Relationships between Oxidation-Reduction Potential, Oxidant, and pH in Drinking Water

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Abstract –Oxidation and reduction (redox) reactions are very important in drinking water. Oxidation-reduction potential (ORP) measurements reflect the redox state of water. Redox measurements are not widely made by drinking water utilities in part because they are not well understood. The objective of this study was to determine the effect of oxidant type and concentration on the ORP of carbonate buffered water as a function of pH. Oxidants that were studied included: chlorine, monochloramine, potassium permanganate, chlorine dioxide, and oxygen. ORP decreased with increasing pH, regardless of the oxidant type or concentration. ORP increased rapidly with increasing oxidant dosage, particularly at lower concentrations. Differences in the redox potentials of different oxidant systems were also observed. Waters that contained chlorine and chlorine dioxide had the highest ORPs. Tests also revealed that there were inconsistencies with redox electrode measurements. In the standard Zobell reference solution, two identical redox electrodes had nearly the same reading, but in test waters the readings sometimes showed a variation as great as 217.7 mV.

Key words: ORP, redox potential, redox chemistry, oxidant, drinking water

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1.0 BACKGROUND

1.1 Redox Theory

Oxidation-reduction (redox) reactions describe the transfer of electrons between atoms, molecules, or ions. Oxidation and reduction reactions occur simultaneously and together make up an electrochemical couple. The oxidation reaction takes place at the anode of an electrochemical cell [1,2,3] and involves the species that loses electrons (referred to as the reductant). In drinking water, examples of reductants include As^{3+}, Fe^{2+}, and Mn^{2+}. In a drinking water distribution pipe (e.g., iron, lead and copper), oxidation (or corrosion) of the base metal takes place at the anode. Reduction takes place at the cathode of an electrochemical cell [1,2,3] and describes the species that accepts electrons (referred to as the oxidant). Chlorine, oxygen, monochloramine, and ozone are examples of oxidants found in drinking waters.

The oxidation–reduction potential (ORP) or redox potential indicates the availability of free electrons and the oxidizing or reducing tendency of a water [1]. The ORP of water is measured in millivolts [mV] using an ORP electrode. Platinum electrodes are most commonly used and typically preferred due to their high current exchange density. The exchange current, I_o, is a fundamental characteristic of electrode behavior, which is defined as the rate of oxidation or reduction at an equilibrium electrode in terms of current (amps). The larger the current exchange, the more stable the electrode response [4]. This current is dependent on the redox species, the concentration of the species in water, and the material of the electrode [7]. Other important

characteristics of oxidation-reduction potential electrodes include the measuring range, accuracy, and response time [4]. Measured ORP values are often normalized with respect to a standard hydrogen electrode (SHE), E_H [8, 4]. Converting ORP measurements to E_H depends on the type of ORP electrode and can be calculated, although electrode manufacturers typically provide conversion factors as a function of temperature (Table 1).

TABLE 1. Example of manufacturer supplied SHE conversation table. Conversion potentials, C, developed by the reference electrode portion relative to the SHE at various temperatures [Thermo Orion Model 9678BN, Platinum–Ag/AgCl combination electrode].

Temperature ^oC	Electrode potential in mV (C) 900001 solution
10	251
20	244
25	241
30	238

Reference—Thermo Orion Manual for Model # 9678BN

The conversion from the electrode mV readings to E_H (respect to the SHE) using the example in Table 1 can be calculated according to:

$$E_H = E_{measured} + C \qquad [1]$$

where E_H is the oxidation-reduction potential of the sample relative to the SHE in mV, $E_{measured}$ is the potential measured by the electrode (i.e., platinum-Ag/AgCl), and C is the potential developed by the reference electrode portion relative to the SHE.

The theoretical ORP of a balanced oxidation-reduction reaction [Equation 2]

$$aA + bB \rightarrow cC + dD \qquad [2]$$

can be calculated based on theoretical considerations according to the Nernst Equation:

$$E_H = E^o - \frac{RT}{nF} \ln(Q) \qquad [3]$$

where the activity coefficient Q is:

$$Q = \frac{Cc \times Dd}{Aa \times Bb} \qquad [4]$$

and E_H is the redox potential (mV), E^o is the standard potential (mV), R is the universal gas constant (8.314 X 10^{-3} kJ/mol-K), T is the temperature (°K), n is the number of moles of electrons transferred in the reaction, and F is Faraday's constant (96,490 C-mol^{-1}) [1].

ORP measurements in drinking water can be easily performed in the field, in either batch or continuous mode, making it a possible process control tool and indicator of distribution system contamination. Although the Nernst equation expresses the thermodynamic relationship of the redox potential and the solution composition at equilibrium [4], the chemistry of natural waters is complex and redox equilibrium is rarely achieved. Because of this limitation, performing accurate ORP measurements in natural waters can be complex and sometimes impossible due to slow kinetics, mixed potentials, and electrode failure [5,6,9]. Therefore, ORP measurements are largely misused, misunderstood, and rarely used by the drinking water community.

1.2 Importance of ORP Measurements in Water and Wastewater Treatment

Oxidation-reduction reactions are extremely important in many drinking water and wastewater processes and applications. For example, the corrosion of distribution system materials, precipitation of iron and manganese compounds, nitrification, and microbial disinfection are all described or dependent on oxidation-reduction reactions. Redox conditions in drinking water systems can widely vary in range from anoxic (e.g., natural source ground water) to disinfected finished water. Therefore a variety of redox-dependent species can exist in drinking water systems.

ORP measurements have been used in various pilot studies and full-scale wastewater treatment plants to monitor disinfection and dechlorination processes. Kim et al. performed ORP testing at a wastewater treatment facility in Simi Valley, California [10, 11]. Since chlorine and other types of oxidants' reactivity in water greatly depend on redox conditions, ORP measurements, in theory, could be used to monitor disinfection success. ORP equipment was established in the plant and correlations from ORP, pH, residual chlorine measurements, and coliform counts were determined. This study showed that the ORP measurements had a higher correlation than the residual chlorine measurements, in terms of coliform inactivation [10, 11]. By using ORP monitoring, the plant saved considerably on chemical supplies (chlorine by 47% by cost). This potential application has sparked a need for further investigation of ORP measurements as a method of water quality control.

1.3 Research Objective

The objective of this work was to examine the effects of pH, and oxidant type and concentration (mg/L) on the ORP of carbonate buffered water. Oxidants evaluated include free chlorine [Cl_2], oxygen [O_2], chlorine dioxide [ClO_2], monochloramine [MCA], and potassium permanganate [$KMnO_4$]. Measurement consistency issues and ORP electrodes operational concerns were also addressed.

2.0 EXPERIMENTAL DESIGN

2.1 Glassware and Sampling Materials

All glassware used during these experiments was thoroughly rinsed in deionized (DI) water using a Milli-Q Plus© cartridge deionized water system (Millipore Corp., Bedford, MA) having a resistivity of 18.2 M Ù-cm.   All plastic used was disposed of after one use (pipette tips, micropipettes, and syringes).

2.2 Chemical Reagents

Unless otherwise specified, all chemicals used in this study were Analytical Reagent (AR) grade. Dilute 0.6 M HCl (Mallinckrodt, Inc., Paris, KY) and 0.5 N NaOH (Fisher Scientific, Fairlawn, NJ) were used to adjust the pH. Sodium bicarbonate (A.C.S. grade, Fisher Scientific, Fairlawn, NJ) was used to buffer the test water. The oxidant stock solutions were made using the following chemicals: chlorine (37 % AR select HOCl, Mallinckrodt, Inc., Paris, KY), potassium permanganate (technical grade, Carus Chemical, Peru, Illinois), and oxygen (air). The chloride dioxide was prepared from sodium chlorite (Spectrum Chemical Mfg. Corp, Gardena, CT) and concentrated H_2SO_4 (95-98% purity, Fisher Scientific, Fairlawn, NJ) according to standard method 4500-ClO_2. The monochloramine stock solution was made using a Cl_2 stock solution (37 % AR select HOCl, Mallinckrodt, Inc., Paris, KY) and ammonium sulfate (($NH_4)_2SO_4$, Fisher Scientific, Fairlawn, NJ) to create a 3:1 ratio of Cl_2 to NH_4. The pH of the Cl_2 solution was adjusted to 9 before adding to the ($NH_4)_2SO_4$ solution. To combine the two solutions, the volumetric flask was placed into an ice bath. The ($NH_4)_2SO_4$ was placed into the volumetric and Cl_2 was slowly added under mixing conditions. The chlorine dioxide was made using standard method 4500-ClO_2. The Zobell Solution was prepared by adding 1.41 grams of potassium ferrocyanide ($K_4Fe(CN)_6$•$3H_2O$, Fisher Scientific, Fairlawn, NJ), 1.01 grams of potassium ferriccyanide ($K_3Fe(CN)_6$, Spectrum Chemical Mfg. Corp, Gardena, CT), and 7.46 grams of potassium chloride (KCl, A.C.S grade, Fisher Scientific, Fairlawn, NJ) into 1 liter of DI water.

2.3 Analytical methods

The pH of the test water was measured with a Hach Company (Loveland, CO) EC40 bench top pH/ISE meter (model 50125) and a Hach Company (Loveland, CO) combination pH electrode (Model 48600) with temperature corrections. The instrument was standardized daily using a two-point calibration with pH 7 and 10 standard solutions (Whatman, Hillsboro, OR). Dissolved oxygen (DO) was measured with a Hach Company (Loveland, CO) Model DO175 dissolved oxygen meter and a Model 50180 dissolved oxygen probe. Redox potential was measured with a Model 450 Corning pH/ion meter (Corning, NY), with Thermo-Orion platinum combination redox electrodes (Model 9678BN, Buerly, MA). The solid chemicals were weighed on an analytical balance (Ainsworth, Denver Instruments).

Concentration measurements for free chlorine and total chlorine were measured using a HACH DR/2010 Portable Datalogging Spectrophotometer (Loveland, CO). The chlorine dioxide was measured using a Palintest Micro 1000 Chlodioxmeter (Palintest Micro 1000, England) using 10 mL glass cuvettes (Palintest, England). Free and total chlorine were measured with a Hach DR/2000 spectrophotometer (Loveland, CO), using the DPD method (standard method 4500-Cl

G, Hach Company 1990). MCA and ammonia concentrations were measured using a HACH pocket colorimeter (as mg Cl_2/L or NH_4 –N mg/L, Loveland, CO). The concentrations of $KMnO_4$ were not measured. The ORP electrodes were stored in Zobell reference solution when not in use. The ORP electrodes were rinsed thoroughly with DI water before each use. Additional cleanings/applications performed when needed and in accordance with the manufacturer's instructions.

2.4 ORP Measurement Experiments

To obtain the ORP data, simple bench-scale tests were performed in a 1-L glass reactor (Ace Glass, Vineland, NJ) with a plexiglass paddle (one 0.75-inch radius blade) continuously stirring the test solutions at 20 RPM (G=3.5 sec^{-1}). The tests were conducted in a weak carbonate buffered (DIC = 5 mg C/L) in double deionized (DDI) water which was prepared by passing distilled water through a Milli-Q Plus© cartridge deionized water system (Millipore Corp., Bedford, MA), having a resistivity $\exists$ 18.2 MΣ. cm. The pH was regulated and maintained at 7, 8, or 9 by a computerized acid and base titration system using Multi_T version 2.0 software (Jensen systems, Germany). The pH was adjusted using 0.6 N HCl and 0.5 N NaOH. The ORP of free chlorine, monochloramine, potassium permanganate, chlorine dioxide, and oxygen solutions were determined at each pH value. Two platinum-Ag/AgCl ORP electrodes were used to measure the ORP. These measurements were recorded every 100 seconds. In addition, at every 200 seconds a small increment [ranging from 0.1 mL and 2 mL at a time] of oxidant was added to the water until electrodes were stabilized. For the experiments using oxygen, the test water was purged of oxygen and then stirred until the water was saturated with air (DO $\approx$ 8 mg/L). Each test was run until the ORP stabilized. All ORP measurements were made in duplicate (two electrodes) to examine measurement reliability and reproducibility issues. All ORP measurements were reported in units of volts to standard hydrogen potential values (E_H).

3.0 RESULTS AND DISCUSSION

3.1 Dissolved Oxygen

The impact of dissolved oxygen concentration on the E_H (calculated from the measured ORP) of carbonate buffered water (DIC = 5 mg C/L, 23°C) was determined in duplicate at pH 7, 8, and 9. The initial E_H of the pH 7 water was approximately 0.421 V (0.46 mg O_2/L) and increased steadily with increasing dissolved oxygen concentration to 0.582 V (Table 2) as the dissolved oxygen concentration reached saturation (approximately 8 mg/L). Similar E_H trends with increasing dissolved oxygen concentration were observed in pH 8 and 9 waters however the magnitude decreased with increasing pH. Final E_H values were 0.551 V (7.83 mg O_2/L) and 0.508 V (8.07 mg O_2/L) for pH 8 and 9, respectively.

Large variations in ORP measurements were observed between the two electrodes at all pH values. The degree of variation decreased with increasing pH from an average of 0.059 V at pH 7 to 0.024 V at pH 8 (Table 3). The maximum variability was observed at low dissolved oxygen levels (<1 mg/L) and maximum differences were 0.094, 0.048, and 0.033 V at pH 7, 8, and 9, respectively.

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TABLE 2. Maximum E_H values (Volts) as a function of pH and oxidant type
(DIC = 5 mg C/L, 23^oC).

Oxidant	pH 7	pH 8	pH 9
Oxygen	0.582	0.552	0.508
Monochloramine	0.806	0.716	0.660
Potassium permanganate	0.812	0.795	0.672
Chlorine dioxide	0.980	0.943	0.912
Chlorine	1.020	0.922	0.769

3.2 Monochloramine

The effect of monochloramine (MCA) concentration on ORP as a function of pH is shown in Figure 1. The initial E_H of the pH 7 water was approximately 0.445 V before MCA was added (close to saturated dissolved oxygen concentration). E_H increased rapidly with increasing MCA dose up to approximately 1.5 mg Cl_2/L. Increasing the MCA concentration beyond 1.5 mg Cl_2/L had little additional impact on E_H which approached a maximum value of approximately 0.806 V by a concentration of 3.5 mg/L (Table 2). The E_H trends at pH 8 and 9 as a function of MCA dose were nearly parallel to the pH 7 trend. The magnitude of the E_H trends and ultimate maximum stabilization values decreased with increasing pH to 0.716 V and 0.660 V at pH 8 and 9, respectively.

The average variability in replicate ORP measurements with separate increased with increasing pH from 0.011 to 0.048, and 0.047 V at pH 7, 8, and 9, respectively. The maximum variation between the two electrode measurements increased to 0.018, 0.072, and 0.071 V at pH 7, 8, and 9.
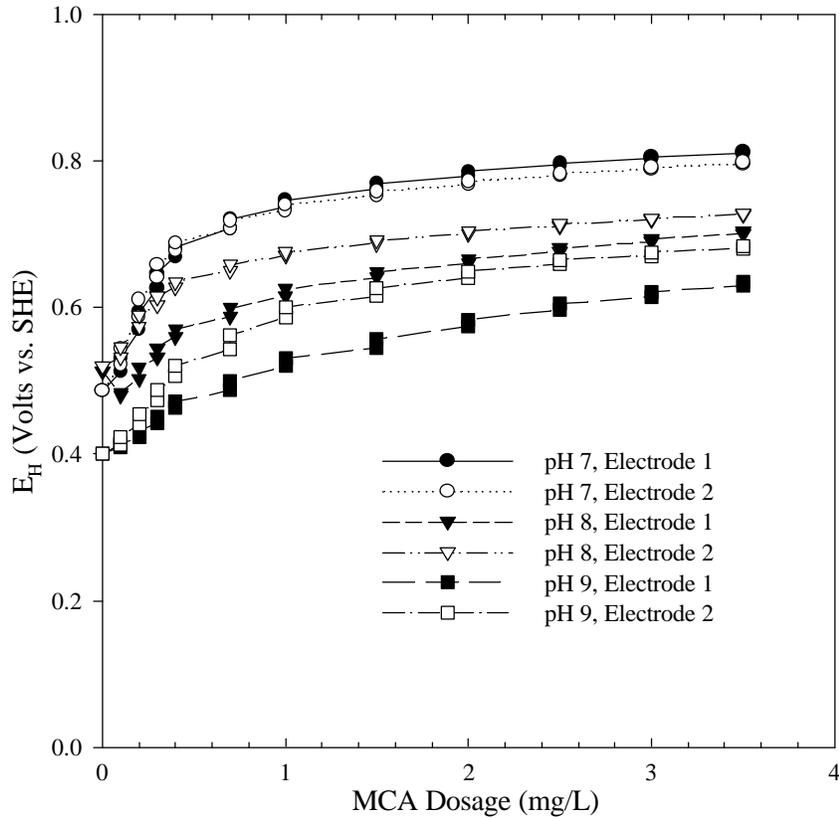
FIGURE 1. The effect of monochloramine concentration and pH on E_H (5 mg C/L, 23°C).

3.3 Potassium Permanganate

The effect of potassium permanganate concentration on E_H was similar to MCA E_H trends in magnitude. The initial E_H of the pH 7 water was approximately 0.619 V before $KMnO_4$ was added (close to saturated dissolved oxygen concentration). E_H increased rapidly with increasing $KMnO_4$ concentration up to approximately 0.6 mg $KMnO_4$/L. Increasing $KMnO_4$ concentration beyond 0.6 mg/L had little additional effect on E_H (not shown). The maximum E_H value reached approximately 0.812 V by a concentration of 3.2 mg $KMnO_4$/L. The E_H trends at pH 8 and 9 as a function of $KMnO_4$ concentration were nearly parallel to pH 7 trends. The magnitude of the trends and ultimate stabilization values decreased with increasing pH to 0.795 V at pH 8 and 0.672 at pH 9 (Table 2).

The average variability in replicate ORP measurements increased with increasing pH from 0.068, 0.050, and 0.073 V at pH 7, 8, and 9, respectively (Table 3). The maximum variation between the two electrode measurements increased to 0.083, 0.081, and 0.121 V at pH 7, 8, and 9.

3.4 Chlorine dioxide

The impact of chlorine dioxide dose on the E_H of carbonate buffered water (DIC = 5 mg C/L, 23°C) was determined in duplicate at pH 7, 8, and 9 (Figure 2). The initial E_H of the pH 7 water was approximately 0.445 V before chlorine dioxide was added (saturated dissolved oxygen concentration). E_H increased rapidly with increasing chlorine dioxide concentration, up to approximately 0.3 mg ClO_2/L. Increasing chlorine concentration beyond 0.3 mg ClO_2/L, had little additional impact on E_H. The E_H approached a maximum value of approximately 1.0 V by a concentration of 0.6 mg ClO_2/L. The E_H trends at pH 8 and 9 as a function of chlorine dose were nearly parallel to pH 7 trends. The magnitude of the trends and ultimate stabilization values decreased with increasing pH to 0.943 V and 0.912 V at pH 8 and 9, respectively.

The average variability in replicate ORP measurements increased with increasing pH from 0.050, 0.078, and 0.112 mV at pH 7, 8, and 9, respectively (Table 3). The maximum variation between the two electrode measurements increased to 0.079, 0.114, and 0.218 V at pH 7, 8, and 9.
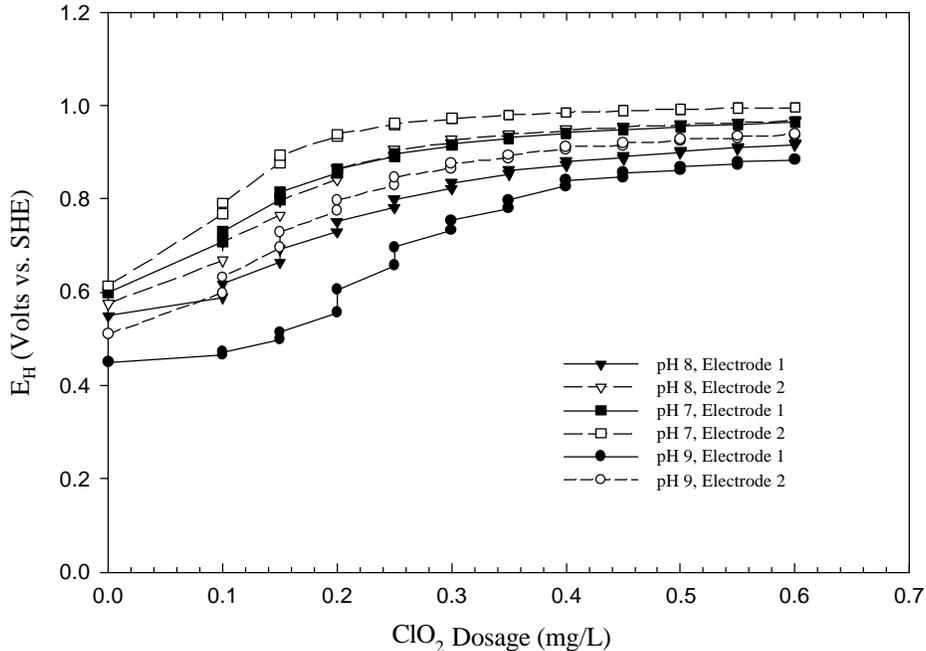

FIGURE 2. The effect of chlorine dioxide concentration and pH on E_H (5 mg C/L, 23°C).

3.5 Chlorine

The chlorine dose impact on the E_H (calculated from the measured ORP) of carbonate buffered water (DIC = 5 mg C/L, 23°C) was determined in duplicate at pH 7, 8, and 9 (Figure 3). The initial E_H of the pH 7 water was approximately 0.445 V before chlorine was added (saturated dissolved oxygen concentration). E_H increased rapidly with increasing chlorine concentration up to approximately 0.6 mg Cl_2/L. Additional increase in E_H beyond a concentration of 0.6 mg Cl_2/L was minimal and approached a maximum value of approximately 1.0 V by as concentration of 3.2 mg Cl_2/L. The E_H trends at pH 8 and 9 as a function of chlorine concentration were nearly

parallel to pH 7 trends. The magnitude of the trends and ultimate stabilization values decreased with increasing pH to 0.922 V and 0.769 V, respectively.

The average variability in replicate ORP measurements increased with increasing pH from 0.025, 0.023, and 0.054 V at pH 7, 8, and 9, respectively (Table 3). The maximum variation between the two electrode measurements increased to 0.067, 0.072, and 0.094 V at pH 7, 8, and 9.
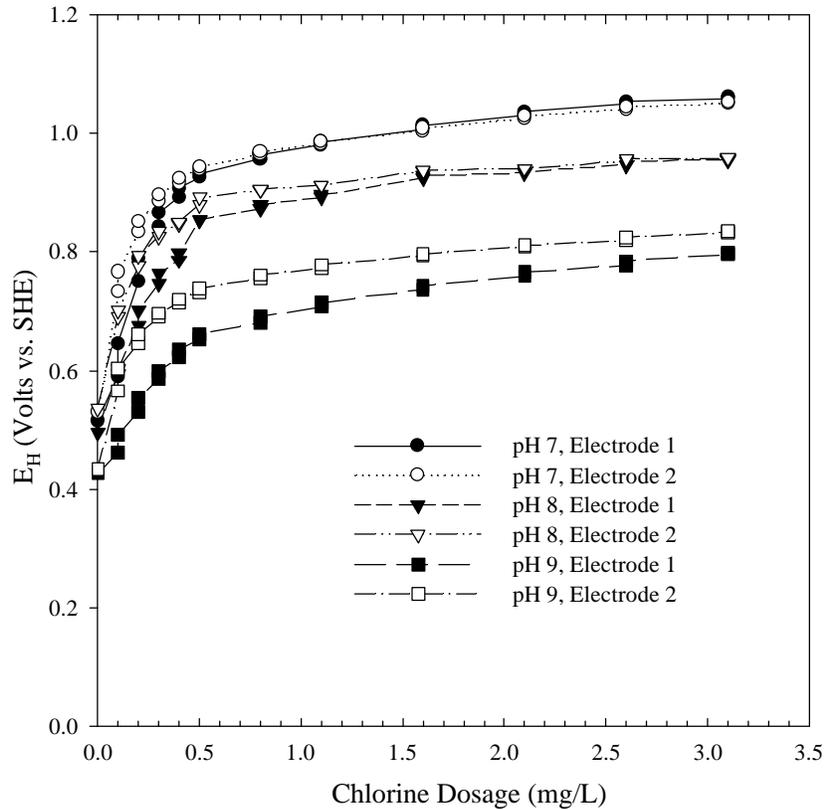

FIGURE 3. The effect of chlorine concentration and pH on E_H (5 mg C/L, 23°C)**.**

3.7 Effect of Oxidant Type on ORP

The ORP of all oxidants in water as a function of concentration are graphically compared at pH 8 in Figure 4. In general, the trends in E_H with increasing oxidant concentration were similar for all oxidants tested; steep E_H increases were observed at low concentrations followed by tendency to level off at higher concentrations. Final E_H values of the oxidant solutions ranked from highest to lowest as follows: $ClO_2 > Cl_2 > KMnO_4 > MCA > O_2$ (Table 2). Chlorine dioxide and free chlorine had similar E_H values (only differed by 0.21 V) while obvious differences between other oxidants were observed.
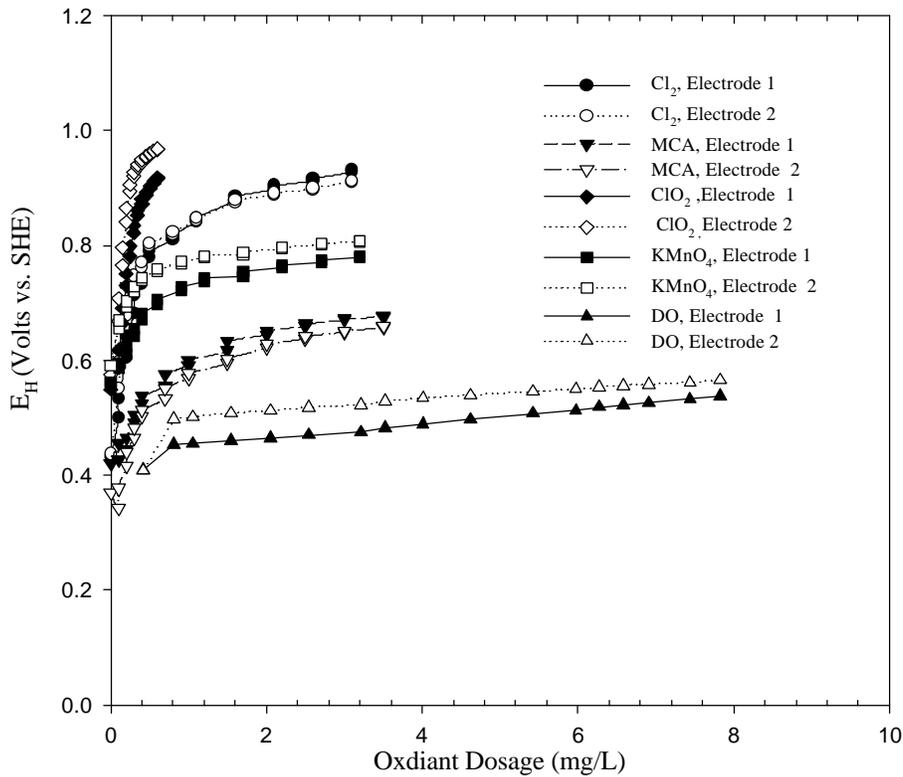
FIGURE 4. The effect of oxidant type on E_H (5 mg C/L, 23°C, pH 8).

The relative strengths of the oxidants in water were the same at pH 9 (Table 2). At pH 7, the relative strengths were also the same with the exception that chlorine was higher than chlorine dioxide (Table 2).

Increasing the pH caused the E_H of all oxidant containing waters to decrease. The degree of decrease was dependent on oxidant type. Chlorine dioxide was least impacted by changing pH only decreasing by 0.068 V between pH 7 and 9. The decrease was similar to the drop in the oxygen system which only dropped by 0.074 V. MCA and permanganate were similar dropping by 0.146 and 0.140 V, respectively between pH 7 and 9. Chlorine was most greatly impacted by pH dropping by 0.251 V between pH 7 and 9.

3.8 Measured Electrode Variability

Tables 3 and 4 show the variation between measurements of two electrodes reported as the average variation (Equation 5) and percent difference (Equation 6) in E_H measurements between the two electrodes as a function of pH and oxidant type.

$$A_V = \frac{\sum M_{ORP1} + M_{ORP2}}{N_{ORP}} \qquad [5]$$

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$$\% D = \frac{A_V}{A_R} \times 100 \qquad [6]$$

A_v is the average variation in ORP readings for a given pH, A_R is the average final ORP reading at stabilization between the two electrodes, M_{ORP1} and M_{ORP2} are the ORP measurements from electrode 1 and 2, N_{ORP} us the number of measurements taken for a given pH range, and %D is the percent difference in ORP readings.

Several trends were observed. With the exception of oxygen and permanganate, replicate electrode measurement variability increased with increasing pH or decreasing ORP. The reverse trend was found in the oxygen system (variability decreased with increasing pH) and the lowest variability in the permanganate system was at pH 8. The greatest variability was observed in the chlorine dioxide system.

TABLE 3. Average variation, A_V, in E_H (based on ORP measurements made with two electrodes, (Equation 5) as a function of pH and oxidant type (DIC = 5 mg C/L, 23 ^{o}C).

Oxidant	pH 7	pH 8	pH 9
Oxygen	0.059	0.038	0.0236
Monochloramine	0.011	0.048	0.047
Potassium permanganate	0.068	0.050	0.073
Chlorine dioxide	0.050	0.078	0.112
Chlorine	0.025	0.024	0.055

TABLE 4. The variation in E_H (ORP measurements made with two electrodes) expressed as a percentage, % (Equation 6), as a function of pH and oxidant type (DIC = 5 mg C/L, 23 ^{o}C).

Oxidant	pH 7	pH 8	pH 9
Oxygen	10.2	6.9	4.6
Monochloramine	1.3	6.7	7.1
Potassium permanganate	8.4	6.3	10.8
Chlorine dioxide	5.1	8.2	12.3
Chlorine	2.5	2.6	7.1

3.8 Electrode Reproducibility and Consistency/Electrode Maintenance

Electrode consistency is a very important aspect in obtaining accurate, reproducible and comparable measurements. During this study, both electrodes' readings were within ± 0.0003 V of each other when placed in the standard Zobell solution suggesting they responded in a similar manner. However, when taking readings during the experiments, the two electrodes often differed significantly (as high as 217.7 mV). The differences in readings could possibly be explained by the redox chemistry of each system, slow kinetics, electrode condition, and other limitations. In addition, redox electrodes cannot be calibrated over a large redox potential range. Zobell solution acts as a measurement to ensure the probes are reading the same ORP values [3,

4]. Additional maintenance and cleaning of the probes may be able to reduce the large variation in the readings. Additionally, probe contamination or precipitation formation may have caused variation in the measurements as well.

4.0 CONCLUSIONS

This research provides an initial step to understanding and interpreting ORP measurements in drinking waters. The results may eventually lead to greater realization of the use of ORP as a tool to monitor drinking water processes such as disinfection effectiveness monitoring or drinking water distribution system corrosion monitoring. Additional investigation is needed to link the relationships of these ORP measurements to natural water systems.

5.0 ACKNOWLEDGMENTS

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