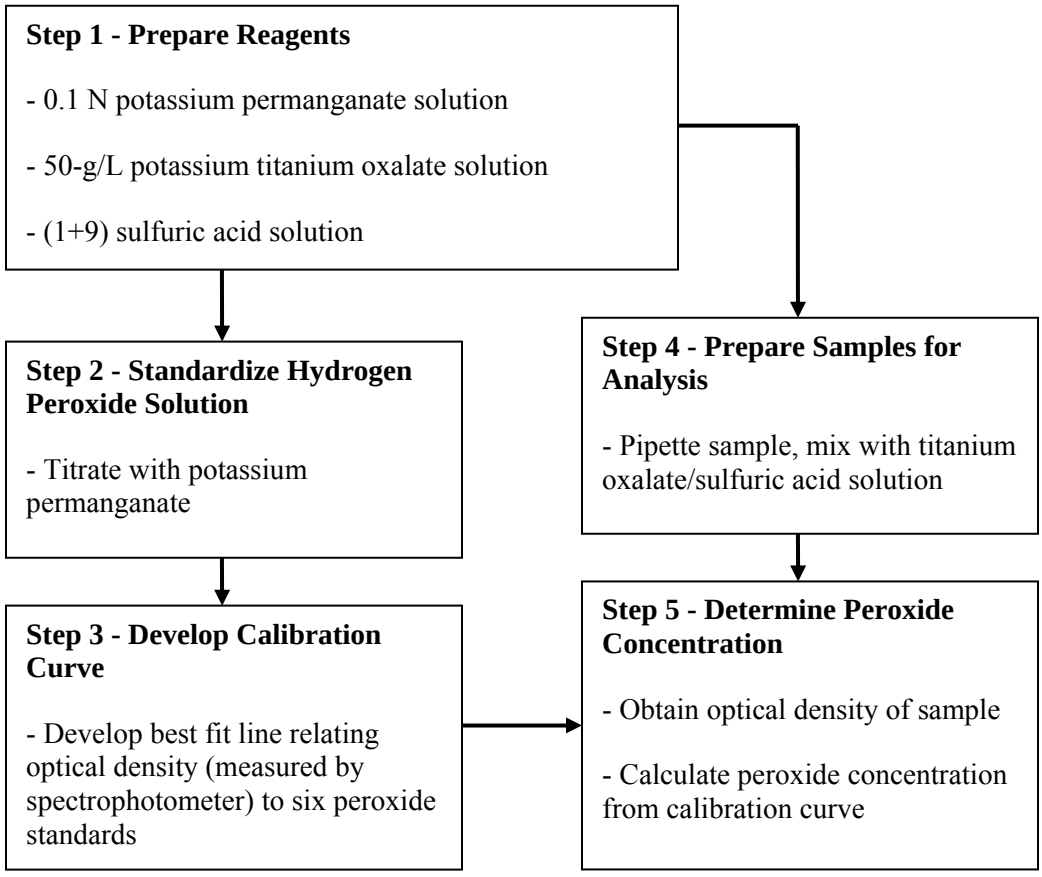

Figure ES-2. Titanium oxalate method for peroxide detection.

Performance of the Titanium Oxalate Method

An assessment of the MDL, bias, and precision was performed by bench-level experiments at the University of Washington and through an interlaboratory effort of the West Basin and OCWD laboratories. The estimated detection limit, bias, and precision of the method (calculated per *Standard Methods* 1040C.3), as determined by bench and interlaboratory evaluation, are presented in Table ES-2.

Table ES-2. MDL, Precision, and Bias for Titanium Oxalate Method

	Value	
Characteristic	**Bench Evaluation**	**Interlaboratory Evaluation**
MDL for H_2O_2	0.05 mg/L[a]	n/a
Precision	4%	5%
Bias	0.4%	−2%

[a]At an H_2O_2 concentration of >0.5 mg/L.

PROJECT RECOMMENDATION

The titanium oxalate method is an effective method for detecting hydrogen peroxide in the presence of chloramine and is suitable for use with AOPs operated by the OCWD and West Basin.

CHAPTER 1

INTRODUCTION AND PROJECT OBJECTIVE

1.1 BACKGROUND

Groundwater recharge with recycled water has been practiced in California since the 1960s. Because groundwater aquifers serve as potable water supply basins, groundwater recharge, including injection as a seawater intrusion barrier, is considered an indirect potable reuse. The California Department of Public Health (CalDPH) requires advanced treatment of recycled water before it is used to recharge groundwater aquifers. These treatment requirements are more restrictive than the typical requirements for discharges to inland surface or coastal waters.

Advanced oxidation processes (AOPs), coupling either ultraviolet (UV) irradiation or ozonation in the presence of hydrogen peroxide, are advanced treatment techniques that have been installed by several utilities to meet CalDPH regulations. AOPs are capable of treating trace contaminants such as 1,4 dioxane and *n*-nitrosodimethylamine (NDMA), as well as some pharmaceutically active compounds (PhACs) and personal care products (PCPs). Of prime importance in monitoring the performance of AOPs is the ability to accurately measure residual hydrogen peroxide concentrations. In addition to monitoring performance, accurate measurement of hydrogen peroxide residuals may also provide an economic benefit, since systems could be operated on the basis of residual concentration rather than on that of applied dose, permitting one to "fine tune" the process.

1.1.1 Hydrogen Peroxide Chemistry

Hydrogen peroxide (H_2O_2) is a clear, colorless liquid, slightly more viscous than water. It is completely miscible in water and alcohol. Structurally, it consists of two oxygens and two hydrogens connected by covalent bonds. The structure of hydrogen peroxide is illustrated in Figure 1-1.

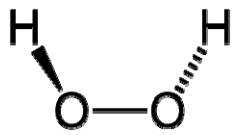

Figure 1-1. Structure of hydrogen peroxide.

Hydrogen peroxide behaves as a weak acid. At alkaline pH it deprotonates and forms a perhydroxyl ion along with a hydrogen ion:

$$H_2O_2 \leftrightarrow H^+ + HO_2^- \qquad pK_a = 11.6$$

In theory H_2O_2 is a strong oxidizing agent. The half-cell reaction for hydrogen peroxide is

$H_2O_2 + 2H^+ + 2e^- \Rightarrow 2H_2O$ $E^0 = 1.76V$

In basic solutions, the half-cell potential is lower because of the presence of the perhydroxyl ion rather than of the hydrogen peroxide molecule. The half-cell reaction in basic solutions is

$HO_2^- + H_2O + 2e^- \Rightarrow 3OH^-$ $E^0 = 0.87V$

Considering the redox potential, one would expect hydrogen peroxide to behave as a strong oxidizing agent. Its E^0 is greater than those of chlorine (1.36 V) and permanganate (1.70 V) but less than that of ozone (2.08 V). Yet hydrogen peroxide behaves as a relatively weak oxidant. It generally requires activation to exhibit oxidizing properties. The activation generally involves the formation of hydroxyl radicals. Many analytical methods include the use of catalysts.

Hydrogen peroxide can also behave as a reducing agent per the following half-cell reaction:

$2H_2O_2^- \Rightarrow 2H^+ + O_2 + 2e^-$ $E^0 = -0.69V$

The corresponding half-cell reaction for the perhydroxyl ion is

$HO_2^- + OH^- \Rightarrow 2H^+ + O_2 + 2H_2O + 2e^-$ $E^0 = -0.08V$

At low and moderate pH, hydrogen peroxide is relatively stable and will rapidly decompose only when catalytic agents (like iron) are present. However, the perhydroxyl ion is inherently more unstable than peroxide, and hydrogen peroxide will decompose at alkaline conditions per the following pathway:

$$H_2O_2 + OH^- \rightarrow HOO^- + H_2O$$

$$\downarrow$$

$$0.5\ O_2 + OH^-$$

1.1.2 AOPs

AOPs involve the in situ generation of the highly potent hydroxyl free radical (OH•) for the treatment of recalcitrant organic compounds. Hydroxyl radicals break down organic contaminants through abstraction of hydrogen atoms. The hydroxyl radical is also one of the most active oxidizing agents known, with an E^0 of 2.8 V. Because of its activity, the hydroxyl radical tends to be short-lived in solution and nonselective in its attack of electron-rich bonds. The half-life of the hydroxyl radical is brief, on the order of microseconds or even nanoseconds. For this reason, it is difficult to analytically quantify its concentration and the ability to measure residual peroxide concentration as a surrogate is important as a means to monitor the AOP.

Hydroxyl radicals are capable of oxidizing contaminants that are immune to attack by traditional water treatment oxidants such as permanganate, chlorine, and ozone. The hydroxyl radical is a powerful oxidant at ambient temperatures and pressures and at moderate pH. However, high concentrations of bicarbonate or carbonate can react with hydroxyl radicals and reduce the effectiveness of the process. Unlike other treatments, such as membranes or ion exchange, AOPs use the hydroxyl radical to destroy the contaminant rather than concentrating it in a separate

residual stream that requires disposal or additional treatment. In general AOP produces low levels of trihalomethanes and haloacetic acids regulated as disinfection by-products in drinking water.

Currently two AOP technologies available on a commercial scale use hydrogen peroxide for the generation of the hydroxyl radical. These include UV/hydrogen peroxide and ozone/hydrogen peroxide systems. The focus of this project is the detection of peroxide for a UV/hydrogen peroxide process, although the results of this work may be applicable to ozone/hydrogen peroxide systems as well.

1.1.2.1 The UV/Hydrogen Peroxide Process

The UV/hydrogen peroxide process employs photolysis to create hydroxyl radicals by using UV light to cleave the O-O bond of the hydrogen peroxide molecule. The process is summarized as follows:

$H_2O_2 + h\nu$ (at $\lambda \approx 200$ to 240 nm) $\Rightarrow$ OH• + OH•

1.1.2.2 The Ozone/Hydrogen Peroxide Process

The chemistry of the ozone/hydrogen peroxide process is more complicated than that of the UV/hydrogen peroxide process. This is because ozone, the hydroxyl radical, and intermediate compounds formed during radical formation and ozone decomposition all can contribute to the oxidation of contaminants. The actual mix of oxidants is determined by factors such as water quality, concentrations of ozone and peroxide present, and the relative ratio of peroxide to applied ozone. A simplified view of the hydroxyl formation process is

$H_2O_2 + 2O_3 \Rightarrow$ OH• + OH• + $3O_2$

1.1.3 Overview of Analytical Methods for Peroxide Detection

At present, *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association, 2005) (referred to as *Standard Methods*) does not include a procedure for measuring hydrogen peroxide concentrations. However, numerous non-standard methods for hydrogen peroxide detection are published in the literature. While these methods have been successfully used for specific applications, they frequently lack simplicity or are subject to positive or negative interference due to components typically present in natural water. In addition, the performance of these methods in the presence of free or combined chlorine is generally unknown. Laboratory methods for the determination of hydrogen peroxide concentrations fall into four categories. The categories include

- Titration
- Spectrophotometry
- Fluorescence
- Chemiluminescence

Methods that fall into each of these four categories will be reviewed in the next chapter of this report. A final category of peroxide detection techniques involves electrochemical methods. Electrochemical detection methods are primarily used to measure the concentration of peroxide in biological samples and for other specialized purposes (Karyakin et al., 2004; Schwake et al., 1998). Electrochemical methods typically are very sensitive and require expensive equipment, extensive calibration, and operator training. These methods are unlikely to be used by a utility. Electrochemical methods were not considered by this project.

In general, titration methods are not accurate in the peroxide concentration range (0.5 to 5 mg/L) of interest to this project. They are also time consuming and require moderate skill. Spectrophotometric methods generally are rapid and well suited for water quality analysis by utilities. If free from interference, or if the extent of interference can be quantified and corrected for, spectrophotometric methods are likely to be effective for determining peroxide in the concentration range of interest to this project. Fluorescence and chemiluminescence methods have been widely used for the quantification of peroxide concentration in environmental samples. In general, these methods have the lowest detection limits. However, these methods are more complex and require instruments and equipment not available in a utility water quality laboratory.

1.2 PROJECT OBJECTIVE

The purpose of this project is to develop a laboratory method for reliable quantification of hydrogen peroxide in the 0.5- to 5-mg/L concentration range that is effective in a natural water matrix, as well as in the presence of combined chlorine (chloramine).

CHAPTER 2

LITERATURE REVIEW

2.1 REVIEW OF ANALYTICAL METHODS

As mentioned in the previous chapter, there are four categories of hydrogen peroxide detection methods considered in the project. These include

- Titration
- Spectrophotometry
- Fluorescence
- Chemiluminescence

Existing literature regarding each of these methods will be reviewed in this chapter.

2.1.1 Titration Methods

2.1.1.1 Iodometric Method

The basis of this method is the oxidation of iodide to iodine in the presence of a molybdate catalyst. The iodine formed by this reaction is titrated with a thiosulfate solution using a starch indicator to indicate the endpoint of the titration. The titration is performed under acidic conditions at an approximate pH of 4. The titration reactions are, according to Scott (1939):

$H_2O_2 + 2KI + H_2SO_4 \leftrightarrow I_2 + K_2SO_4 + 2H_2O$

$I_2 + 2Na_2S_2O_3 \leftrightarrow Na_2S_4O_6 + 2NaI$

When the iodine has been formed by reaction with peroxide, it is titrated against thiosulfate. The resulting solution turns pale yellow. Adding starch forms a deep blue that changes to colorless at the end point of the titration (Kieber and Helz, 1986; US Peroxide). Starch is added near the end of the titration to avoid the formation of insoluble complexes between the starch and iodine. It is recommended that peroxide–iodide solution be stored 5 min in the dark prior to titration with thiosulfate (Gordon et al., 1992). The overall stoichiometry of the reaction is 1 mol of H_2O_2 reacts with 2 mol of $Na_2S_2O_3$. The method is valid for peroxide determinations from 0.1 wt % to 6 wt % (US Peroxide). The basic method has been called Kingzett's method in honor of the author who first proposed it (Kingzett, 1880).

This method is primarily used to standardize stock peroxide solutions. Factors that may affect the accuracy of this method include the possible volatility of iodide; catalysis or interference from transition metals such as iron, copper, nickel, and chromium; and the fading of color (Gordon et al., 1992).

2.1.1.2 Permanganate Method

In contrast to the iodometric method, which depends on the oxidizing properties of peroxide, the permanganate method depends on peroxide's reducing properties. For this method, potassium(VII) is reduced to potassium(II) per the following reaction (FMC Corporation, 1978; Klassem et al., 1994; Masschelein et al., 1977; Schumb et al., 1955; US Peroxide):

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \leftrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

The overall stoichiometry of the reaction is 5 mol of H_2O_2 reacts with 2 mol of $KMnO_4$. Similar to the iodometric method, the titration is performed under acidic conditions. The peroxide solution is titrated with permanganate until a permanent pinkness develops. This method is subject to interference caused by both organic and inorganic substances that react with permanganate (Gordon et al., 1992). The method is valid for peroxide determinations from 0.25 wt % to 70 wt % (US Peroxide). This method is sometimes termed the Ghormley method (Hochanadel, 1952).

2.1.1.3 Ceric Sulfate Method

This method consists of determining hydrogen peroxide concentrations by titration with cerium(IV) in the form of ceric sulfate ($Ce[SO_4]_2$). The basis of the titration is the reduction of cerium(IV) to cerium(III) by hydrogen peroxide under acidic conditions. The titration should be performed at a temperature of <10 °C, with $Ce(SO_4)_2$ added in the presence of a ferroin indicator. The titration is ended after the transition from orange to pale blue is complete (Solvay Chemical Inc., 2004a; US Peroxide). The method is valid for peroxide determinations from 1 wt % to 13 wt % (US Peroxide). Little information is available regarding possible interference with this method. It is probable the method is sensitive to other oxidants or reductants that may be present in the sample.

2.1.2 Spectrophotometric Methods

2.1.2.1 Cobalt Carbonate Method

The basis of this method is the oxidation of cobalt(II) to cobalt(III) by hydrogen peroxide (Gordon et al., 1992; Masschelein et al., 1977; US Peroxide). In a concentrated bicarbonate solution, a cobalt(III) carbonate ($[Co\{CO_3\}_3]Co$) complex is formed after cobalt(II) has been oxidized (Masschelein et al., 1977). The cobalt(III) carbonate complex produces an intense green. The complex presents absorption bands in the visible region at 440 nm and 635 nm and in the UV region at 260 nm. The 260-nm band is recommended for analysis. Although the green is claimed to be stable (Masschelein et al., 1977), others disagree (Bader et al., 1988). This author had difficulties with this method in natural water due to background absorption from organic matter at 260 nm. The reported detection limit for the method is 100 μg/L (US Peroxide). Possible sources of interference for the method include reducing agents, turbidity, nitrate, and chlorite (Gordon et al., 1992) and organic matter.

2.1.2.2 Iodometric Method

The basis of this procedure is similar to the iodometric titration method discussed above in that iodide is oxidized to iodine in the presence of a molybdate catalyst. However, rather than titrating the iodine formed by this reaction with thiosulfate, the I_3^- species, which is in equilibrium with I_2 and I^-, is measured spectrophotometrically. Overall, the pertinent reactions (according to Klassem et al. [1994]) are

$$H_2O_2 + 2I^- + 2H^+ \leftrightarrow I_2 + + 2H_2O$$

$$I_2 + I^- \leftrightarrow I_3^-$$

At near-neutral pH, a pale yellow will form with a maximum absorbance of 351 nm. The solution can be measured immediately (or alternatively after 5 min stored in the dark). The detection level for this method is 50 μg/L. Possible interfering agents include transition metals and oxidants such as chlorine.

2.1.2.3 Titanium Method

The basis of this method is the reaction of hydrogen peroxide with titanium to form a peroxotitanium complex under acidic conditions (Gordon et al., 1992; Solvay Chemical Inc., 2004b; US Peroxide). The peroxotitanium complex is yellowish and possesses maximum absorbance at 400 nm. The best performance is reported when using potassium titanium oxalate ($K_2TiO[C_2O_4]_2 \bullet 2H_2O$) (Allsopp, 1941; Wanger and Rusk, 1984). The detection limit, when using potassium titanium oxalate, is reported as 100 μg/L (Solvay Chemical Inc., 2004b). While several authors report success using this method (Karpel vel Leitner and Dore, 1997; Price et al., 1994; Sunder and Hempel, 1997; Volk et al., 1993), others (Bader et al., 1988) do not agree, concluding the method has low sensitivity. Possible inferring agents include turbidity, color, and reducing agents.

2.1.2.4 HRP Method

A number of methods involve the use of horseradish peroxidase (HRP). HRP is a hemoprotein capable of catalyzing the oxidation of a number of substrates by hydrogen peroxide (Gordon et al., 1992; Worthington Biochemical Corporation). Substrates that can be oxidized include ascorbate, ferrocyanide, and the leuco form of dyes. The HRP–peroxide reaction is highly selective and relatively immune to interference (US Peroxide). The reaction of HRP with hydrogen peroxide proceeds along these lines (Gordon et al., 1992):

$$2H_2O_2 + \text{reduced species} \xrightarrow{\text{HRP}} 3H_2O + \text{oxidized species}$$

Because of the specificity of the HRP–peroxide reaction, a number of peroxide detection strategies have been developed involving HRP. These detection strategies include

- The oxidation of chemiluminescent compounds (Andreae, 1955);
- The destruction of fluorescent compounds (Kieber and Helz, 1986);
- The formation of a product that can be detected spectrophotometrically with greater sensitivity (Andreae, 1955; Mottola et al., 1970).

Methods based on the first two strategies listed above will be discussed later in this review. The two methods discussed immediately below are based on the third detection strategy.

2.1.2.4.1 Leuco Crystal Violet Method

The most widely used spectrophotometric method involves the HRP-catalyzed oxidation of leuco crystal violet (Mottola et al., 1970; US Peroxide). Analysis is performed by successively adding a leuco crystal violet solution, HRP, and an acetate buffer to the peroxide-containing solution. After incubation, violet forms with maximum absorbance at 596 nm. The reported incubation time varies between 5 min (US Peroxide) and 60 min (Gordon et al., 1992). Detection levels as low as 20 μg/L are reported. Concerns regarding this method include slow development of color, interference from turbidity, nonlinearity of the response, and sensitivity to sunlight (Gordon et al., 1992). Humics in the sample may also adversely impact the performance of the method (Bader et al., 1988).

2.1.2.4.2 DPD Method

A second spectrophotometric peroxide detection method is based on the HRP-catalyzed oxidation of *N*,*N*-diethyl-*p*-phenylenediamine (DPD). The basis of this method is assumed to be a sequence of reactions starting with the oxidation of HRP to a higher valence state. The oxidized HRP then oxidizes two DPD molecules to form the radical cation $DPD\bullet^{+}$. This cation is stabilized by resonance and forms a color with adsorption peaks at 510 and 551 nm (Bader et al., 1988). The color is not stable, and the sample must be analyzed within a few minutes of oxidation (Gordon et al., 1992). A detection level of 0.2 μg/L is reported for the DPD method. An advantage of this method is that DPD is frequently used for the detection of chlorine, so the technique is widely accepted by utilities. However, because of the sensitivity of DPD to the presence of chlorine and other oxidants, it is unlikely this method will be effective if other oxidants are present.

2.1.2.4.3 Copper–DMP Method

The basis of this method takes advantage of peroxide's reducing properties. For this method, hydrogen peroxide reduces copper(II) ions to copper(I) ions in the presence of excess 2,9-diemethyl-1,10-phenanthroline (DMP). The copper(I) forms a bright yellow cationic complex with DMP that has a maximum absorbance of 454 nm. The reported detection level is < 30 μg/L. The proposed stoichiometry (Nogueira et al., 2005; Perschke and Broda, 1961) is

$$2Cu^{2+} + 4DMP + H_2O_2 \rightarrow 2Cu(DMP)^{2+} + O_2 + 2H^{+}$$

The method is effective over a wide pH range (pH 5 to pH 9), and the reaction is rapid, essentially completed in the time it takes to mix the reagents (Baga et al., 1988). The color is stable and not sensitive to light (Baga et al., 1988). The method appears to be simple, robust, and rather insensitive to interference. By-products such as formaldehyde, acetaldehyde, formate, and acetate, which are formed by the decomposition of organic matter exposed to AOPs, do not interfere with the method. The method is effective in waters with humic content of <10 mg/L as carbon. Chlorine residuals of up to 0.8 mg/L also do not interfere with the method (Kosaka et al., 1998).

2.1.2.5 Peroxovanadium Method

This method also takes advantage of hydrogen peroxide's reducing properties to reduce vanadium(V) to vanadium(III). The basis of the method is the reaction of hydrogen peroxide with ammonium metavanadate under acidic conditions. After reduction, a red-orange peroxovanadium cation is formed with a maximum absorbance at 450 nm (Nogueira et al., 2005). The proposed reaction between peroxide and vanadium is as follows (Sandel, 1959):

$$VO_3^- + 4H^+ + H_2O_2 \rightarrow VO_2^{3+} + 3H_2O$$

The method is rapid, and the samples are stable up to 180 h at room temperature. However, the reported hydrogen peroxide detection limit is rather high, approximately 4 mg/L. The method appears robust, with little interference detected from the presence of chloride, nitrate, or ferric iron (Nogueira et al., 2005). The possible interference from oxidants, including free and combined chlorine, is unknown.

2.1.3 Fluorescence Methods

2.1.3.1 HRP Method

As discussed above, HRP is capable of catalyzing the oxidation of a number of substrates by hydrogen peroxide. Two fluorescence methods involving HRP are discussed below.

2.1.3.1.1 POHPAA Method

The *p*-hydroxyphenylacetic acid (POHPAA) method is based on the dimerization of POHPAA to form fluorochrome. A complex mechanism is proposed (Miller and Kester, 1988) in which peroxide oxidizes peroxidase from the +3 to the +5 state. The oxidized peroxidase is in turn reduced by POHPAA to form POHPAA radicals through two related pathways. The two POHPAA radicals formed by reaction with peroxidase then dimerize to form a fluorescent product. The overall stoichiometry is 1:1, peroxide to dimer. The dimer is excited at 313 nm and emits at 400 nm. The dimer is stable for up to 5 days, and the detection level is estimated to be less than 1 μg/L (Kok et al., 1986). The method has been used to detect peroxide in both precipitation (Miller and Kester, 1988) and seawater (Kok et al., 1986). The method is insensitive to the presence of major cations and anions found in natural water (Kok et al., 1986). It is also insensitive to the presence of nitrate (Schick et al., 1997). However, the presence of oxidants in the form of chlorine/hyperchloride positively interferes with the method. Chlorine/hyperchloride solutions were found to generate a fluorescence signal at 400 nm in the absence of peroxide (Schick et al., 1997). A residual chlorine concentration of 0.1 mg/L in the absence of peroxide generated a response equivalent to a peroxide concentration of 2.2 mg/L. Lastly, dissolved organic matter in the water may fluoresce in the 400-nm range, possibly interfering with peroxide detection by this method.

2.1.3.1.2 Scopoletin Method

The 7-hydroxy-6-methoxy-2H-1-benzopyran-2-one (scopoletin) method has been widely accepted as a fluorescence-based procedure for the detection of low concentrations of peroxide (Gordon et al., 1992; Kieber and Helz, 1986; Perschke and Broda, 1961; Price et al., 1994). Scopoletin is a fluorochrome and a naturally occurring component in cotton leaf and citrus peel (Corbett, 1989). The scopoletin method is based on the decay of the fluorescent signal from scopoletin caused by the oxidation of HRP by peroxide. Excitation is at 350 nm, and emission occurs at 395 nm. The method is very sensitive, and peroxide detection levels of approximately 0.05 μg/L are possible. Similar to the POHPAA method, the scopoletin method may be

susceptible to interference from organic matter in water (Gordon et al., 1992). Additional research is required to determine the method's performance in the presence of oxidants such as chlorine or chloramines. It is anticipated that positive interference similar to that found in the POHPAA method will be observed.

2.1.4 Chemiluminescence Methods

2.1.4.1 Luminol Method

5-Amino-2,3-hihydro-1,4-phathlazinedione (luminol) is a chemical phosphor. When peroxide is mixed with luminol in the presence of a catalyst, the decomposition of peroxide sets off a sequence of reactions resulting in the release of photons from a luminal by-product. Specifically, it is speculated that a multistep reaction process proceeds along these lines (Yamashiro et al., 2004). First, in the presence of a catalyst, peroxide decomposes into OH• radicals. The OH• radicals then react with luminol anions to form luminol radicals. Oxygen radicals, which are formed by the reaction between peroxide and OH• radicals, react with the luminol radicals to form a hyproperoxide intermediate. This intermediate decays into 3-aminophthalate at an excited energy level. Photons are released as the 3-aminophthalate proceeds to the ground state. The emitted photons are detected by a photomultiplier tube. To promote this sequence of reactions, a pH of approximately 10 must be maintained to assure the presence of luminol anions. The decomposition of peroxide can be catalyzed by either cobalt(II) (Burdo and Seitz, 1975; Price et al., 1994; Yamashiro et al., 2004) or copper(II) (Madsen and Kromis, 1984). While the luminol method is capable of detection limits of 0.2 μg/L, it is subject to positive interference in natural water (Gordon et al., 1992). It is reported (Madsen and Kromis, 1984) that the use of copper(II) rather than of cobalt(II) as a catalyst eliminates interference from manganese(II) and iron(III).

2.2 SUMMARY OF METHODS

A number of analytical methods are documented in the literature. Most appear to be subject to interference from constituents commonly present in natural water. Only a handful of methods have been evaluated for possible interference from the presence of oxidants like free or combined chlorine. For comparison purposes, a tabular summary of the analytical methods reviewed by this paper is presented in Table 2.1. Based on the available information, the spectrophotometric methods appear to be the most suitable for the requirements of this project.

Table 2.1. Summary of Analytical Methods

Type	Method	H_2O_2 range	Reaction mechanism and detection conditions	Performance assessment/interference
Titration	Iodometric	0.1–6 wt %	Oxidize iodide to iodine, titrated with thiosulfate and starch.	Not accurate at low concentration; subject to interference.
	Permanganate	0.25–70 wt %	Reduce permanganate to manganous ion.	Not accurate at low concentration.
	Ceric sulfate	1–13 wt %	With ferroin indicator, titrate to a pale blue.	Not accurate at low concentration.
Spectrophotometry	Cobalt carbonate	Up to 0.1 mg/L	Formation of a UV-absorbing complex between Co^{3+} and carbonate, detection at 260 nm.	Reducing and complexing agents; combined and free chlorine effects not known.
	Iodometric	0.05–10 mg/L	Oxidize iodide to iodine with molybdate catalyst at pH 5; detection at 351 nm.	Evidence of interference from oxidants.
	Titanium oxalate	0.1–50 mg/L	Formation of colored peroxotitanium complex; detection at 400 nm.	Some UV-absorbing species, turbidity, color; combined and free chlorine effects not known.
	Peroxidase enzyme –leuco crystal	0.1–10 mg/L	Oxidation of leuco crystal violet dye by H_2O_2 in presence of peroxidase enzyme catalyst; detection at 596 nm.	Usually interference-free; slow color development; sensitive to sunlight; combined and free chlorine effects not known.
	Peroxidase enzyme –DPD	0.02–10 mg/L	Oxidation of DPD by H_2O_2 in presence of peroxidase enzyme catalyst; detection at 551 nm.	Likely interference from combined and free chlorine; color unstable.
	Copper–DMP	0.03–10 mg/L	Reduction of Cu(II) and formation of copper–DMP complex; detection at 454 nm.	Reported to be effective in presence of chlorine; stable color.
	Peroxovanadium	4–10 mg/L	Reduction of V(V) and formation of peroxovanadium cation; detection at 450 nm.	High detection limit; interference not known.
Fluorescence	Peroxidase enzyme –POHPAA	>0.001 mg/L	Peroxidase catalyzed oxidation of POHPAA by H_2O_2; fluoresces at 400 nm.	Known positive interference with chlorine.
	Peroxidase enzyme –scopoletin	>0.00005 mg/L	Peroxidase catalyzed oxidation of scopoletin by H_2O_2; measure decay of fluorescence at 395 nm.	Possible positive interference with chlorine.
Chemi-luminescence	Luminol	>0.0002 mg/L	Catalyzed decomposition of luminol by H_2O_2 in presence of cobalt or copper; detect luminescence of decomposition product.	Positive interference from natural water (possibly organic matter); interference from combined and free chlorine unknown.

CHAPTER 3

SCREENING OF METHODS

3.1 SCREENING APPROACH

Table 2.1 in Chapter 2 outlines a number of methods that are capable of peroxide detection. It was neither feasible nor desirable to validate the performance of all these methods. Hence, the methods in Table 2.1 were screened in order to select the most suitable detection method for monitoring peroxide residual from a UV/peroxide process. This chapter will discuss how the methods were screened, describe the initial bench-level evaluations of the copper–DMP and titanium oxalate methods, and document the reasons why the titanium oxalate method was selected for additional study.

3.2 DESIRED METHOD CHARACTERISTICS

The first step in the screening process was to determine the characteristics of a desirable peroxide detection method suited to detecting residual peroxide from a UV/peroxide treatment system. Method requirements were discussed in detail at the December 2005 Project Advisory Committee (PAC) meeting. At this meeting the following basic requirements for the method were agreed upon:

- The method should be a laboratory method. An online or real-time measurement is not required. A rapid method is desirable but not essential. It was anticipated that the method will be used on a daily-to-weekly frequency.
- The method should be able to reliably quantify hydrogen peroxide in the 0.5- to 5.0-mg/L concentration range.
- The method should be effective in a natural water matrix. However, the specific focus of the project should be on the Orange County Water District (OCWD) and West Basin water matrices.
- The method should be effective in the presence of combined chlorine (chloramine).
- The method should be relatively simple and not require highly specialized equipment or instrumentation.
- If possible, a spectrophotometric method is preferred over a fluorescence method.

The key concern regarding method development was determined to be the possible impact of chloramine on the performance of the method. For this reason, much of the subsequent evaluation of the method at the bench and interlaboratory levels focused on the possible interference of chloramine on the method performance.

3.3 PRIORITIZATION OF METHODS TO BE EVALUATED

The December 2005 PAC meeting prioritized the order in which the methods identified by the literature review should be evaluated. At the PAC meeting, it was agreed that the focus of the project should be on improving a promising, existing method rather than on exhaustively testing all possible methods or developing a new method. Based upon PAC recommendations and the literature review, the spectrophotometric methods were judged to be most promising in meeting the method characteristics described above. The methods deemed worthy of investigation were ranked in the following order from highest to lowest priority:

- Copper–DMP
- Titanium oxalate
- Peroxidase–leuco crystal violet
- Peroxidase–DPD
- Peroxovanadium
- Cobalt carbonate

3.4 BENCH-LEVEL EVALUATION OF METHODS

By use of the prioritization of methods established at the December 2008 PAC meeting, bench-level evaluations of the methods were initiated at the University of Washington. The initial evaluation was limited to the copper–DMP and titanium oxalate methods. If either of these methods was determined to be unsatisfactory, lower-priority methods would be evaluated.

3.4.1 Initial Bench-Level Assessment of the Copper–DMP Method

3.4.1.1 Absorbance Spectra

Absorbance spectra generated for deionized water containing various amounts of hydrogen peroxide (0.4 to 2 mg/L) are shown in Figure 3-1. Absorbance spectra generated for West Basin and Orange County water, without added hydrogen peroxide, are also shown in the figure.

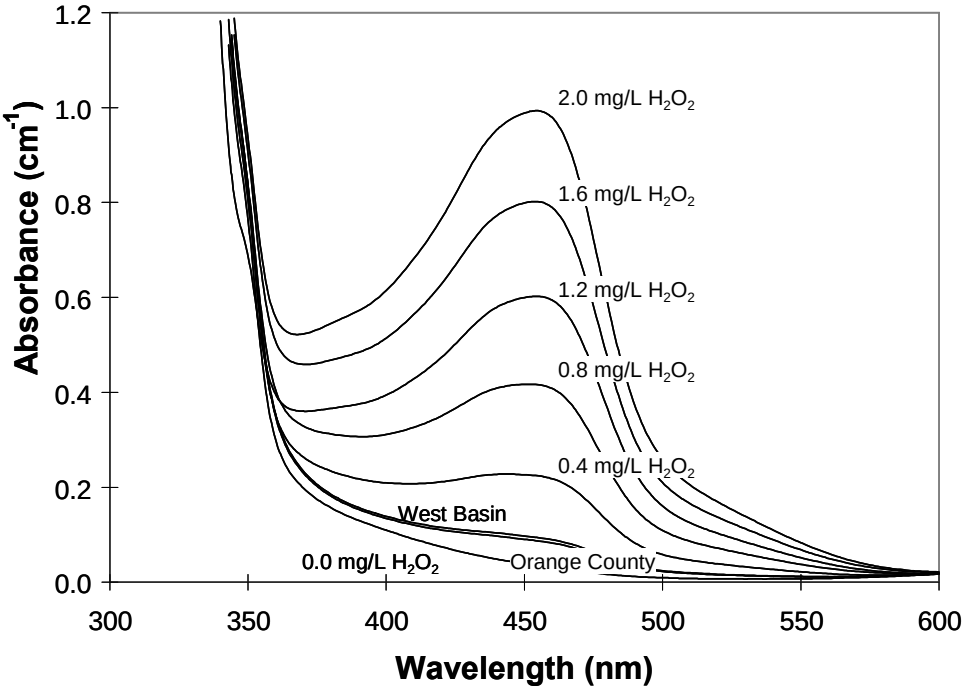

Figure 3-1. Absorbance spectra of DMP–copper solutions with various concentrations of hydrogen peroxide.

Several features of the spectra shown in Figure 3-1 are notable. First, the absorbance band in the range of wavelengths from 360 to 550 nm with a maximum at 454 nm is very distinct from any absorbance features that can be observed for most untreated or treated waters or surface waters. Second, the intensity of this absorbance band is very high. It approaches almost 1 absorbance unit for a 2-mg/L hydrogen peroxide concentration.

However, for West Basin and Orange County water even in the absence of added hydrogen peroxide, a small but notable development of the characteristic absorption band was observed (Figure 3-1). This is likely to have been caused by the reduction of Cu(II) to Cu(I) by natural organic matter or other organic species present in these waters and attendant formation of the colored Cu(I)–DMP complex. Hence, this method appears to be subject to interference by natural organic matter or other organic species. No such effect was observed for the titanium oxalate method, as discussed below.

3.4.1.2 Calibration and Sensitivity to Chloramine

The calibration curve for the DMP method is shown in Figure 3-2. It exhibits nearly perfect linearity and consistency with the high absorbance of the copper–DMP complex.

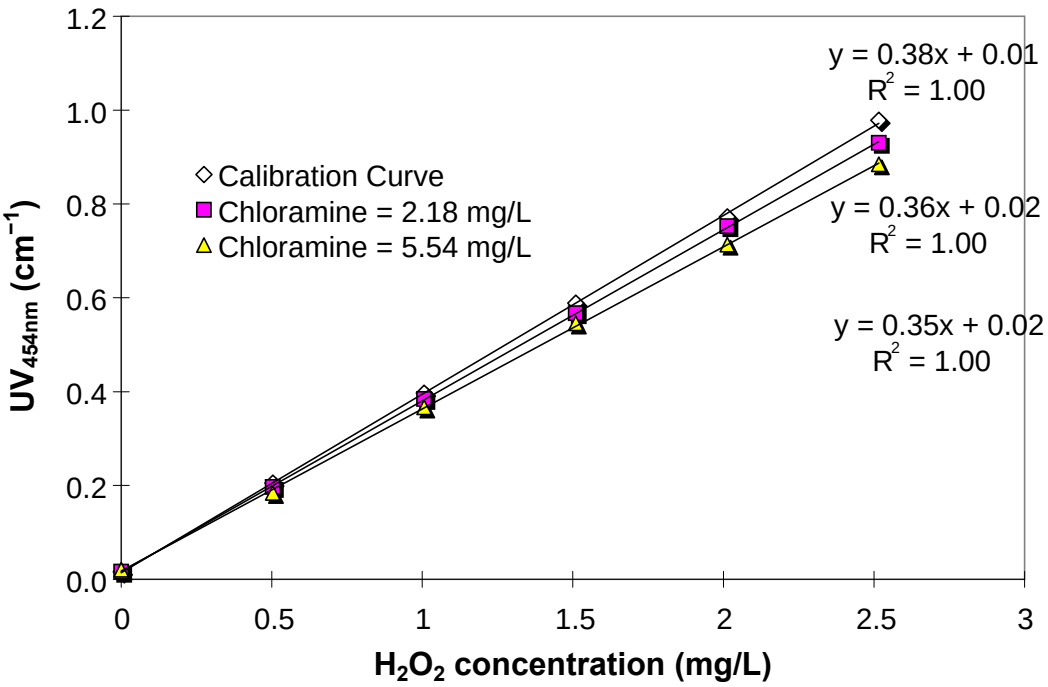

Figure 3-2. Comparison of calibration data for hydrogen peroxide in deionized water in the absence of chloramine and in the presence of 2.18- and 5.54-mg/L chloramine (as N).

However, in contrast with reports in the literature (Kosaka et al., 1998), the performance of the DMP method was affected by the presence of chloramine. This is demonstrated by small but not insignificant changes in the slope of the calibration curve at increased chloramine concentrations in deionized water as seen in Figure 3-2. Although less consistent, similar effects were observed for two fixed hydrogen peroxide concentrations and widely varying chloramine levels in Orange County (Figure 3-3) and West Basin water.

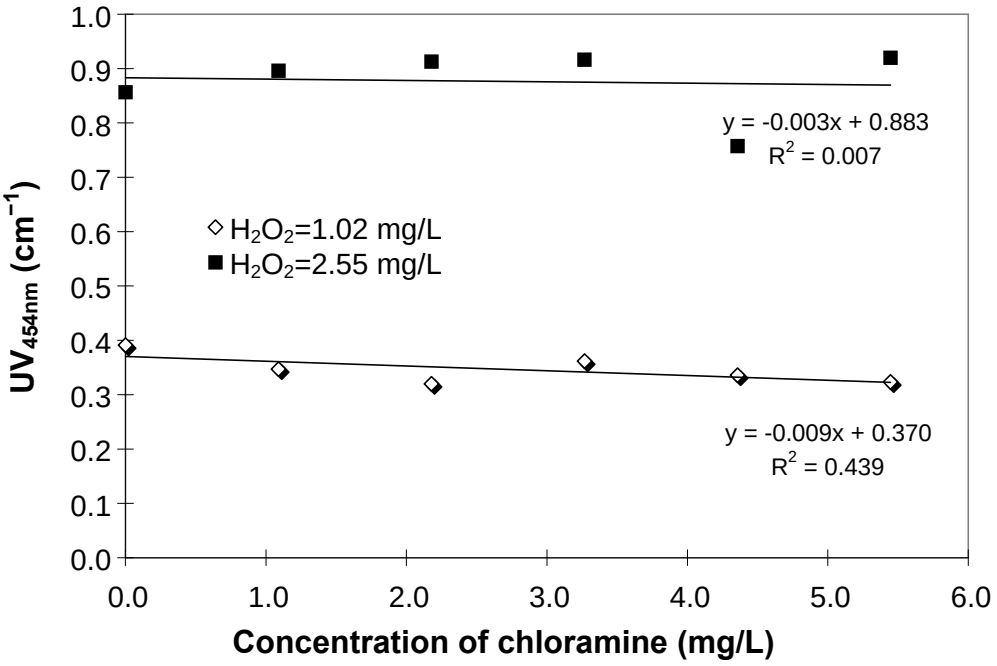

Figure 3-3. Effects of various chloramine concentrations in Orange County water on the absorbance of H_2O_2 at 454 nm.

Based on this evidence, it was concluded that, despite an evidently high sensitivity of the copper–DMP method to low concentrations of hydrogen peroxide, its performance is affected by the presence of organic species (natural organic matter) that do not interfere with other techniques. No less important, it is also affected by the presence of chloramine. For this reason, attention was turned to evaluating the performance of the titanium oxalate method.

3.4.2 Initial Bench-Level Assessment of the Titanium Oxalate Method

3.4.2.1 Absorbance Spectra

The absorbance spectra of titanium oxalate with various concentrations of hydrogen peroxide are shown in Figure 3-4. It can be observed that a band at wavelengths of >380 nm develops in the presence of H_2O_2, while absorbance arises in the absence of this compound either in deionized water or in water from West Basin or OCWD sites (Figure 3-4).

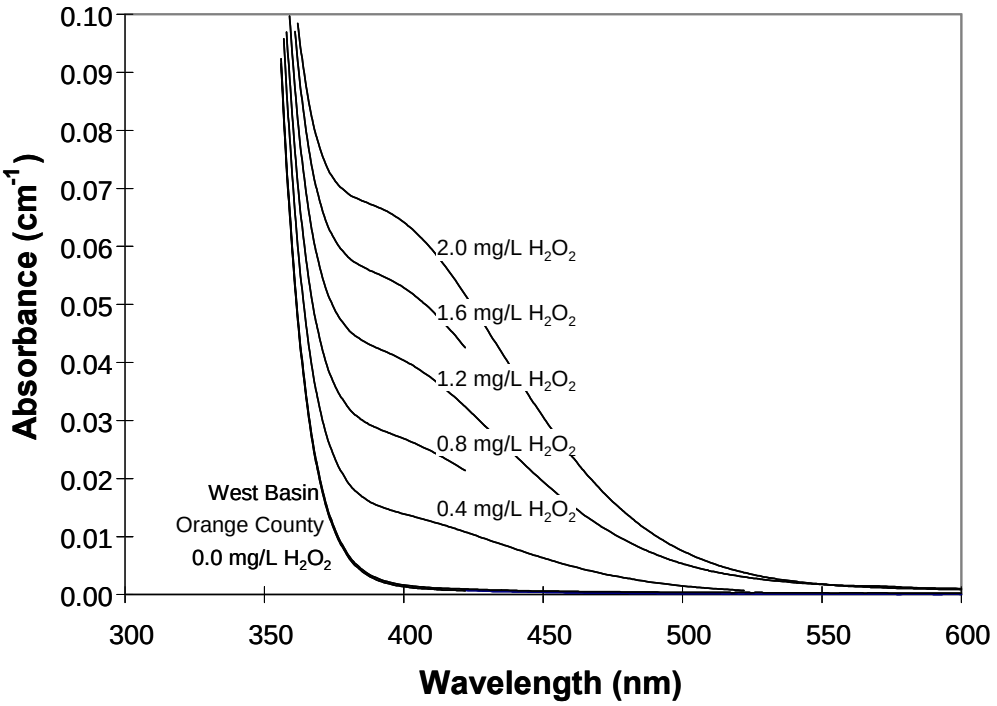

Figure 3-4. Absorbance spectra of titanium oxalate solution with various concentrations of hydrogen peroxide.

The calibration data for deionized water with various concentrations of chloramine are shown in Figure 3-5. Similar calibration data for Orange County water are presented for comparison in Figure 3-6.

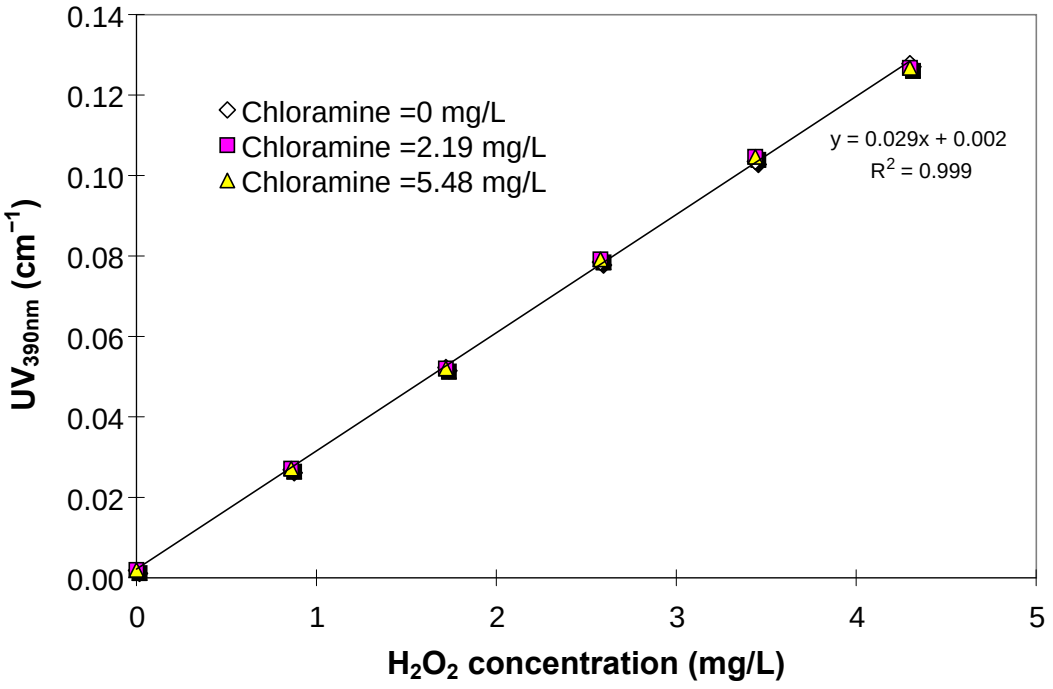

Figure 3-5. Comparison of calibration data for hydrogen peroxide in deionized water in the absence of chloramine and in the presence of 2.19- and 5.48-mg/L chloramine.

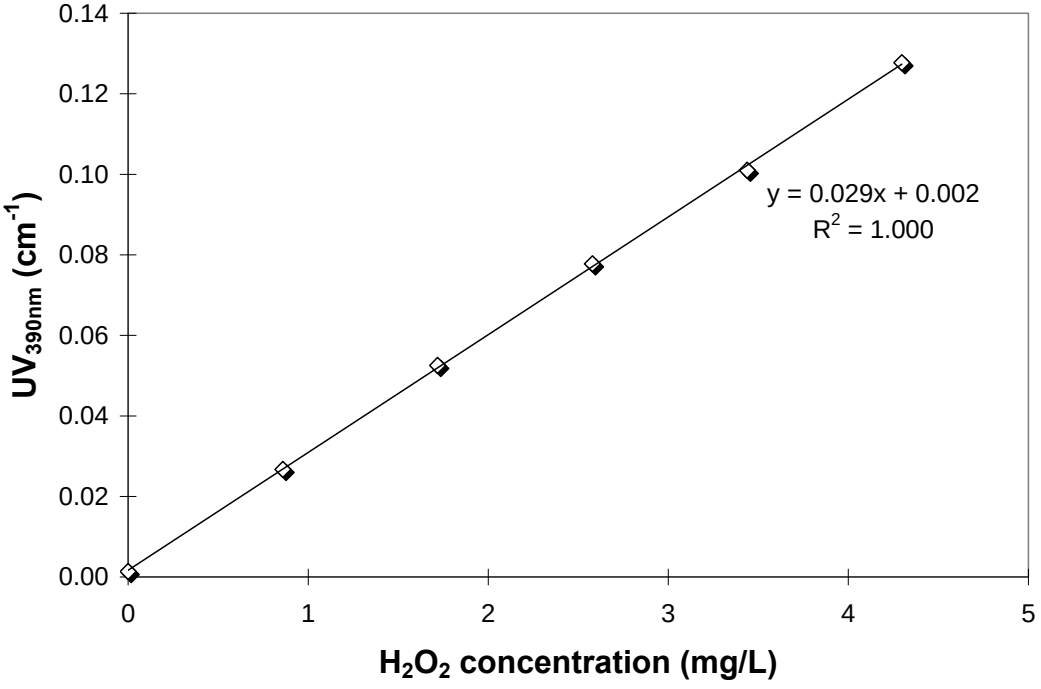

Figure 3-6. Calibration data for hydrogen peroxide in Orange County water.

The data show that although the slope of the H_2O_2-absorbance correlation for the titanium oxalate method is much less than that for the copper–DMP method, it is not affected by the presence of chloramine and/or organic matter in water. Additional experiments performed on Orange County water spiked with two constant concentrations of hydrogen peroxide and widely varying chloramine concentrations showed the existence of very small, if any, effects of chloramine on the absorbance of the titanium/hydrogen peroxide complex at 390 nm (Figure 3-7).

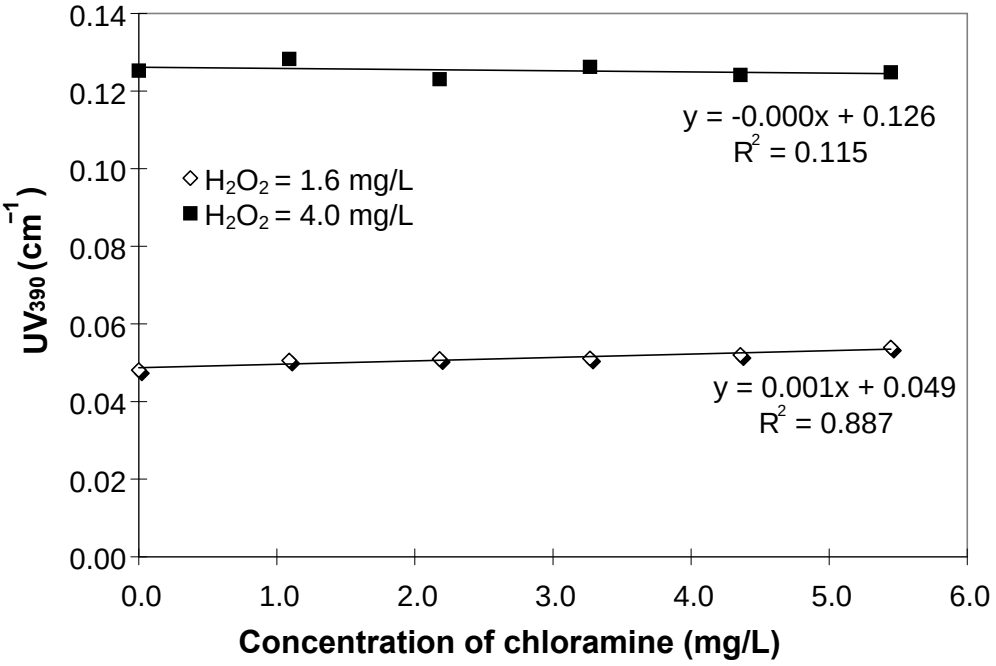

Figure 3-7. Effects of various chloramine concentrations in Orange County water on the absorbance at 390 nm.

3.4.3 Recommendation for Additional Evaluation of the Titanium Oxalate Method

Based on these results, literature-reported interference, and the reported performance of the other spectrophotometric methods in the literature, it was concluded that titanium oxalate appears to be the best option for hydrogen peroxide analyses of the West Basin and OCWD waters.

CHAPTER 4

BENCH-LEVEL EVALUATION OF TITANIUM OXALATE METHOD

4.1 INTRODUCTION

As discussed in Chapter 3, the titanium oxalate method was found to be a relatively simple spectrophotometric method with little interference from chloramine. Additional evaluations of the titanium oxalate method were performed by the University of Washington at bench level to determine the MDL, precision, and bias. These experiments and their interpretation were performed in accord with recommendations and definitions set forth by *Standard Methods*.

4.2 DETERMINATION OF MDL, PRECISION, AND BIAS

4.2.1 Determination of MDL

The MDL values for the low levels of hydrogen peroxide in deionized water and West Basin water in the absence and presence of chloramine are calculated from experimental analysis. Results of MDL measurements for various water matrices are compiled in Table 4.1. The analytical data that were employed for this calculation are included in Appendix D, Tables A1 to A4.

Table 4.1. Comparison of MDLs for Hydrogen Peroxide in Deionized Water and West Basin Water in the Absence and Presence of Chloramine[a]

Sample	Concn (mg/L) of H_2O_2
Deionized water without chloramine	0.050
Deionized water with 5.54-mg/L chloramine	0.049
Water without chloramine	0.069
Water with 5.54-mg/L chloramine	0.046
Average H_2O_2 detection limit	0.054

[a]These data averages are calculated for hydrogen peroxide concentrations that are > 0.5 mg/L.

The data indicate that all MDL values found for all water matrices utilized in this study were very close and ranged from 0.046 mg of H_2O_2/L in West Basin water with chloramine to 0.069 mg of H_2O_2/L in the same water without chloramine. The average MDL value obtained in all experiments is 0.054 mg/L. Overall, these results indicate that the sensitivity of the titanium oxalate method is adequate for determination of hydrogen peroxide concentrations that exceed 0.05 mg/L.

4.2.2 Determination of Method Bias and Precision

Method bias and precision were determined at hydrogen peroxide concentrations that varied from 0.1 to 10 mg/L. Bias and detection measurements were carried in the same water matrices that were utilized for MDL determinations.

The bias and precision of the titanium oxalate method are best understood when represented in relative, not in absolute, terms. Correspondingly, in the discussion that follows, the bias and precision data are calculated as percentage of nominally expected concentrations of hydrogen peroxide.

The primary results that were used to determine the values of bias and precision are shown in Table 4.2 and Figures 4-1 to 4-5, respectively. Note that in Figure 4-1, each data point represents an average calculated for measurements of deionized water with 0- and 5.54-mg/L chloramine concentrations. In Figure 4-2, each data point represents an average calculated for measurements of West Basin water with 0- and 5.54-mg/L chloramine concentrations. In Figure 4-3, each data point represents an average calculated for measurements in deionized and West Basin water without chloramine. In Figure 4-4, each data point represents an average calculated for measurements in deionized and West Basin water (5.54-mg/L chloramine in each case). In Figure 4-5, each data point represents an average calculated for all measurements in deionized and West Basin water. The analytical data that were employed in bias and precision calculations are included in Appendix D, Tables A5 to A9.

Table 4.2. Comparison of Averaged Relative Bias and Precision Values Found for Titanium Oxalate Hydrogen Peroxide Determinations in Deionized Water and West Basin Water in the Absence and Presence of Chloramine

Sample	Relative Bias	Relative Precision
Deionized water without chloramine	−0.6%	3.3%
Deionized water with 5.54-mg/L chloramine	−2.0%	2.8%
West Basin water without chloramine	2.6%	6.3%
West Basin water with 5.54-mg/L chloramine	1.5%	3.6%
All averaged samples	0.4%	4.0%
All deionized water samples	−1.3%	3.0%
All West Basin water samples	2.1%	5.0%
All samples without chloramine	1.0%	4.8%
All samples with 5.54-mg/L chloramine	−0.2%	3.2%
All averaged samples	0.4%	4.0%

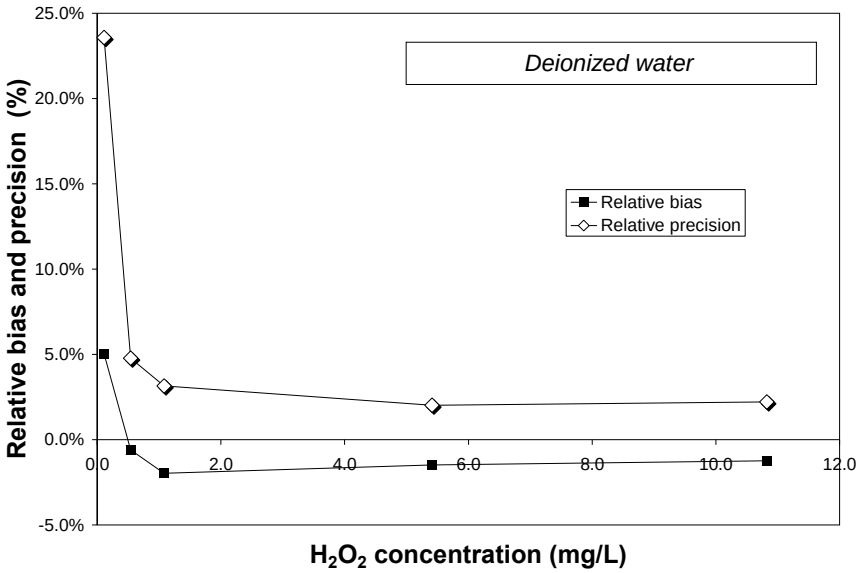

Figure 4-1. Behavior of relative bias and precision for titanium oxalate measurements at various nominal H_2O_2 concentrations.

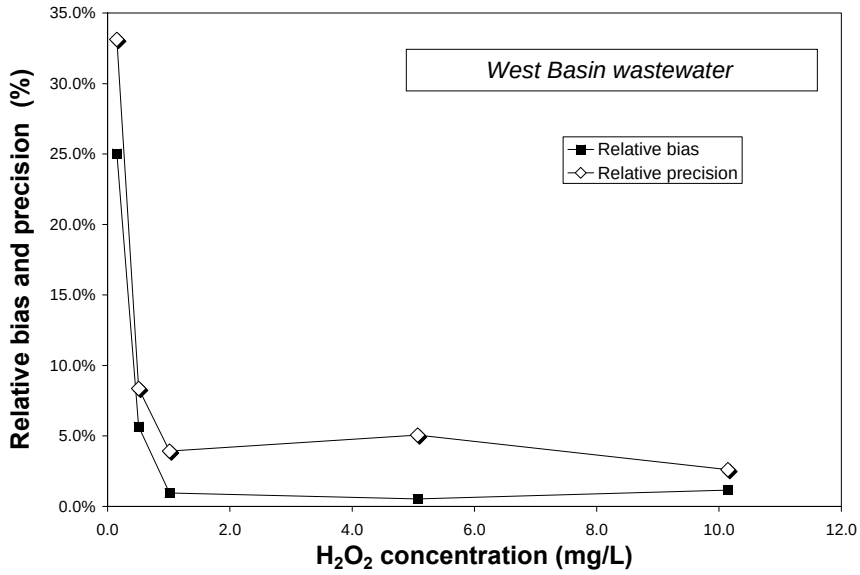

Figure 4-2. Behavior of relative bias and precision for titanium oxalate measurements at various nominal H_2O_2 concentrations.

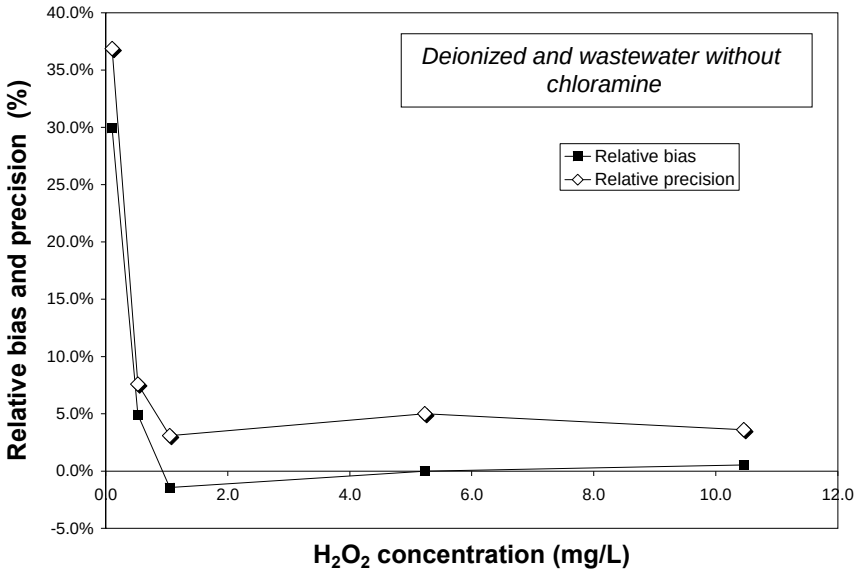

Figure 4-3. Relative bias and precision for titanium oxalate measurements at various nominal H_2O_2 concentrations.

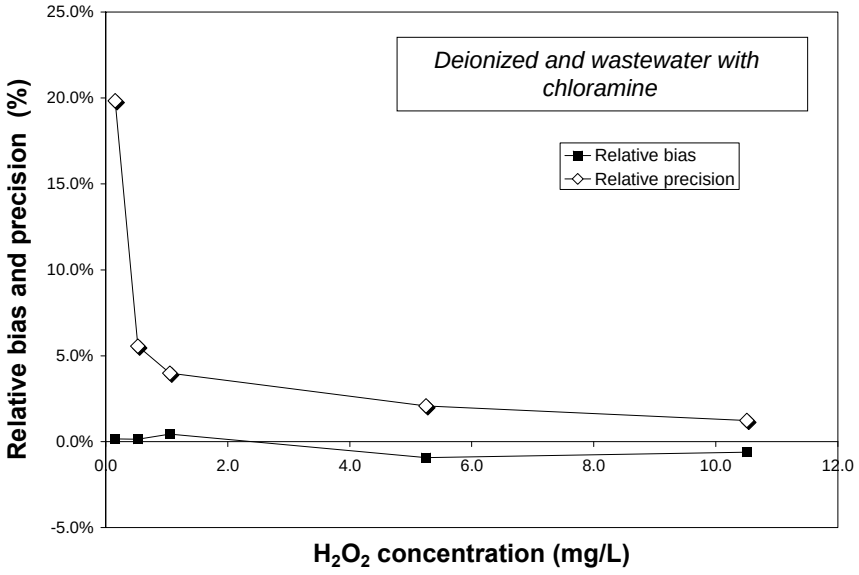

Figure 4-4. Relative bias and precision for titanium oxalate measurements at various nominal H_2O_2 concentrations.

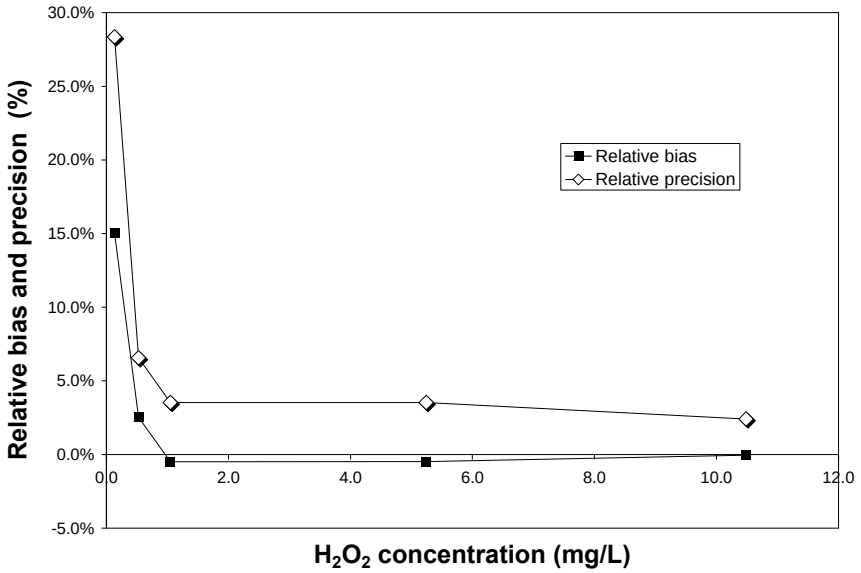

Figure 4-5. Relative bias and precision for titanium oxalate measurements at various nominal H_2O_2 concentrations.

The behavior of relative bias and precision was very similar in all water matrices (Figures 4-1 to 4-5). As expected, the relative bias and precision of the titanium oxalate measurements for a 0.1-mg/L H_2O_2 concentration, which is very close to the detection limit, were greater than those for hydrogen peroxide concentrations of >0.5 mg/L. However, in absolute terms the performance of the titanium oxalate method, even at a hydrogen peroxide concentration as low as 0.1 mg/L, appears to be acceptable (see the compilation of both absolute and relative bias and precision data in Appendix D, Tables A5 to A10.)

Comparison of values of relative bias and precision generated in different water matrices for all nominal hydrogen peroxide concentrations exceeding a 0.5-mg/L threshold yields the following conclusions: first, the values of bias of the titanium oxalate method do not seem to be affected by the presence or absence of chloramine. However, there was a slight negative bias in deionized water and slight positive bias in West Basin water. Second, the relative precision of the hydrogen peroxide measurements was similar in all cases, as illustrated in Table 4.2.

Because of the similarity of relative bias and precision measurements in all matrices that have been tested, the estimated overall values of relative bias and precision of the titanium oxalate method are 0.4 and 4.0%, respectively, for hydrogen peroxide concentrations that exceed a 0.5-mg/L level.

CHAPTER 5

INTERLABORATORY EVALUATION OF TITANIUM OXALATE METHOD

5.1 OBJECTIVE OF INTERLABORATORY EVALUATION

The objective of the interlaboratory evaluation was to determine the method's bias and precision that would occur in normal practice when the procedure is performed by independent laboratories. In addition, the evaluation provided an opportunity to compare method performance in different waters as well as to evaluate the method sensitivity to different concentrations of hydrogen peroxide and chloramine.

5.2 INTERLABORATORY EVALUATION PLAN

5.2.1 Roles and Responsibilities for Evaluation

The interlaboratory study was a cooperative effort among all the study participants. The divisions of responsibility were as follows:

- Develop an interlaboratory evaluation plan, coordinate evaluations, and reduce data—HDR Engineering;
- Perform laboratory analysis—West Basin Municipal Water District (laboratory operated by United Water) and the OCWD;
- Provide a titanium oxalate procedure—University of Washington.

5.2.2 Evaluation Method

5.2.2.1 Overview of Evaluation Process

Water samples for the interlaboratory evaluation were collected from specific points from the advanced oxidation (UV/hydrogen peroxide) treatment systems in West Basin and Orange County. Known quantities of hydrogen peroxide and chloramine were added to these samples in predetermined amounts. The samples were distributed between both laboratories so that each laboratory analyzed both the samples it had collected and prepared as well as the samples collected and prepared by the other laboratory. Measurement of the residual hydrogen peroxide concentration was performed per the method validated by the University of Washington. Figure 5-1 illustrates the evaluation process.

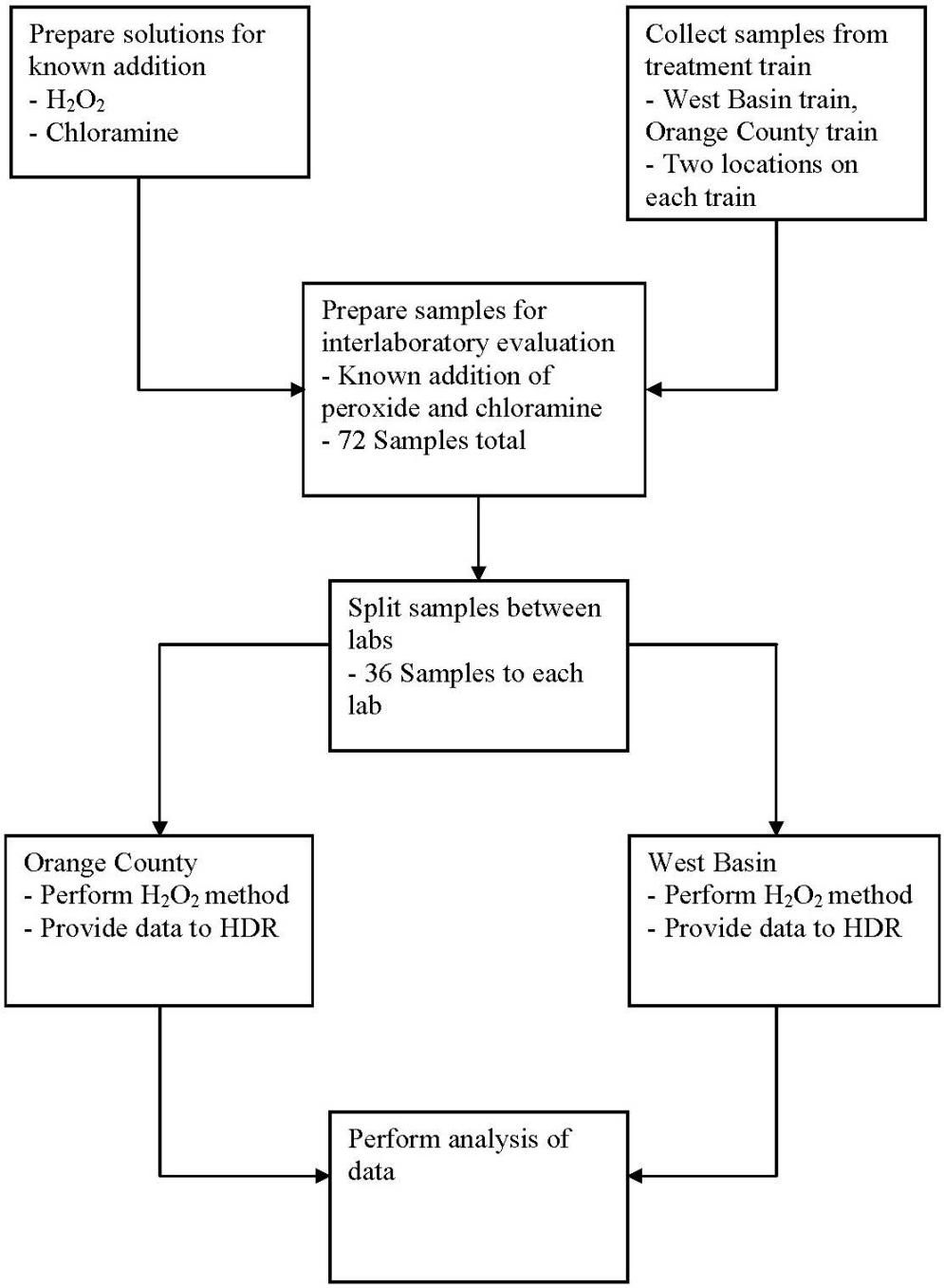

Figure 5-1. Overview of the interlaboratory evaluation process.

5.2.2.2 Sample Collection Points

Samples were collected at two similar points on the Orange County and West Basin treatment trains. The two points from which samples were collected were located immediately upstream of peroxide addition and, following pH adjustment (lime addition), downstream of the UV reactor. Figure 5-2 illustrates the locations from which the two samples were taken from the treatment train.

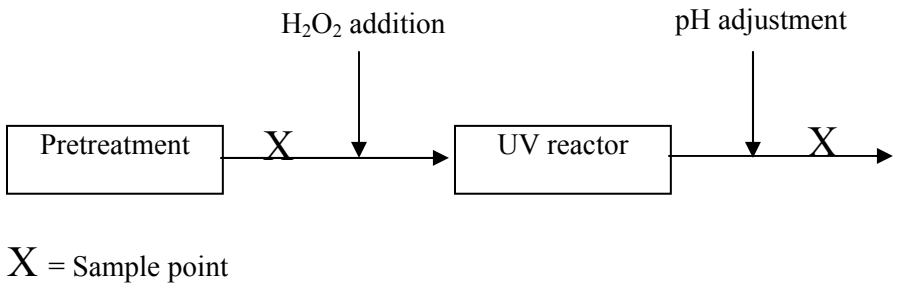

Figure 5-2. Locations of interlaboratory samples.

5.2.2.3 Interlaboratory Sample Matrix

As described above, each sample collected from the treatment train was spiked with known concentrations of hydrogen peroxide and preformed chloramines. The known spiking concentrations were:

Hydrogen peroxide: 0 mg/L, 2.5 mg/L, 5 mg/L

Chloramine: 0 mg/L, 1 mg/L, 2 mg/L

The samples were spiked in combination, forming a 3 × 3 validation matrix of samples. This means each sample was spiked with nine different combinations of peroxide and chloramine. The spiking conditions ranged from 0-mg/L hydrogen peroxide and 0-mg/L chloramine to 5-mg/L hydrogen peroxide and 2-mg/L chloramine. Table 5.1 presents the complete list of spiking conditions.

Table 5.1. Matrix of Known Additions to Treatment Train Samples[a]

Upstream of Peroxide Injection Sample					
Sample	**Known Addition (mg/L)**		**Sample**	**Known Addition (mg/L)**	
	Peroxide	**Chloramine**		**Peroxide**	**Chloramine**
10WB	0	0	10OC	0	0
20WB	0	1	20OC	0	1
30WB	0	2	30OC	0	2
40WB	2.5	0	40OC	2.5	0
50WB	2.5	1	50OC	2.5	1
60WB	2.5	2	60OC	2.5	2
70WB	5	0	70OC	5	0
80WB	5	1	80OC	5	1
90WB	5	2	90OC	5	2

Downstream of Peroxide Injection Sample					
Sample	**Known Addition (mg/L)**		**Sample**	**Known Addition (mg/L)**	
	Peroxide	**Chloramine**		**Peroxide**	**Chloramine**
100WB	0	0	100OC	0	0
200WB	0	1	200OC	0	1
300WB	0	2	300OC	0	2
400WB	2.5	0	400OC	2.5	0
500WB	2.5	1	500OC	2.5	1
600WB	2.5	2	600OC	2.5	2
700WB	5	0	700OC	5	0
800WB	5	1	800OC	5	1
900WB	5	2	900OC	5	2

[a]WB = West Basin, OC = Orange County.

5.2.2.4 Peroxide Detection Method

The titanium oxalate method, provided by the University of Washington, was used to determine residual peroxide concentration in the samples listed in Table 5.1. The method is included in Appendix A.

5.2.2.5 Preparation of Spiking Solutions and Spiking of Samples

The procedure used to collect and spike samples is included in Appendix B. The procedure used for preparing stock solutions of peroxide and chloramine is included in Appendix C.

5.2.2.6 Timing of Analysis

Since peroxide residual is inherently unstable and will decay with time, spiking of the samples with known concentrations will occur within 24 h of collection and the analysis will be performed within 24 h of spiking. It was anticipated that 2 days would be required to perform the interlaboratory evaluation.

Day 1: Collect samples, exchange samples between laboratories, perform known addition

Day 2: Exchange spiked samples between laboratories, perform peroxide detection method

When performed, the evaluation was completed in a single day and overnight storage was not required. During shipment between laboratories, the samples were kept on ice and in the dark until the analysis was performed.

5.3 INTERLABORATORY EVALUATION RESULTS

5.3.1 Peroxide Detection Results

The laboratory results for the upstream and downstream samples are included in Tables 5.2 and 5.3, respectively.

Table 5.2. Measured Peroxide Concentration for Upstream Samples[a]

		Known Addition (mg/L)		Measured Peroxide Concn (mg/L)	
Source	**Sample**	**Peroxide**	**Chloramine**	**OCWD**	**West Basin**
West Basin	10WB	0	0	0.30	0.009
	20WB	0	1	<0.1	0.008
	30WB	0	2	0.50	0.010
	40WB	2.5	0	2.35	2.37
	50WB	2.5	1	2.42	2.32
	60WB	2.5	2	2.37	2.26
	70WB	5	0	5.16	4.72
	80WB	5	1	5.42	4.63
	90WB	5	2	4.71	4.58
OCWD	10WB	0	0	0.50	0.020
	20WB	0	1	<0.1	0.001
	30WB	0	2	<0.1	0.007
	40WB	2.5	0	2.80	2.52
	50WB	2.5	1	2.02	2.48
	60WB	2.5	2	3.03	2.50
	70WB	5	0	5.37	5.04
	80WB	5	1	5.35	5.02
	90WB	5	2	5.00	5.01

Table 5.3. Measured Peroxide Concentration for Downstream Samples

		Known Addition (mg/L)		Measured Peroxide Concentration (mg/L)	
Source	**Sample**	**Peroxide**	**Chloramine**	**OCWD**	**West Basin**
West Basin	100WB	0	0	2.23	2.09
	200WB	0	1	2.16	2.14
	300WB	0	2	2.12	2.05
	400WB	2.5	0	4.28	4.59
	500WB	2.5	1	4.45	4.45
	600WB	2.5	2	4.89	4.37
	700WB	5	0	6.87	6.92
	800WB	5	1	6.61	6.55
	900WB	5	2	6.73	6.49
OCWD	100WB	0	0	1.57	1.86
	200WB	0	1	1.96	1.72
	300WB	0	2	2.31	1.79
	400WB	2.5	0	4.42	4.28
	500WB	2.5	1	4.50	4.15
	600WB	2.5	2	4.44	4.08
	700WB	5	0	7.19	6.56
	800WB	5	1	6.89	6.53
	900WB	5	2	6.24	6.52

[a]Measured peroxide concentration in Tables 5.2 and 5.3 is greater than known addition because of background peroxide concentration in downstream water.

5.3.2 Estimate of Method Precision and Bias

The method precision and bias were calculated per *Standard Methods* 1040C.3. The method bias is defined as the difference between the grand average of measured values and the known concentration:

$$\text{Method bias} = \frac{\sum_{i=1}^{n} x}{n} - \text{known concentration} \qquad (5.1)$$

Where x = the measured concentration

n = number of measurements

Method precision is the standard deviation of the measured values divided by the grand average of the measured values:

$$\text{Method precision} = \frac{s}{\sum_{i=1}^{n} x} \qquad (5.2)$$

Where x = the measured concentration

n = number of measurements

s = standard deviation

The upstream samples were used to calculate method precision and bias between the two laboratories for each water. These values were then averaged to provide an overall estimate of precision and bias at each known peroxide concentration. Downstream samples were not used in this calculation since they contained a background hydrogen peroxide concentration. As can be seen in Table 5.4, the method returned a false positive for hydrogen peroxide (0.13 mg/L) in samples not containing a peroxide spike. However, at detectable concentrations of hydrogen peroxide, the method was quite accurate and precise. The overall method precision and bias for detectable levels of peroxide were 5 and −2% respectively.

Table 5.4. Estimate of Method Precision and Bias (*n* = 36)

	Values for:								
	West Basin Water			Orange County Water			Overall		
Known Peroxide Concn (mg/L)	Found Peroxide Concn (mg/L)	Method Precision (%)	Method Bias (%)	Found Peroxide Concn (mg/L)	Method Precision (%)	Method Bias (%)	Found Peroxide Concn (mg/L)	Method Precision (%)	Method Bias (%)
0	0.15	141.7	—	0.10	186.1	—	0.13	141.7	—
2.5	2.35	2.3	−6.1	2.56	13.3	2.3	2.45	2.3	−1.9
5	4.87	7.0	−2.6	5.13	3.5	2.6	5.00	4.8	0.0

5.3.3 Comparison of Results between Laboratories

Figure 5-3 presents a comparison of peroxide concentrations measured in split samples; that is, identical samples measured by each laboratory. As can be seen in the figure, the measured peroxide concentrations were highly correlated (r = 0.984) between laboratories. The straight line indicated by $y = x$ in the figure indicates a perfect match between laboratories with a slope of 1. The best fit line correlating the two laboratories' results is slightly less than 1 (slope = 0.981), indicating the West Basin laboratory in general returned a slightly lower concentration than the Orange County laboratory did for identical samples.

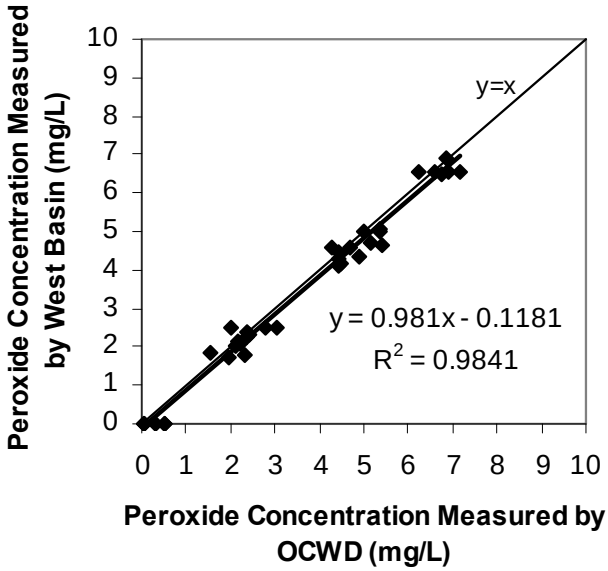

Figure 5-3. Comparison of split samples analyzed by West Basin and Orange County laboratories.

In order to determine if this difference between laboratories is statistically significant, a two-tailed paired *t* test was performed comparing the results for the split sample. At a 95% confidence level (α = 5%), the difference between the concentrations measured by the laboratories was found to be statistically significant. Hence, there is a small but systematic difference between the hydrogen peroxide measurements made by the West Basin and Orange County laboratories.

5.3.4 Comparison of Results between Waters

A similar comparison was performed to determine if there are differences in hydrogen peroxide quantification between the two water sources when they are spiked with equal concentrations of hydrogen peroxide. Figure 5-4 presents this comparison. In this case, the comparison is limited to 18 points for the upstream water. The comparison was limited to upstream water since there are different background hydrogen peroxide concentrations in the downstream water that could bias the analysis. As can be seen in the figure, the hydrogen peroxide detection results between water sources are highly correlated (r = 0.985). The best fit line correlating the data falls slightly below the $y = x$ line, indicating a possible bias in the data. In general, at equal spiked hydrogen peroxide concentrations, the titanium oxalate method detected slightly lower hydrogen peroxide concentrations in the West Basin water than in the Orange County water.

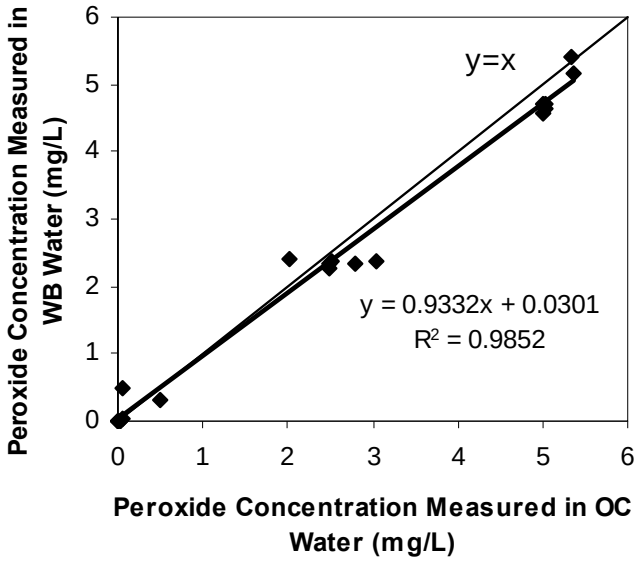

Figure 5-4. Comparison of equally spiked Orange County and West Basin water samples.

A two-tailed paired *t* test was again used to determine if this difference in hydrogen peroxide detection between waters was statistically significant. At a 95% confidence level (α = 5%), the difference between the hydrogen peroxide concentrations measured in the two waters was found not to be statistically significant. Hence, based on these data, there is no systematic difference in hydrogen peroxide detection between the two waters.

5.3.5 Comparison of Results between Sample Locations

A third comparison was performed to determine if there are differences in hydrogen peroxide quantification in the two water sources when drawn from sample points upstream and downstream of UV/hydrogen peroxide treatment. This analysis is complicated because background hydrogen peroxide was present in the downstream sample. Table 5.5 summarizes the calculation of the background hydrogen peroxide concentration for the OCWD and West Basin downstream waters. There was close agreement in the measurement of the background hydrogen peroxide concentrations in the respective OCWD and West Basin downstream samples.

Table 5.5. Background Peroxide Concentration Measured in Unspiked Downstream Samples

Water Source	Measured Hydrogen Peroxide Concn for: OCWD Laboratory Sample A	OCWD Laboratory Sample B	OCWD Laboratory Sample C	West Basin Laboratory Sample A	West Basin Laboratory Sample B	West Basin Laboratory Sample C	OCWD Average	West Basin Average	Grand Average
OCWD	1.57	1.96	2.31	1.86	1.72	1.79	1.95	1.79	1.87
West Basin	2.23	2.16	2.12	2.09	2.14	2.05	2.17	2.09	2.13

Figure 5-5 presents the comparison of upstream and downstream samples. In order to adjust the downstream samples for background hydrogen peroxide, the measured background concentration (Table 5.4) was subtracted from all the downstream samples. Overall, a total of 36 points were compared. As can be seen in the figure, the hydrogen peroxide detection results of the upstream and downstream samples are highly correlated ($r = 0.981$). The best fit line correlating the data falls slightly below the $y = x$ line, indicating a possible bias in the data. In general, at equal spiked hydrogen peroxide concentrations, the titanium oxalate method detected slightly lower hydrogen peroxide concentrations at the downstream sample point than at the upstream sample point.

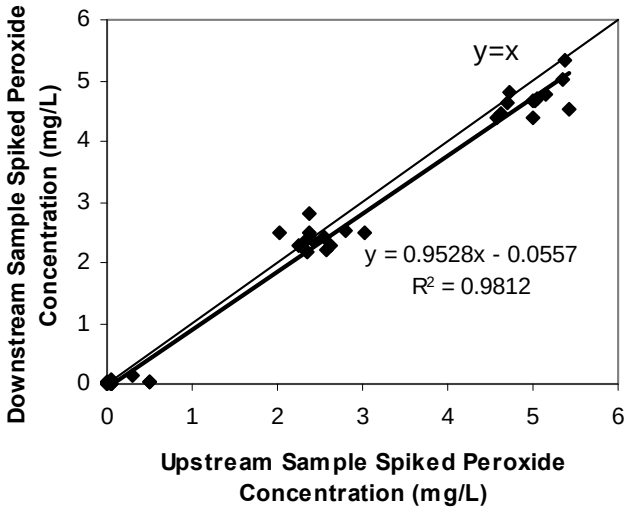

Figure 5-5. Comparison of equally spiked upstream and downstream samples.

Again a two-tailed paired *t* test was used to determine if this difference in hydrogen peroxide detection between the upstream and downstream locations was statistically significant. At a 95% confidence level ($\alpha = 5\%$), the difference between the hydrogen peroxide concentrations

measured at the two locations was found to be statistically significant. Therefore, there appears to be a systematic difference in measurements made at the two locations.

The reason for this difference is not clear. It should be noted that the absolute differences between the upstream and downstream measurements are quite small and probably have no practical importance. The difference may be due to the inherent variability in spiking or in the background hydrogen peroxide concentration.

5.3.6 Influence of Hydrogen Peroxide and Chloramine Concentration on Results

The potential influence of different peroxide and chloramine concentrations on the accuracy of the hydrogen peroxide detection method was evaluated by a two-way analysis of variance (ANOVA). The upstream samples were used for this analysis. In order to perform the ANOVA, the measurement error of each of the hydrogen peroxide measurements was calculated for all of the known hydrogen peroxide and chloramine spikes. The measurement error is defined as the difference between the known (spiked) hydrogen peroxide concentration and measured concentration:

Measurement error = Known concentration – Measured concentration (5.3)

A table of measurement errors was created by pooling all the upstream hydrogen peroxide measurements for both laboratories and waters. Since the two laboratories tested two upstream samples at each condition and there was a combination of nine hydrogen peroxide and chloramine conditions, the table of measurement errors consists of 36 entries. Table 5.6 presents the table of measurement errors that formed the basis of the ANOVA.

Table 5.6. Table of Measurement Errors Used for ANOVA

Chloramine Concn (mg/L)	Errors Found for Hydrogen Peroxide Concn (mg/L) of:		
	0	**2.5**	**5**
0	−0.30	0.15	−0.16
	−0.50	−0.30	−0.37
	−0.01	0.13	0.28
	−0.02	−0.02	−0.04
1	−0.05	0.08	−0.42
	−0.05	0.48	−0.35
	−0.01	0.18	0.37
	0.00	0.02	−0.02
2	−0.50	0.13	0.29
	−0.05	−0.53	0.00
	−0.01	0.24	0.42
	−0.01	0.00	−0.01

The ANOVA was performed by using the two-way ANOVA data analysis tool in Microsoft Excel.

At a 95% confidence level (α = 5%), the ANOVA concluded that, at the conditions tested, there is no statistically significant relationship between:

- Hydrogen peroxide concentration and measurement error, or
- Chloramine concentration and measurement error, or
- The combination of hydrogen peroxide and chloramine and measurement error.

A summary of the F-statistic is presented in Table 5.7. Statistical significance is indicated when the calculated F-statistic exceeds the critical F-statistic at the assumed confidence level. As seen in the table, the calculated F-statistic is less than the critical F-statistic in all cases. Hence, none of the potential sources of variation is statistically significant.

Table 5.7. Two-Way ANOVA Table Evaluating the Impacts of Differing Chloramine And Hydrogen Peroxide Concentrations on the Performance of the Titanium Oxalate Method

Sample of Variation	F-Statistic		Significant at 95% Confidence Level?
	Calculated	Critical	
Hydrogen Peroxide	1.507	3.354	No
Chloramine	0.724	3.354	No
Interaction	1.145	2.728	No

5.4 CONCLUSIONS FOR THE INTERLABORATORY EVALUATION

Overall, the titanium oxalate hydrogen peroxide detection method was effective in determining hydrogen peroxide concentrations in the West Basin and OCWD water. Within the range of concentrations tested, the overall precision of the method was 5% and the bias was −2%. There was a slight but statistically significant difference between the two laboratories in quantifying hydrogen peroxide. In general, the West Basin laboratory measured a lower concentration than the OCWD laboratory. A small difference in detecting hydrogen peroxide was also observed when quantifying hydrogen peroxide in the two different waters, but this difference was not statistically significant. A slight and statistically significant difference in hydrogen peroxide values was found when quantifying hydrogen peroxide concentration upstream and downstream of UV/hydrogen peroxide treatment. The difference may be related to the background hydrogen peroxide concentration present in the downstream samples. No statistically significant relationships were found between the hydrogen peroxide or chloramine concentration and hydrogen peroxide concentration measurement error.

CHAPTER 6

COMPARISON OF THE TITANIUM OXALATE METHOD DEVELOPED BY THIS PROJECT TO OTHER PUBLISHED TITANIUM OXALATE METHODS

6.1 INTRODUCTION

The purpose of this chapter is to compare the titanium oxalate method developed by this project (termed WRF-04-019 method) to similar methods reported in the literature.

6.1.1 Overview of the Method

The WRF-04-019 titanium oxalate method can be divided into five steps. The first step involves the preparation of reagents. These include a 0.1 N potassium permanganate solution, a 50-g/L potassium titanium oxalate solution, a (1+9) sulfuric acid solution, a (1+17) sulfuric acid solution, and a 1000-mg/L hydrogen peroxide solution. The second step, which should be performed on the day of analysis, is the standardization of an approximately 1000-mg/L hydrogen peroxide solution. The standardization is performed by potassium permanganate titration. Permanganate is used to drop-wise titrate the clear hydrogen peroxide solution to the appearance of pinkness, indicating the point at which excess manganese(VII) is present and at which all hydrogen peroxide has been consumed by the reduction of manganese(VII) to manganese(II).

The third step of the method consists of the development of a calibration curve, relating measured optical density to the known concentration of six hydrogen peroxide standards in the presence of titanium oxalate and sulfuric acid. The calibration curve is developed at 390 nm using either 10-mm or 50-mm quartz cells. Step 4 is the preparation of the sample for analysis. This step involves pipetting the unknown hydrogen peroxide sample into deionized water, titanium oxalate and sulfuric acid, forming the titanium(IV)–peroxide complex. Step 5 completes the analysis by determining the optical density of the unknown sample and determining its hydrogen peroxide concentration from the calibration curve developed in step 3. Figure 6-1 provides a graphic illustration of the method. The detailed steps for performing the method are presented in Appendix A.

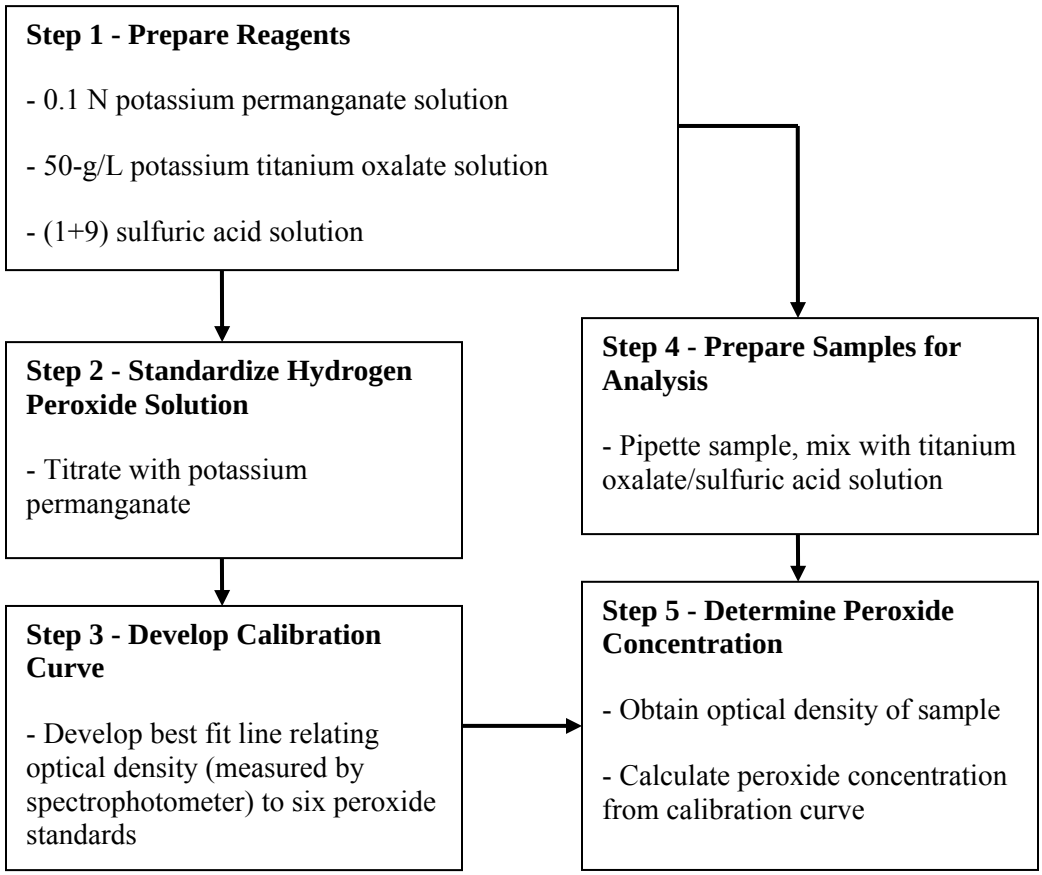

Figure 6-1. Titanium oxalate method for hydrogen peroxide detection.

6.1.2 Comparison to Other Versions of the Titanium Oxalate Method

The titanium oxalate method was initially proposed by Sellers in 1980. According to Sellers, the primary advantages of the method were

- A specific titanium(IV)–peroxide complex is formed for detection, making it less susceptible to interference by other oxidants,
- Titanium, in the Ti(IV) valence state, is commercially available as a salt in the form of potassium titanium oxalate, and
- The method is relatively simple.

Subsequently, the method has evolved to make it more robust. US Peroxide recommends a version of the titanium oxalate method for low-level residual hydrogen peroxide detection. The OCWD has created a slightly modified standard operating procedure (SOP) based on the US Peroxide procedure. The procedure modified by the University of Washington (termed the WRF-

04-019 method), which is presented here, is similar to the Orange County standard procedure. Differences between the Orange County procedure and the one developed by the University of Washington are

- Pretreatment for the sample was determined to be unnecessary in low-turbidity water.
- Sample volume was reduced from 20 to 10 ml.
- Absorbance measurements were performed at 390 rather than at 400 nm.

Table 6.1 provides a detailed comparison of the Sellers, US Peroxide, Orange County, and WRF-04-019 methods.

Table 6.1. Comparison of Key Aspects of Various Versions of the Titanium Oxalate Method

	Findings for:			
Description	**Sellers**	**US Peroxide**	**Orange County Standard Procedure**	**WRF-04-019 Method**
$KMnO_4$	n/a	0.1 N	0.1 N	0.1 N
Aluminum Chloride	n/a	484 g /L	484 g /L	484 g /L
Titanium Oxalate	35.4 g/L (in H_2SO_4 solution)	50 g/L	50 g/L	50 g/L
NaOH	n/a	240 g/L	240 g/L	240 g/L
H_2SO_4	n/a	(1+9)	(1+9)	(1+9)
H_2SO_4	n/a	(1+17)	(1+17)	(1+17)
Stock H_2O_2 Solution	n/a	7.5 mL, 27.5%, in 2 L	7.5 mL, 29–30%, in 2 L	7.5 mL, 29–30%, in 2 L
Standardized H_2O_2 Solution	None	50 mL of deionized water + 10 mL of (1+9) H_2SO_4 0.1 N $KMnO_4$ added to pink Calc H_2O_2 concentration G = T × N × 340 mg/mL	50 mL of deionized water + 10 mL of (1+9) H_2SO_4 0.1 N $KMnO_4$ added to pink Add 50 mL of H_2O_2 and titrate with 0.1 N $KMnO_4$ Calc H_2O_2 concentration G = T × N × 340 mg/L	50 mL of deionized water + 10 mL of (1+9) H_2SO_4 0.1 N $KMnO_4$ added to pink Calc H_2O_2 concentration G = T × N × 340 mg/L

Table 6.1 (cont.). Comparison of Key Aspects of Various Versions of the Titanium Oxalate Method

Description	Sellers	US Peroxide	OC SOP	WRF-04-019 Method
Working Standard Solution	None	Dilute standardized solution to 0.1 G	Dilute standardized solution to 0.02 G	
Development of Calibration Curve	None	Standards of 0, 1 ppm, 2 ppm, 3 ppm, 4 ppm, 5 ppm, made from working standard diluted to 25 mL Measured with 10-mm cell @ 400 nm	Standards of 0, 1 ppm, 2 ppm, 3 ppm, 4 ppm, 5 ppm, 6 ppm made from working standard diluted to 25 mL Measured with 10-mm cell @ 400 nm	Standards of 0, 1 ppm, 2 ppm, 3 ppm, 4 ppm, 5 ppm, made from working standard diluted to 25 mL Measured with 10-mm or 50-mm cell @ 390 nm
Sample Pretreatment	None	1 mL of aluminum chloride and 1 mL of NaOH added to 500-mL sample, allow precipitate to settle	1 mL of aluminum chloride and 1 mL of NaOH added to 300-mL sample, allow precipitate to settle for >30 min	None
Blank Analysis	5-mL sample + 5 mL of titanium oxalate, dilute to 25 mL without peroxide Measured @ 400 nm	20-mL sample + 2.5 mL of (1+17) H_2SO_4, dilute to 25 mL Measured with 10-mm cell @ 400 nm	20-mL sample + 2.5 mL of (1+17) H_2SO_4, dilute to 25 mL Measured with 10-mm cell @ 400 nm	10-mL sample + 1 mL of (1+17) H_2SO_4, dilute to 25 mL Measured with 10-mm cell @ 390 nm

Table 6.1 (cont.). Comparison of Key Aspects of Various Versions of the Titanium Oxalate Method

Description	Sellers	US Peroxide	OC SOP	WRT-04-019 Method
Sample Analysis	5-mL sample + 5 mL of titanium oxalate, dilute to 25 mL Measured @ 400 nm	20-mL sample + 2.5 mL of (1+17) H_2SO_4 + 2 mL of titanium oxalate, dilute to 25 mL Measured with 10-mm cell @ 400 nm	20-mL sample + 2.5 mL of (1+17) H_2SO_4 + 2 mL of titanium oxalate, dilute to 25 mL Measured with 10-mm cell @ 400 nm	10-mL sample + 1 mL of (1+17) H_2SO_4 + 1 mL of titanium oxalate, dilute to 25 mL Measured with 10-mm or 50-mm cell @ 390 nm
Calculation of Concn	$[H_2O_2]$ = (A-Ab)/(37.4 xl) A, Ab = absorbance x = sample volume l = path length	Optical density related to calibration graph	Optical density related to calibration graph	Optical density related to calibration graph

CHAPTER 7

CONCLUSION AND RECOMMENDATIONS

7.1 CONCLUSION

The titanium oxalate method (WRF-04-019) is an effective detection method for hydrogen peroxide in the presence of chloramine and is suitable for use with AOPs. The version of the procedure presented here is recommended for use in determining hydrogen peroxide concentrations for AOP systems.

7.2 RECOMMENDATIONS FOR ADDITIONAL STUDY

While the titanium oxalate method was found to be effective for the treatment of reuse water at West Basin and Orange County, additional study should be focused on:

- Evaluation in additional water matrices; and
- Evaluation at additional laboratories.

As previously noted, at present, there is no method for hydrogen peroxide detection included in *Standard Methods*. Therefore, this titanium oxalate method could be considered for inclusion in *Standard Methods*.

REFERENCES

Allsopp, C. Colorimetric estimation of hydrogen peroxide with titanium sulfate. *Analyst* **1941**, *66,* 371.

American Public Health Association (APHA). *Standard Methods for the Examination of Water and Wastewater*, 21st ed. American Public Health Association: Washington, DC, 2005.

Andreae, W. A sensitive method for the estimation of hydrogen peroxide in biological materials. *Nature* **1955**, *175,* 859–860.

Bader, H.; Sturzenegger, V.; Hoigne, J. Photometric method for the determination of low concentrations of hydrogen peroxide by the peroxidase catalyzed oxidation of N-N diethyl-*p*-phenylenediamine. *Water Res*. **1988**, *22,* 1109–1115.

Baga, A.; Johnson, G. R. A.; Nazhat, N. B.; Saadalla-Nazhat, R. A. A simple spectrophotometric determination of hydrogen peroxide at low concentrations in aqueous solution. *Anal. Chim. Acta* **1988**, *204,* 349–353.

Burdo, T.; Seitz, W. Mechanisms of cobalt catalysis of luminal chemiluminescence. *Anal. Chem.* **1975**, *47,* 1639.

Corbett, J. The scopoletin assay for hydrogen peroxide. A review and a better method. *J. Biochem. Biophys. Methods* **1989**, *18,* 297–307.

FMC Corporation, Industrial Chemical Group. *Analysis of Hydrogen Peroxide Solutions;* Technical Data Bulletin No. 59; Princeton, NJ, 1978.

Gordon, G.; Cooper, W. J.; Rice, R. G.; Pacey, G. E. *Disinfectant Residual Measurement Methods*, 2nd ed. AwwaRF: Denver, CO, 1992; pp 429–445.

Hochanadel, C. Effects of cobalt γ-radiation on water and aqueous solutions. *J. Phys. Chem.* **1952**, *56,* 587–594.

Karpel vel Leitner, N.; Dore, M. Mechanism of the reaction between hydroxyl radicals and glycolic, glyoxylic, acetic and oxalic acids in aqueous solution: consequence on hydrogen peroxide consumption in the H2O2/UV and O3/H2O2 systems. *Water Res*. **1997**, *31,* 1383–1397.

Karyakin, A.; Puganova, E.; Budashov, I.; et al. Prussian blue based nanoelectrode arrays for H_2O_2 detection. *Anal. Chem.* **2004**, *76,* 474–478.

Kieber, R.; Helz, G. Two-method verification of hydrogen peroxide determinations in natural waters. *Anal. Chem.* **1986**, *58,* 2312–2315.

Kingzett, C. *J. Chem. Soc.* **1880**, *37,* 792.

Klassem, N.; Marchington, D.; McGowan, H. H_2O_2 determination by I_3^- method and by $KMnO_4$ titration. *Anal. Chem*. **1994**, *66,* 2921–2925.

Kok, G. L.; Thompson, K.; Lazrus, A.; McLaren, S. E. Derivatization technique for the determination of peroxides in precipitation. *Anal. Chem*. **1986**, *58,* 1192–1194.

Kosaka, K.; Yamada, H.; Matsui, S.; Echigo, S.; Shishida, K. Comparison among the methods for hydrogen peroxide measurements to evaluate advance oxidation processes: application of a spectrophotometric method using copper(II) ion and 2,9-diemethyl-1,10-phenanthroline. *Environ. Sci. Technol*. **1998**, *32,* 3821–3824.

Madsen, B.; Kromis, M. Flow injection and photometric determination of hydrogen peroxide in rainwater with N-ethyl-N-(sulfopropyl)aniline sodium salt. *Anal. Chem*. **1984**, *56,* 2849–2850.

Masschelein, W.; Denis, M.; Ledent, R. Spectrophotometric determination of residual hydrogen peroxide. *Water Sewage Works* **1977**; August, pp 69–72.

Miller, W.; Kester, D. Hydrogen peroxide measurement in seawater by (*p*–hydroxyphenyl)acetic acid dimerization. *Anal. Chem*. **1988**, *60,* 2711–2715.

Mottola, H.; Simpson, B.; Gorin, G. Absorptiometric determination of hydrogen peroxide in submicrogram amounts with leuco crystal violet and peroxidase as catalyst. *Anal. Chem.* **1970**, *42,* 410.

Nogueira, R.; Oliveira, M.; Paterlini, W. Simple and fast spectrophotometric determination of H2O2 in photo-fenton reactions using metavanadate. *Talanta* **2005**, *66,* 86–91.

Perschke, H.; Broda, E. Determination of very small amounts of hydrogen peroxide. *Nature* **1961**, *190,* 257–258.

Price, D.; Worsfold, P.; Mantoura, R. Determination of hydrogen peroxide in sea water by flow injection analysis with chemiluminescence detection. *Anal. Chim. Acta* **1994**, *298,* 121.

Sandel, E. *Colorimetric Determinations of Trace Metals,* 3rd ed. Interscience Publishers: New York, NY, 1959, p 929.

Schick, R.; Strasser, I.; Stabel, H. Fluorometric determination of low concentrations of H_2O_2 in water: comparison with two other methods and application to environmental samples and drinking water treatment. *Water Res*. **1997**, *31,* 1371–1378.

Schumb, W.; Satterfield, C.; Wentworth, L. *Hydrogen Peroxide.* Reinhold Publishers: New York, NY, 1955.

Schwake, A.; Ross, B.; Camann, K. Chrono amperometric determination of hydrogen peroxide in swimming pool water using an ultramicroelectrode array. *Sens. Actuators, B* **1998**, *46,* 242–248.

Scott, W. W. *Scott's Standard Methods of Chemical Analysis,* 5th ed. D. Van Nostrand Co.: New York, NY, 1939.

Sellers, R. M. Spectrophotometric determination of hydrogen peroxide using potassium titanium(IV) oxalate. *Analyst* **1980**, *105,* 950–954.

Solvay Chemical Inc. *Determination of Hydrogen Peroxide; Ceric Sulfate Method;* TDS HH-5201; Brussels, Belgium, 2004a.

Solvay Chemical Inc. *Determination of Hydrogen Peroxide Concentration;* TDS HH-118; Brussels, Belgium, 2004b.

Sunder, M.; Hempel, D. Oxidation of tri- and perchloroethene in aqueous solution with ozone and hydrogen peroxide in a tube reactor. *Water Res.* **1997**, *31,* 33–40.

US Peroxide. http://www.h2o2.com (accessed Dec 2008).

Volk, C.; Roche, P.; Joret, J. Effects of ozone-hydrogen peroxide combination on the formation of biodegradable dissolved organic carbon. *Ozone Sci. Eng.* **1993**, *15,* 405–418.

Wanger, H.; Rusk, W. Determination of hydrogen peroxide and other peroxy-compounds. *Z. Wasser-Abwasser-Forsch*. **1984**, *17,* 262–267.

Worthington Biochemical Corporation. http://www.worthington-biochem.com/HPO/default.html (accessed Dec 2008).

Yamashiro, N.; Uchida, S.; Yamada, R. Determination of hydrogen peroxide in water by chemiluminescence detection. *J. Nucl. Sci. Technol.* **2004**, *41,* 890–897.

APPENDIX A

WRF-04-019 TITANIUM OXALATE METHOD FOR ANALYSIS OF HYDROGEN PEROXIDE IN WATER

INTRODUCTION

This document describes operating procedures that are required to carry out analyses for hydrogen peroxide (H_2O_2) using the titanium oxalate method.

The goal of this document is to provide step-by-step guidance concerning relevant analytical procedures.

BACKGROUND INFORMATION

Fundamentally, the titanium oxalate method is a spectrophotometric technique. It is designed to measure the absorbance of light caused by a spectrophotometrically active species the concentration of which is proportional to that of H_2O_2.

In this method, H_2O_2 is made to react with potassium titanium oxalate in acid solution. This reaction causes an intensely yellow complex of pertitanic acid with H_2O_2 to form. Because of its high level of absorbance and lack of interference caused by species typically present in water, the concentration of the colored complex can be measured spectrophotometrically with a high precision and accuracy. The wavelength of 390 nm is recommended for these measurements. The absorbance of the H_2O_2–pertitanate complex formed in the conditions specified for this method is expected to be directly proportional to that of the analyte (H_2O_2).

INTENDED USE AND INTERFERENCE

This method is suitable for the determination of H_2O_2 in aqueous effluents originating from the treatment of water by AOPs. The range of H_2O_2 concentrations that can be well quantified by the method is 0.1 to 10 mg/L as H_2O_2.

The method is expected to be largely interference free for AOP samples because the formation of the peroxotitanium complex is highly H_2O_2 specific. However, sample preparation (e.g., coagulation with alum and filtration) may be required for measurements of H_2O_2 concentrations in highly colored waters.

APPARATUS AND GLASSWARE

Spectrophotometric equipment. Use a spectrophotometer capable of measuring absorbance at a wavelength of 390 nm and fitted with 10- or 50-mm-path-length quartz cells. (A Perkin-Elmer Lambda 18 spectrometer was used in the University of Washington laboratory.). Other spectrophotometers can be used for measurements described in this document, provided that their spectrophotometric precision and accuracy are adequate. This is to be tested using the calibration procedure described in the sections that follow.

Note: Glass cells can also be used for spectrophotometric measurements described in this document; however, quartz cells are generally preferable because of their higher chemical stability and transparency in a broader range of wavelengths.

Glassware and other equipment. 25-mL, 500-mL, 1-L, and 2-L volumetric flasks; 500-mL beakers; 250-mL Erlenmeyer flask; a titration burette (10 or 25 mL); and Eppendorf pipettes.

REAGENTS

All reagents should be reagent-grade chemicals unless otherwise stated. The following solutions need to be prepared:

1. Potassium permanganate solution (0.1 N)

Preparation: Dissolve 3.2 g of $KMnO_4$ in 400 to 600 mL of deionized water placed in a 1-L volumetric flask. Adjust the volume to the mark.

Caution: Potassium permanganate is a strong oxidant. Safety goggles and gloves should be worn while handling it.

Note: 0.1 N $KMnO_4$ can also be purchased as a standard solution (for instance, item 319406-500ML or 319406-2L in the Aldrich catalog).

2. Potassium titanium oxalate solution (50 g/L)

Preparation: Dissolve 25.0 g of potassium titanium oxalate in 400 mL of deionized water, warming it slightly if necessary. Cool and dilute to 500 mL with deionized water in a volumetric flask and mix well.

Caution: Potassium titanium oxalate is toxic, and its solutions must be handled using a safety pipette or a burette.

Sources of this reagent are listed in the end of this document. Its CAS number is 14402-67-6 or 14481-26-6.

3. Sulfuric acid solution (1 + 9)

Preparation: Slowly add 50 mL of concentrated sulfuric acid (density, 1.84 g/mL) to 450 mL of demineralized water placed in a 1-L beaker. Be sure to continuously stir during the process and then allow the solution to cool.

Caution: Safety goggles must be worn when handing concentrated sulfuric acid.

4. Sulfuric acid solution (1 + 17)

Preparation: Slowly add 20 mL of concentrated sulfuric acid (density, 1.84 g/mL) to 340 mL of demineralized water placed in a 1-L beaker. Water needs to be continuously stirred. Following this operation, allow the solution of sulfuric acid to cool.

5. H_2O_2 stock solution (1000 mg/L)

Because of the potential instability of H_2O_2, its stock solution must be standardized as described below on the day of use. The following procedure is to be followed:

Caution: Safety goggles and gloves must be worn when handing stock solutions of H_2O_2.

Preparation: Add 7.50 mL of stock H_2O_2 solution (e.g., ACS reagent, 30 wt % in water; Aldrich no. 216763-500ML) to a 2-L volumetric flask, dilute to volume with deionized water, and mix well. The target concentration of H_2O_2 in this solution is 1000 mg/L.

Standardization: To determine the actual concentration of H_2O_2, the solution must be standardized before use.

For that purpose, do the following: using measuring cylinders, add 10 mL of sulfuric acid solution (1 + 9) and 50 mL of deionized water to a 250-mL Erlenmeyer (or conical) flask. Pipette 10.0 or 50 mL of H_2O_2 stock solution into the flask and titrate drop-wise with solution potassium permanganate (0.1 N) to the appearance of a faint permanent pinkness (initially, the pinkness of added permanganate will fade in the initial phase of titration, but it reappears at the end point).

Calculate the weight concentration of H_2O_2 in the stock solution using the following formula:

$$[H_2O_2]_{stock} = \frac{T_{MnO_4} \times N_{MnO_4} \times 17 \times 1000}{V_{stock}} (mg/L)$$

In this formula,

T_{MnO_4} is the volume of potassium permanganate titrant (in milliliters),

N_{MnO_4} is the normality of potassium permanganate titrant (nominally 0.1 N), and

V_{stock} is the volume of stock solution of H_2O_2 subject to titration (in milliliters).

For 10-mL and 50-mL aliquots of H_2O_2 stock solution, the above formulas can be rewritten as

For a 10-mL aliquot $[H_2O_2]_{stock} = 1700 \times T_{MnO_4} \times N_{MnO_4} (mg/L)$

For a 50-mL aliquot $[H_2O_2]_{stock} = 340 \times T_{MnO_4} \times N_{MnO_4} (mg/L)$

6. H_2O_2 standard solution: (20 mg/L)

Preparation: Pipette 10.0 mL of H_2O_2 stock solution prepared in step 5 into a 500-mL volumetric flask. Dilute to volume with deionized water and mix well. This solution must be prepared for use daily.

Note: If the preceding standardization step reveals a H_2O_2 concentration that is slightly different from 1000 mg/L in the H_2O_2 stock, it may be easier to adjust the volume of stock solution added to prepare the 20-mg/L standard solution, rather than trying to prepare stock solution at exactly 1000 mg of H_2O_2/L. The decision to adjust the volume added to obtain 20-mg/L H_2O_2 solution or adjust the concentration of H_2O_2 in standard solution no. 5 to have exactly 1000 mg/L is the operator's.

PREPARATION OF CALIBRATION GRAPH

Method calibration is necessary prior to measurements of unknown H_2O_2 concentrations. Preparation of samples and measurements necessary to generate a calibration curve is described below.

1. Pipette 10 mL of deionized water into each of six 25-mL volumetric flasks.
2. Using a volumetric pipette, add to the flasks amounts of the H_2O_2 standard solution (solution 6 above) that are outlined in the table below.

Variable (Unit Used)	Properties for Sample No.:					
	1	2	3	4	5	6
H_2O_2 Standard (mL)	0	1	2	3	4	5
Concn (mg/L)	0	0.8	1.6	2.4	3.2	4.0

3. Sequentially add 1.0 mL of sulfuric acid solution (1 + 17) (solution 4) and 1.0 mL of potassium titanium oxalate solution (solution 2) to each flask.
4. Adjust the volume of solutions in each flask with deionized water. Mix well.
5. Allow the color to develop for at least 5 min.
6. Set the spectrophotometer to measure absorbance at a wavelength of 390 nm and select a pair of 10-mm-path-length quartz cells. Fifty-millimeter quartz cells can be used for higher sensitivity (as long as the absorbance does not exceed 1 absorbance unit at 390 nm).
7. Adjust the instrument for zero absorbance against deionized water in one of the cells. Using the other cell, measure the absorbance of each of the standard solutions.
8. Plot the optical densities against the corresponding H_2O_2 content of the standard solutions.
9. Draw the line of best fit through the series of points and the origin to obtain the required calibration graph.

PREPARATION OF SAMPLES CONTAINING HYDROGEN PEROXIDE FOR SPECTROPHOTOMETRIC MEASUREMENTS

As described above, no pretreatment prior to the spectrophotometric analysis is normally required for water samples originating from the AOP and/or related water treatment systems.

Given the potential instability of H_2O_2-containing samples, they should be analyzed as soon as possible and in no case be held for more than a day. To prevent effects of illumination, wrap them in aluminum foil.

Sequence of steps to process the samples:

1. Pipette 10 mL of the H_2O_2-containing sample into a 25-mL volumetric flask.
2. Add 1.0 mL of sulfuric acid (1 + 17) (solution 4).
3. Add 1.0 mL of potassium titanium oxalate solution (solution 2).
4. Adjust the volume to 25 mL with deionized water.
5. Mix well.
6. Allow the color to develop for at least 5 min.
7. Measure the absorbance of the sample solution.
8. Relate the optical density thus obtained to the calibration curve to obtain the apparent weight concentration of H_2O_2. Record this weight as "A." To calculate the actual concentration of H_2O_2 in the sample, use the following formula (which is applicable for 10-mL aliquots):

   A = weight concentration of H_2O_2 (mg/L)

$$H_2O_2\,(mg/L) = 2.5 \times A$$

INFORMATION CONCERNING VENDORS OF POTASSIUM TITANIUM OXALATE

Company	Phone	Website	Other Information
Alfa Aesar	(978) 521-6401	www.alfa.com	Item no. 42898
City Chemical	(800) 248-2436	www.citychemical.com	Item no. T8835; only technical grade is listed
MP Biomedicals	(800) 854-0530	www.mpbio.com	Item no. 220580; appears to be extremely expensive
Pfaltz & Bauer	(203) 574-0075	www.pfaltzandbauer.com	Item no. P24013

APPENDIX B

PROCEDURE FOR SAMPLE COLLECTION PREPARATION—INTERLABORATORY EVALUATION

1) Collected Samples: from four locations, each 2000 ml and in an amber glass jar.

- WB upstream of peroxide addition
- WB downstream of peroxide addition
- OC upstream of peroxide addition
- OC downstream of peroxide addition

2) Known Hydrogen Peroxide Addition

- Obtain 1000-mg/L stock H_2O_2 solution
- Prepare two (2) 500-ml volumetric flasks—labels A and B
- Add approximately 400 ml of sample to each volumetric
- Add 1.25 mL of hydrogen peroxide solution to flask A (2.5 mg/L addition), then fill
- Add 2.5 mL of hydrogen peroxide solution to flask B (5.0 mg/L addition), then fill to line

3) Chloramine Addition

- Obtain 500-mg/L chloramine solution
- Prepare six 100-mL volumetric flasks—labels C, D, E, F, G, and H
- Add approximately 80 ml of the following sample to each flask and add chloramine (see table below.)
- Fill to line with appropriate water

Table of Chloramine Addition

100 mL	Condition (mg/L)			Amount or chloramine to add
Volumetric	Peroxide	Chloramine	Take water from	mL
C	0	1	2000 mL sample	0.2
D	0	2	2000 mL sample	0.4
E	2.5	1	Volumetric A	0.2
F	2.5	2	Volumetric A	0.4
G	5	1	Volumetric B	0.2
H	5	2	Volumetric B	0.4

4) Sample preparation

- Obtain and label 72 40-mL amber glass EPA vials per the table below. Two labels are required for each sample. Fill two vials per table.

Table of Sample Conditions

Sample	Source Water	Location	Source of sample	Condition (mg/L) Peroxide	Chloramine
10 WB	WB	Up Stream	2000 mL container	0	0
20 WB	WB	Up Stream	Volumetric C	0	1
30 WB	WB	Up Stream	Volumetric D	0	2
40 WB	WB	Up Stream	Volumetric A	2.5	0
50 WB	WB	Up Stream	Volumetric E	2.5	1
60 WB	WB	Up Stream	Volumetric F	2.5	2
70 WB	WB	Up Stream	Volumetric B	5	0
80 WB	WB	Up Stream	Volumetric G	5	1
90 WB	WB	Up Stream	Volumetric H	5	2
100 WB	WB	Down Stream	2000 mL container	0	0
200 WB	WB	Down Stream	Volumetric C	0	1
300 WB	WB	Down Stream	Volumetric D	0	2
400 WB	WB	Down Stream	Volumetric A	2.5	0
500 WB	WB	Down Stream	Volumetric E	2.5	1
600 WB	WB	Down Stream	Volumetric F	2.5	2
700 WB	WB	Down Stream	Volumetric B	5	0
800 WB	WB	Down Stream	Volumetric G	5	1
900 WB	WB	Down Stream	Volumetric H	5	2
10 OC	OC	Up Stream	2000 mL container	0	0
20 OC	OC	Up Stream	Volumetric C	0	1
30 OC	OC	Up Stream	Volumetric D	0	2
40 OC	OC	Up Stream	Volumetric A	2.5	0
50 OC	OC	Up Stream	Volumetric E	2.5	1
60 OC	OC	Up Stream	Volumetric F	2.5	2
70 OC	OC	Up Stream	Volumetric B	5	0
80 OC	OC	Up Stream	Volumetric G	5	1
90 OC	OC	Up Stream	Volumetric H	5	2
100 OC	OC	Down Stream	2000 mL container	0	0
200 OC	OC	Down Stream	Volumetric C	0	1
300 OC	OC	Down Stream	Volumetric D	0	2
400 OC	OC	Down Stream	Volumetric A	2.5	0
500 OC	OC	Down Stream	Volumetric E	2.5	1
600 OC	OC	Down Stream	Volumetric F	2.5	2
700 OC	OC	Down Stream	Volumetric B	5	0
800 OC	OC	Down Stream	Volumetric G	5	1
900 OC	OC	Down Stream	Volumetric H	5	2

5) Split samples

- One full set to Orange County and one full set to West Basin for analysis per peroxide detection method. Analysis performed in duplicate. Samples should remain chilled and in the dark during transport.

APPENDIX C

PROCEDURE FOR PREPARATION OF STOCK SOLUTIONS FOR KNOWN ADDITION—INTERLABORATORY EVALUATION

STOCK PEROXIDE SOLUTION PREPARATION

See peroxide detection method for 1000-mg/L H_2O_2 stock solution preparation.

STOCK CHLORAMINE SOLUTION PREPARATION

Preparation of chlorine solution

1) Add 20 mL of 5–6% sodium hypochlorite to 1000 mL of volumetric-containing deionized water; fill to the line. Concentration should be approximately 1000 mg of Cl_2/L.

2) Standardize the solution using the iodometric method (SM 4500-Cl) or similar technique.

3) Stock solution should be stored chilled.

Preparation of ammonia solution

1) Adjust 1000 mL of deionized water to pH 8 with sodium hydroxide.

2) Add 381 mg of ammonium chloride to 500 mL of pH 8 deionized water, mixing with stir plate.

3) Chill ammonia solution to 5 ºC.

Preparation of monochloramine solution

1) *** This step should be performed under hood or with adequate ventilation***

After chilling, slowly add 500 ml of 1000-mg/L stock chlorine solution to ammonium chloride solution, mixing with stir plate. Concentration should be 500 mg/L as Cl_2 or 353 mg/L as NH_2Cl.

2) Standardize solution using iodometric method (SM 4500-Cl) or similar technique.

3) Stock solution should be stored chilled.

APPENDIX D

DATA FROM BENCH-LEVEL TITANIUM OXALATE EVALUATION

Table A1. Analytical Data Used to Calculate MDLs for Titanium Oxalate Hydrogen Peroxide Measurements in Deionized Water without Chloramine

Sample #	1	2	3	4	5	6	7
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Abs_{390nm}	0.0028	0.0024	0.0019	0.0022	0.0023	0.0026	0.0029
H_2O_2 (mg/L)	0.06	0.05	0.02	0.04	0.04	0.06	0.07
Standard Deviation (mg/L)	**0.014**						
MDL (mg/L)	**0.045**						

Sample #	1	2	3	4	5	6	7
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Abs_{390nm}	0.0027	0.0030	0.0032	0.0037	0.0032	0.0026	0.0036
H_2O_2 (mg/L)	0.06	0.07	0.08	0.10	0.08	0.05	0.09
Standard Deviation (mg/L)	**0.017**						
MDL (mg/L)	**0.053**						

Table A2. Analytical Data Used to Calculate MDLs for Titanium Oxalate Hydrogen Peroxide Measurements in Deionized Water with 5.54-mg/L Chloramine

Sample #	1	2	3	4	5	6	7
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Abs_{390nm}	0.0028	0.0024	0.0019	0.0022	0.0023	0.0026	0.0029
H_2O_2 (mg/L)	0.06	0.05	0.02	0.04	0.04	0.06	0.07
Standard Deviation (mg/L)	**0.014**						
MDL (mg/L)	**0.045**						

Sample #	1	2	3	4	5	6	7
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Abs_{390nm}	0.0027	0.0030	0.0032	0.0037	0.0032	0.0026	0.0036
H_2O_2 (mg/L)	0.06	0.07	0.08	0.10	0.08	0.05	0.09
Standard Deviation (mg/L)	**0.017**						
MDL (mg/L)	**0.053**						

Table A3. Analytical Data Used to Calculate MDLs for Titanium Oxalate Hydrogen Peroxide Measurements in West Basin Water without Chloramine

Sample #	1	2	3	4	5	6	7
H_2O_2 stock (mL)	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Abs_{390nm}	0.008	0.008	0.008	0.009	0.009	0.008	0.008
H_2O_2 (mg/L)	0.21	0.22	0.23	0.25	0.26	0.22	0.21
Standard Deviation (mg/L)	**0.017**						
MDL (mg/L)	**0.054**						

Sample #	1	2	3	4	5	6	7
H_2O_2 stock (mL)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Abs_{390nm}	0.007	0.006	0.006	0.007	0.005	0.005	0.005
H_2O_2 (mg/L)	0.15	0.14	0.12	0.16	0.10	0.10	0.10
Standard Deviation (mg/L)	**0.027**						
MDL (mg/L)	**0.085**						

Table A4. Analytical Data Used to Calculate MDLs for Titanium Oxalate Hydrogen Peroxide Measurements in West Basin Water with 5.54-mg/L Chloramine

Sample #	1	2	3	4	5	6	7
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Abs_{390nm}	0.0076	0.0075	0.0075	0.0081	0.0083	0.0078	0.0075
H_2O_2 (mg/L)	0.20	0.19	0.19	0.22	0.23	0.20	0.19
Standard Deviation (mg/L)	**0.014**						
MDL (mg/L)	**0.045**						

Sample #	1	2	3	4	5	6	7
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Abs_{390nm}	0.0086	0.0092	0.0091	0.0094	0.0090	0.0096	0.0087
H_2O_2 (mg/L)	0.24	0.27	0.26	0.27	0.26	0.29	0.25
Standard Deviation (mg/L)	**0.015**						
MDL (mg/L)	**0.048**						

Table A5. Bias and Precision Determined for Various Levels of Hydrogen Peroxide Measurements in Deionized Water (DI) without Chloramine

H_2O_2 concentration	Bias DI w/o chloramine	Precision DI w/o chloramine	Relative bias, DI w/o chloramine	Relative precision, DI w/o chloramine
0.1	0.02	0.03	18.2%	27.2%
0.5	0.01	0.03	2.4%	5.0%
1.1	-0.02	0.03	-2.0%	2.8%
5.4	-0.04	0.08	-0.7%	1.4%
10.8	-0.23	0.43	-2.1%	3.9%

Table A6. Bias and Precision Determined for Various Levels of Hydrogen Peroxide Measurements in Deionized Water (DI) with 5.54-mg/L Chloramine

H_2O_2 concentration	Bias DI with chloramine	Precision DI with chloramine	Relative bias, DI with chloramine	Relative precision, DI with chloramine
0.1	-0.01	0.02	-8.1%	20.0%
0.5	-0.02	0.02	-3.6%	4.5%
1.1	-0.02	0.04	-1.9%	3.5%
5.4	-0.12	0.14	-2.3%	2.6%
10.9	-0.04	0.05	-0.4%	0.5%

Table A7. Bias and Precision Determined for Various Levels of Hydrogen Peroxide Measurements in West Basin Water without Chloramine

H_2O_2 concentration	Bias wastewater w/o chloramine	Precision wastewater w/o chloramine	Relative bias, wastewater w/o chloramine	Relative precision, wastewater w/o chloramine
0.1	0.04	0.05	41.6%	46.6%
0.5	0.04	0.05	7.4%	10.1%
1.0	-0.01	0.03	-0.9%	3.4%
5.1	0.03	0.43	0.7%	8.6%
10.1	0.32	0.33	3.2%	3.3%

Table A8. Bias and Precision Determined for Various Levels of Hydrogen Peroxide Measurements in West Basin Water with 5.54-mg/L Chloramine

H_2O_2 concentration	Bias wastewater with chloramine	Precision wastewater with chloramine	Relative bias, wastewater with chloramine	Relative precision, wastewater with chloramine
0.2	0.02	0.04	8.5%	19.7%
0.5	0.02	0.03	3.9%	6.6%
1.0	0.03	0.05	2.8%	4.5%
5.1	0.02	0.08	0.4%	1.6%
10.2	-0.09	0.20	-0.9%	1.9%

Table A9. Analytical Data Used to Calculate Bias and Precision for Various Levels of Hydrogen Peroxide Measurements in Deionized Water without Chloramine

H_2O_2 spiked	10.80 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
H_2O_2 stock (mL)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Abs_{390nm}	0.252	0.257	0.256	0.256	0.236	0.252	0.250	0.254	0.248	0.234
H_2O_2 (mg/L)	10.69	10.91	10.85	10.85	9.99	10.69	10.62	10.75	10.50	9.90
Difference	-0.12	0.11	0.05	0.05	-0.81	-0.11	-0.19	-0.05	-0.30	-0.90
Squared Difference	0.0133	0.0128	0.0024	0.0028	0.6519	0.0114	0.0344	0.0028	0.0929	0.8041

H_2O_2 spiked	5.40 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
H_2O_2 stock (mL)	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Abs_{390nm}	0.128	0.124	0.127	0.127	0.128	0.130	0.129	0.128	0.127	0.129
H_2O_2 (mg/L)	5.36	5.21	5.35	5.33	5.39	5.45	5.42	5.38	5.32	5.41
Difference	-0.04	-0.19	-0.05	-0.07	-0.01	0.05	0.02	-0.02	-0.08	0.01
Squared Difference	0.00	0.03	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00

H_2O_2 spiked	1.08 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
H_2O_2 stock (mL)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Abs_{390nm}	0.027	0.026	0.026	0.027	0.027	0.028	0.026	0.027	0.027	0.027
H_2O_2 (mg/L)	1.06	1.04	1.03	1.06	1.07	1.09	1.03	1.08	1.05	1.08
Difference	-0.02	-0.04	-0.05	-0.02	-0.01	0.01	-0.05	0.00	-0.03	-0.01
Squared Difference	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

H_2O_2 spiked	0.54 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
H_2O_2 stock (mL)	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Abs_{390nm}	0.016	0.015	0.015	0.015	0.015	0.015	0.015	0.016	0.014	0.015
H_2O_2 (mg/L)	0.60	0.56	0.56	0.54	0.54	0.53	0.55	0.59	0.52	0.54
Difference	0.06	0.02	0.02	0.00	0.00	-0.01	0.01	0.05	-0.02	0.00
Squared Difference	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

H_2O_2 spiked	0.11 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
H_2O_2 stock (mL)	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Abs_{390nm}	0.004	0.004	0.005	0.005	0.005	0.006	0.006	0.006	0.005	0.006
H_2O_2 (mg/L)	0.10	0.09	0.13	0.12	0.12	0.15	0.15	0.15	0.12	0.15
Difference	-0.01	-0.01	0.02	0.01	0.01	0.05	0.04	0.04	0.01	0.04
Squared Difference	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A10. Bias and Precision Determined for Various Levels of Hydrogen Peroxide Measurements in Deionized Water with 5.54-mg/L Chloramine

H_2O_2 spiked	10.85 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Abs_{390nm}	0.254	0.253	0.253	0.254	0.253	0.255	0.254	0.254	0.253	0.253
H_2O_2 (mg/L)	10.81	10.79	10.76	10.83	10.79	10.87	10.80	10.83	10.77	10.79
Difference	-0.04	-0.06	-0.09	-0.02	-0.05	0.03	-0.04	-0.02	-0.08	-0.05
Squared Difference	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00

H_2O_2 spiked	5.42 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Abs_{390nm}	0.126	0.126	0.123	0.125	0.127	0.126	0.126	0.124	0.126	0.125
H_2O_2 (mg/L)	5.34	5.32	5.18	5.28	5.38	5.34	5.33	5.23	5.30	5.29
Difference	-0.08	-0.10	-0.24	-0.14	-0.04	-0.08	-0.09	-0.19	-0.12	-0.14
Squared Difference	0.0072	0.0102	0.0571	0.0193	0.0018	0.0070	0.0078	0.0363	0.0141	0.0184

H_2O_2 spiked	1.08 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Abs_{390nm}	0.028	0.027	0.028	0.026	0.026	0.027	0.026	0.027	0.027	0.027
H_2O_2 (mg/L)	1.12	1.05	1.10	1.05	1.03	1.07	1.03	1.05	1.09	1.05
Difference	0.04	-0.03	0.02	-0.04	-0.06	-0.02	-0.05	-0.03	0.00	-0.03
Squared Difference	0.0014	0.0009	0.0003	0.0015	0.0032	0.0002	0.0030	0.0011	0.0000	0.0011

H_2O_2 spiked	0.54 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Abs_{390nm}	0.014	0.014	0.015	0.014	0.014	0.014	0.015	0.014	0.014	0.014
H_2O_2 (mg/L)	0.51	0.51	0.55	0.52	0.50	0.52	0.54	0.53	0.52	0.51
Difference	-0.03	-0.03	0.00	-0.02	-0.04	-0.02	0.00	-0.01	-0.02	-0.03
Squared Difference	0.0008	0.0009	0.0000	0.0005	0.0015	0.0004	0.0000	0.0001	0.0003	0.0008

H_2O_2 spiked	0.11 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Abs_{390nm}	0.004	0.004	0.005	0.004	0.004	0.004	0.005	0.004	0.005	0.004
H_2O_2 (mg/L)	0.08	0.09	0.11	0.08	0.10	0.08	0.15	0.10	0.12	0.09
Difference	-0.02	-0.02	0.00	-0.03	-0.01	-0.02	0.04	-0.01	0.01	-0.01
Squared Difference	0.0006	0.0004	0.0000	0.0008	0.0002	0.0006	0.0014	0.0001	0.0001	0.0002

Table A11. Bias and Precision Determined for Various Levels of Hydrogen Peroxide Measurements in West Basin Water without Chloramine

H_2O_2 spiked	10.12 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Abs_{390nm}	0.245143	0.244083	0.241968	0.245718	0.246574	0.245939	0.243056	0.245062	0.241602	0.242636
H_2O_2 (mg/L)	10.44	10.40	10.31	10.47	10.51	10.48	10.35	10.44	10.29	10.34
Difference	0.33	0.28	0.19	0.35	0.39	0.36	0.24	0.33	0.18	0.22
Squared Difference	0.1082	0.0803	0.0371	0.1250	0.1524	0.1318	0.0573	0.1059	0.0313	0.0490

H_2O_2 spiked	5.06 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Abs_{390nm}	0.124506	0.124606	0.124217	0.123442	0.124271	0.124326	0.116594	0.092711	0.124524	0.125077
H_2O_2 (mg/L)	5.27	5.27	5.25	5.22	5.26	5.26	4.93	3.90	5.27	5.29
Difference	0.21	0.21	0.20	0.16	0.20	0.20	-0.13	-1.16	0.21	0.23
Squared Difference	0.0436	0.0454	0.0386	0.0266	0.0395	0.0405	0.0171	1.3357	0.0439	0.0545

H_2O_2 spiked	1.01 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Abs_{390nm}	0.025995	0.025647	0.025156	0.025083	0.023871	0.024104	0.025183	0.026363	0.025011	0.025235
H_2O_2 (mg/L)	1.04	1.02	1.00	1.00	0.95	0.96	1.00	1.05	1.00	1.01
Difference	0.03	0.01	-0.01	-0.01	-0.06	-0.05	-0.01	0.04	-0.02	-0.01
Squared Difference	0.0007	0.0001	0.0001	0.0001	0.0041	0.0029	0.0001	0.0018	0.0002	0.0000

H_2O_2 spiked	0.51 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Abs_{390nm}	0.013804	0.014298	0.013863	0.015138	0.013851	0.013809	0.016094	0.014088	0.014708	0.015022
H_2O_2 (mg/L)	0.52	0.54	0.52	0.57	0.52	0.52	0.61	0.53	0.55	0.57
Difference	0.01	0.03	0.01	0.07	0.01	0.01	0.11	0.02	0.05	0.06
Squared Difference	0.0001	0.0009	0.0001	0.0044	0.0001	0.0001	0.0116	0.0005	0.0023	0.0038

H_2O_2 spiked	0.10 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Abs_{390nm}	0.00548	0.004811	0.0049	0.005233	0.005285	0.005408	0.004815	0.004573	0.005017	0.005743
H_2O_2 (mg/L)	0.16	0.13	0.13	0.15	0.15	0.15	0.13	0.12	0.14	0.17
Difference	0.06	0.03	0.03	0.05	0.05	0.05	0.03	0.02	0.04	0.07
Squared Difference	0.0032	0.0008	0.0010	0.0021	0.0023	0.0029	0.0008	0.0003	0.0014	0.0046

Table A12. Bias and Precision Determined for Various Levels of Hydrogen Peroxide Measurements in West Basin Water with 5.54-mg/L Chloramine

H_2O_2 spiked	10.17 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Abs_{390nm}	0.236	0.236	0.236	0.245	0.237	0.228	0.237	0.237	0.238	0.238
H_2O_2 (mg/L)	10.04	10.03	10.06	10.45	10.09	9.72	10.07	10.09	10.11	10.12
Difference	-0.13	-0.13	-0.10	0.28	-0.07	-0.45	-0.09	-0.08	-0.05	-0.04
Squared Difference	0.02	0.02	0.01	0.08	0.01	0.20	0.01	0.01	0.00	0.00

H_2O_2 spiked	5.08 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Abs_{390nm}	0.122	0.120	0.122	0.121	0.121	0.116	0.122	0.120	0.122	0.122
H_2O_2 (mg/L)	5.15	5.08	5.15	5.11	5.12	4.90	5.16	5.08	5.15	5.13
Difference	0.07	0.00	0.06	0.02	0.04	-0.18	0.07	0.00	0.07	0.05
Squared Difference	0.0047	0.0000	0.0040	0.0006	0.0017	0.0329	0.0055	0.0000	0.0049	0.0023

H_2O_2 spiked	1.02 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Abs_{390nm}	0.027	0.026	0.027	0.026	0.025	0.025	0.027	0.026	0.026	0.028
H_2O_2 (mg/L)	1.08	1.04	1.06	1.05	1.00	1.00	1.07	1.02	1.03	1.11
Difference	0.07	0.02	0.04	0.03	-0.02	-0.02	0.05	0.00	0.01	0.09
Squared Difference	0.0043	0.0004	0.0017	0.0011	0.0002	0.0002	0.0026	0.0000	0.0002	0.0082

H_2O_2 spiked	0.51 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Abs_{390nm}	0.014	0.015	0.014	0.014	0.014	0.014	0.013	0.014	0.015	0.015
H_2O_2 (mg/L)	0.50	0.55	0.54	0.53	0.51	0.53	0.48	0.53	0.57	0.55
Difference	-0.01	0.05	0.03	0.02	0.00	0.02	-0.02	0.02	0.06	0.04
Squared Difference	0.0001	0.0021	0.0007	0.0003	0.0000	0.0004	0.0006	0.0004	0.0041	0.0014

H_2O_2 spiked	0.20 mg/L									
Sample #	1	2	3	4	5	6	7	8	9	10
Chloramine dosing (mL)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
TOTCl (mg/L)	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54	5.54
NH_3-N (mg/L)	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18
H_2O_2 stock (mL)	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Abs_{390nm}	0.007	0.008	0.007	0.009	0.007	0.006	0.007	0.007	0.007	0.006
H_2O_2 (mg/L)	0.21	0.24	0.21	0.31	0.22	0.19	0.21	0.20	0.22	0.19
Difference	0.01	0.04	0.00	0.11	0.02	-0.01	0.01	0.00	0.01	-0.02
Squared Difference	0.0001	0.0014	0.0000	0.0114	0.0004	0.0001	0.0000	0.0000	0.0002	0.0003

ABBREVIATIONS

AOP	Advanced oxidation process
APHA	American Public Health Association
ANOVA	Analysis of variance
AWWA	American Water Works Association
CalDPH	California Department of Health
DMP	2,9-Diemethyl-1,10-phenanthroline
DPD	*N*,*N*-Diethyl-*p*-phenylenediamine
HRP	Horseradish peroxidase
MDL	Method detection limit
NDMA	*N*-Nitrosodimethylamine
OC	Orange County
OCWD	Orange County Water District
PAC	Project Advisory Committee
PCPs	Personal care products
PHACs	Pharmaceutically active compounds
POHPAA	*p*-Hydroxyphenylacetic acid
SM	Standard Methods
SOP	Standard operating procedure
UV	Ultraviolet
WB	West Basin
WBMWD	West Basin Municipal Water District
WEF	Water Environment Foundation
WRF	WateReuse Foundation

Advancing the Science of Water Reuse and Desalination



WATEREUSE FOUNDATION

1199 North Fairfax Street, Suite 410
Alexandria, VA 22314 USA
(703) 548-0880
Fax (703) 548-5085
E-mail: Foundation@WateReuse.org
www.WateReuse.org/Foundation