Oxidation-reduction (redox) reactions can affect drinking water treatment and distribution in significant ways. Measurements of oxidation-reduction potential (ORP) in water reflect the tendency of major constituents in the water to accept or lose electrons. Although ORP measurements are valuable and can provide useful information toward protecting public health, they are not widely undertaken by the drinking water community for a variety of reasons. The objective of this research was to determine the effect of five oxidants commonly used in drinking water treatment as well as the effect of pH on measured ORP. Results showed that the ORP of each oxidant system increased with increasing oxidant concentration to a maximum. The ORP also decreased with increasing pH. Water treated with chlorine and chlorine dioxide had the greatest ORP followed by water containing monochloramine and permanganate and water containing only oxygen. Duplicate ORP measurements revealed some inconsistencies with redox electrode measurements.

**Keywords:** chlorine, chlorine dioxide, monochloramine, oxidants, oxidation-reduction potential

Oxidation and reduction reactions control many chemical and biochemical processes in nature and in engineered systems such as water treatment and distribution operations. Redox potential (also referred to as reduction potential, oxidation-reduction potential, or ORP) refers to the tendency of water’s constituents to gain or lose electrons. Oxidation involves a loss of electrons, and reduction involves a gain of electrons. The ORP of drinking water is controlled by the presence of major constituents such as iron (Fe), chlorine (Cl₂), and oxygen (O₂). Therefore, ORP measurements can provide water utility operators with useful water quality and process information. For example, ORP measurements indicate the presence and concentration of a disinfectant, the tendency for corrosion of distribution system materials, and conditions that support biofilm growth and iron and manganese removal.

Measuring the ORP of water is a simple task that requires only well-established and readily available methods (Carlson, 1991; Grundl & Macalady, 1989; Bricker, 1982; Victorin et al, 1972; Lund, 1965; Ives & Hills, 1961). Despite the value and availability of the technology, ORP measurements are not widely or routinely performed by drinking water utilities for numerous reasons, including electrode reliability issues, the lack of a regulatory requirement, and, perhaps most important, the absence of a reference as to what the measurements should be for a given water quality. Very little research has been reported on the effect of pH, oxidant type, and oxidant concentration on the ORP of water on the basis of actual measurements. The objective of this study was to measure the ORP of water over a range of pH values and a range of concentrations of five oxidants commonly used in water treatment: Cl₂, monochloramine (MCA), chlorine dioxide (ClO₂), potassium permanganate (KMnO₄), and dissolved oxygen (DO). Although ozone (O₃) is another oxidant used in drinking water applications, an O₃ generator was not available to allow the ORP of water containing O₃ to be evaluated in this research. The study’s results will serve as a useful reference for water utilities and engineers in predicting anticipated field ORP measurements.

**BACKGROUND**

Redox reactions describe the transfer of electrons between atoms, molecules, or ions. The ORP is the measurement of the electromotive force created when an oxidant or reductant is present in water. Oxidation and reduction reactions occur simultaneously, and together they make up an electrochemical, or redox, couple. The oxidation reaction takes place at the anode of an electrochemical cell (Sigg, 2000; Stumm & Morgan, 1970) and is where a species loses electrons (referred to as the reductant). Reduction takes place at the cathode of the electrochemical cell and is where a species accepts electrons (referred to as the oxidant). Important redox couples in drinking water include the arsenic couples As(III)–As(V), the iron couples Fe(II)–Fe(III), the manganese couples Mn(II)–Mn(IV), and the lead couples Pb(II)–Pb(IV). The ORP of a half-cell potential is described by the Nernst equation (Eq 1):

\[ E_h = E_h^o - \frac{RT}{nF} \log Q \]

1Black & Veatch, Centennial, Colo.
2US Environmental Protection Agency, Cincinnati, Ohio
in which \( E_b \) is the half-reaction electrode potential (measured in millivolts), \( E^0_b \) is the standard half-reaction potential relative to that of hydrogen (also measured in millivolts), \( R \) is the universal gas constant (8.314 J/mol K), \( T \) is the temperature (measured in degrees kelvin), \( F \) is the Faraday constant (96485 C/mol), \( n \) is the number of electrons transferred in the reaction, and \( Q \) is the reaction quotient (activity of the reductant divided by reactivity of the oxidant).

**ORP measurements.** ORP measurements are similar to pH measurements and are defined by the Nernst equation. ORP measurements are typically made using platinum silver–silver chloride (Ag–AgCl) electrodes, but a variety of other probes are commercially available. ORP measurements are determined between the inert electrode, usually platinum, in contact with a redox couple in solution and a reference electrode, such as a standard hydrogen electrode or Ag–AgCl reference electrode. The platinum (or other inert material) allows the electrons to be transferred between the oxidized and reduced species of the redox couple through the electrode interface. The electrode does not contribute to this interaction, making it a pure measurement of the electron transfer of the species (Peiffer, 2000). ORP measurements are often standardized to compare measured values with the work of others or with references based on fundamental chemistry relationships. The standard hydrogen electrode is the reference from which standard redox potential is reported, and the corresponding ORP measurement is defined as the \( E_b \). If a standard hydrogen reference electrode is used to make ORP measurements, the \( E^0_b \) in the Nernst equation is zero and the \( E_b \) is measured directly. ORP measurements, however, are rarely made using a standard hydrogen electrode, and ORP measurements (\( E_{\text{measured}} \) mV) using commercially available electrodes can be converted to \( E_b \) by means of a reference electrode material-specific conversion factor (\( E_{\text{reference}} \) mV) provided by the manufacturer or found in reference textbooks (Eq 2):

\[
E_{\text{measured}} = E_b - E_{\text{reference}}
\]

Water quality influences ORP measurements. Temperature, for example, directly affects ORP, as described in the Nernst equation, and so does pH when hydrogen ion is part of the redox reaction. Temperature and ionic strength can affect the rate of electrode response (decreasing temperature or ionic strength results in a decrease in electrode response). Maintenance and care of ORP electrodes are critical in making meaningful ORP measurements. ORP electrodes are not calibrated with a regression plot established from a set of standards as is the case for a pH probe. Typically, the electrodes are placed in ZoBell’s solution, a very concentrated solution that has a specific ORP with a variance of < 0.0001 V (Standard Methods, 1995). ZoBell’s solution consists of a mixture of potassium chloride (KCl), potassium ferrocyanide + water \([K_{4}Fe(CN)_{6}] + H_{2}O\), and potassium ferricyanide \([K_{4}Fe(CN)_{6}]\). This approach simply provides an indication of the electrode’s functionality, which is necessary to ensure its accuracy.

**Importance of ORP in aqueous systems.** Because redox reactions describe chemical and biological systems, they are especially relevant to drinking water treatment. Reductants that occur naturally in water include Fe and Mn in the +2 oxidation state, whereas \( O_2 \) is a naturally occurring oxidant. Common oxidants used in drinking water treatment for microbial disinfection and oxidation of inorganic and organic contaminants include free chlorine (hypochlorous acid \([HOCl]\) and hypochlorite ion \([OCl^-]\)), MCA, and \( O_3 \). Table 1 shows the \( E_b \) of common oxidants used in drinking water treatment in acidic and basic conditions (25°C).

Water quality parameters such as pH and temperature greatly affect the ORP of an oxidant. Chlorine, for example, dissociates to hypochlorous acid and hypochlorite ions, with the relative concentrations of each dependent on pH. Table 1 shows that for more effective disinfection and oxidation, hypochlorous acid as the dominant species in water is desirable because of its higher \( E_b \).

The type and amount of reductants and oxidants in a water system directly affect the ORP and can greatly change the water quality of an aqueous system. \( E_b \)-pH diagrams for particular species of interest can be useful in examining the effect of \( E_b \) and pH on the distribution of chemical species of interest. These diagrams, derived from fundamental chemistry relationships and experimentally developed parameters, are well-accepted and frequently used by engineers and scientists. The information contained within \( E_b \)-pH diagrams does not take into account kinetic limitations and should be interpreted accordingly.

\( E_b \)-pH diagrams are used to predict the oxidation state and speciation of chemical constituents found in water. The information gained from \( E_b \)-pH diagrams by utility staff, engineers, and other drinking water professionals can influence the type of water treatment techniques adopted and help predict the quality of water in the distribution system. One of the most important examples of the relationship between redox reactions and water quality in the distribution system is the corrosion of pipe networks. Corrosion affects the amount of metal released into

| TABLE 1 | Standard electrode potential for some common oxidants used in drinking water treatment* under standard conditions (1 atm and 25°C) |
|---|---|---|
| Oxidant | Reduction half-reaction | \( E^0_b \) Volts |
| Chlorine dioxide | \( ClO_2 + 2H_2O + 5e^- \rightarrow Cl^- + 4OH^- \) | 1.71 |
| Chlorine | \( Cl_2(g) + 2e^- \rightarrow 2Cl^- \) | 1.36 |
| Hypochlorous acid | \( HOCl + H^+ + 2e^- \rightarrow 2Cl^- \) | 1.49 |
| Hypochlorite | \( ClO^- + H_2O \rightarrow Cl^- + OH^- \) | 0.9 |
| Monochloramine (basic) | \( NH_2Cl + H_2O + 4e^- \rightarrow 2Cl^- + NH_3 + 2OH^- \) | 0.75 |
| Dichloramine (basic) | \( NHCl_2 + 3H_2O + 4e^- \rightarrow 2Cl^- \) | 0.79 |
| Monochloramine (acidic) | \( NH_2Cl + H^+ + 2e^- \rightarrow 2Cl^- + NH_3^+ \) | 1.4 |
| Dichloramine (acidic) | \( NHCl_2 + 3H^+ + 4e^- \rightarrow 2Cl^- + NH_3^+ \) | 1.34 |
| Permanganate (basic) | \( MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \) | 0.58 |
| Permanganate (acidic) | \( MnO_4^- + 4H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \) | 1.68 |
| Permanganate (acetic) | \( MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \) | 1.49 |
| Oxygen (basic) | \( O_2 + 2H^+ + 4e^- \rightarrow 4OH^- \) | 1.23 |
| Oxygen (acidic) | \( O_2 + 2H^+ + 4e^- \rightarrow 2H_2O \) | 0.4 |

*Glaze, 1990

\( E^0_b \)—standard half-reaction potential relative to that of hydrogen
treated drinking water and can ultimately lead to pipe failure. In addition, corrosion by-products can harbor biofilms and cause head loss buildup leading to increased pumping costs. ORP measurements in drinking water distribution systems reflect the tendency of plumbing materials to corrode. Furthermore, ORP has a direct effect on the oxidation state and mineralogy of associated metal corrosion by-products, thereby influencing metal solubility.

The most recently recognized and perhaps most important drinking water corrosion relationship between ORP and metal geochemistry is associated with lead. Both Pb(II) (typically lead carbonates) and Pb(IV) (lead dioxide, or PbO2) corrosion by-products have been identified in drinking water distribution systems (Schock et al, 2005; Schock & Giani, 2004; Schock et al, 1996). The significance is that PbO2 is far less soluble than Pb(II) carbonate or hydroxycarbonate in water, and transformations in the lead oxidation state can readily occur with changes in ORP. A highly publicized, widespread outbreak of elevated lead concentrations in the Washington, D.C., distribution system (Renner, 2004) has been attributed to solubility difference and oxidation state transformations following the application of a chemical disinfectant. Examination of an $E_h$–pH diagram for lead shows that PbO2 is stable only at very high $E_h$ values starting near the upper stability boundary for water (Figure 1). An understanding of the link between ORP measurement, $E_h$–pH relationships, and geochemistry in drinking water distribution systems can help water professionals control corrosion and metal concentrations in drinking water and better protect public health.

**ORP measurements in drinking water and wastewater applications.** ORP measurements can be a useful process control tool in drinking water and wastewater applications including disinfection, biological treatment, anaerobic digestion, determination of whether groundwater is influenced by surface water, protection of membranes from contact with chlorinate, hydrogen sulfide treatment, biological nutrient reduction, and corrosion control. Redox monitoring devices have been tested, installed, and used

---

**FIGURE 1**

$E_h$–pH diagram for a lead–water–carbonate system

<table>
<thead>
<tr>
<th>pH</th>
<th>$E_h$—Vols Versus SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Water oxidized (partial pressure of $O_2$ = 0.21 atm)</td>
</tr>
<tr>
<td>10</td>
<td>Water reduced (partial pressure of $O_2$ = 1 atm)</td>
</tr>
</tbody>
</table>

$H_2CO_3^*$—carbonic acid, $HCO_3^*$—bicarbonate ion, $O_2$—oxygen, $Pb^{2+}$—lead ion in the +2 oxidation state, $PbCO_3^0$—aqueous lead carbonate, $PbO_2(s)$—lead oxide, $Pb(OH)_2^0$—lead hydroxide, SHE—standard hydrogen electrode

The following formulas have no designated chemical names: $CO_3^{2-}$, $Pb(CO_3)^{2-}$, $PbO_3^{2-}$, $Pb(OH)_3^{2-}$, $Pb(OH)^{2-}$, $Pb(s)$.

Lead species = 0.015 mg Pb/L; dissolved inorganic carbon = 10 mg C/L; ionic strength = 0; temperature = 25°C

*Lytle et al, 2009
to monitor and chemically dose water on a daily basis in various treatment plants in the United States. These monitoring systems were made possible by various studies that investigated the correlation of ORP and microorganism kill rates.

The idea of using ORP measurements as a means of evaluating disinfection efficiency has been considered. Victorin et al. (1972) discovered that *Escherichia coli* kill rates in chlorinated water were more strongly correlated with ORP measurements than with chlorine residual measurements. Lund (1965) found the same correlation using the poliovirus in sewage and concluded that the time required to inactivate the virus was related to millivolt potential. Carlson (1991) conducted a study using chlorine and *E. coli* and found that the intensity of the *E*ₚ (650–700 mV) was responsible for killing the microorganisms. Carlson (1991) also examined the effect of colloidal concentrations on *E. coli* kill rates. Colloids were found to interfere with killing the microorganisms; however, the use of flocculation and filtration as part of the treatment process can eliminate this problem (Carlson, 1991). Carlson’s work ultimately defined the rate of inactivation as a function of ORP and pH without dependence on the chlorine concentration.

On the basis of these studies and many others, redox systems have been developed and implemented in wastewater treatment plants to monitor microbial kill and chlorine concentrations in order to ensure regulatory compliance. For example, the Guelph (Ont.) Wastewater Treatment Plant had difficulty monitoring and maintaining accurate chlorine residuals and consistently had high microorganism counts even in the presence of very high concentrations of chlorine. Installation of a redox system that regulated the oxidant dosage saved the plant $2,000 per month (Kiser, 1992). Similar results were observed at plants in the United States, along with reduced damage caused by corrosion and reduced biofouling (Kim & Hensley, 1997; Kim & Strand, 1997; Kiser, 1992).

**Limitations of ORP measurements.** Despite the success of ORP measurement devices, limitations to this technology exist and are addressed in the literature (Lindberg & Runnells, 1984; Whitfield, 1974; Stumm & Morgan, 1970). The limitations of electrodes in measuring ORP in natural water systems have been investigated by comparing measured ORP values with theoretical ORP calculations based on the Nernst equation (Kölling, 2000). These measured results and theoretical calculations typically differed greatly (Kölling, 2000; Lindberg & Runnells, 1984). Lindberg & Runnells measured the ORP of several different redox couples in a large number of groundwater supplies and then calculated the theoretical ORP for each couple, but they found no correlation between the electrode measure and the calculated measurement.

One reason for this discrepancy in measured and calculated data may be instrument contamination, especially of key probe components such as the junction (Galster, 2000). In addition, platinum oxide or other materials may build up or adsorb to the surface of the electrode, compromising its ability to measure ORP. This buildup or adsorption on the electrode’s surface can delay the exchange current between the redox couple and the electrode, impairing accuracy (Galster, 2000). The redox couples within the water matrix can also contribute to the inaccuracy of ORP measurements in natural water sources. A natural body of water typically contains many different redox couples. Redox-sensitive couples—*O₂*, *H₂O*, nitrate ion (*NO₃⁻*)—nitrogen gas (*N₂*), *NO₃⁻*–ammonium (*NH₄⁺*), sulfate—hydroxysulfide ion, and carbon dioxide—methane—often react slowly by microbial catalysis (Sigg, 2000). Typically, redox couples with very slow or very fast reaction rates cannot be accurately measured using an electrode because a sufficient exchange current cannot occur or cannot remain constant (Sigg, 2000). Mixed potentials can also interfere with obtaining representative ORP measurements in natural water systems (Galster, 2000). A mixed potential is defined as a galvanic potential lying between different redox potentials (Galster, 2000). Typically, this occurs when any or all redox couples in the water are irreversible; that is, they are unable to reach equilibrium (Sigg, 2000). The ideal conditions for ORP measurements occur in systems with reversible redox couples and relatively fast exchange current kinetics such as Fe(II)–Fe(III) under acidic conditions and ferrocyanide [Fe(CN)₆⁴⁺]–ferricyanide [Fe(CN)₆³⁻] (Sigg, 2000; Stumm & Morgan, 1970).

Other causes of ORP measurement issues include development of bubbles on the electrode tip, adherence of biofilm to the electrode surface, and the presence of other materials on the electrode surface (e.g., mineral deposits, oil and grease, organic matter). Solutions with low ionic strength and low temperature can also slow electrode response.

**Knowledge gap.** Despite the importance of redox relationships in drinking water applications and the amount of research dedicated to ORP measurement accuracy and usable monitoring devices, established ORP ranges for common oxidants in water are still somewhat uncertain. The experience of the authors is that many water treatment plant personnel are aware of ORP but do not fully understand the usefulness of the measurement. For example, ORP measurements could be a useful process control tool for manganese, iron, and arsenic removal; disinfection; and corrosion control. Water utility operators who have made ORP measurements or are currently doing so are often not clear on how to interpret the readings, are unable to sense an expected value for the quality of their water, and do not know whether the electrode is functioning properly. Therefore determining expected ORP ranges for water containing commonly used oxidants over a broad range of pH values would be a useful guide to many. Water utility staff could use such information as a check on the reliability of their field ORP measurements, gain confidence in the value of the measurement for identifying problems within the treatment plant and distribution system, and reduce public health risks.

**MATERIALS AND METHODS**

**Glassware and sampling materials.** All glassware used during these experiments was thoroughly rinsed in deionized water with a resistivity ≥ 18.2 MΩ-cm. All plastics (pipette tips, micropettes, and syringes) were disposed of after one use.

**Chemical reagents.** Unless otherwise specified, all chemicals used in this study were analytical reagent (AR) grade. Diluted 0.6M hydrochloric acid (HCl) and 0.5N sodium hydroxide
(NaOH) were used to adjust the pH. Sodium bicarbonate was used to buffer the test water. The oxidant stock solutions were made using the following chemicals: Cl₂ (37% AR select HOCl), KMnO₄ (technical grade), and O₂ (air). The ClO₂ was prepared from sodium chloride and concentrated sulfuric acid (95–98% purity) according to method 4500-ClO₂ (Standard Methods, 1995). The MCA stock solution was made using a Cl₂ stock solution (37% AR select HOCl) and ammonium sulfate [(NH₄)₂SO₄] to create a 3:1 ratio of Cl₂ to ammonium (NH₄). These solutions were formulated so that approximately equal volumes of the two, when combined, would produce the desired ratio of Cl₂ to nitrogen (N). The Cl₂ solution was adjusted to 9 pH before it was added to the (NH₄)₂SO₄ solution. To combine the two solutions, the volumetric flask was placed into an ice bath. The (NH₄)₂SO₄ was placed into the volumetric flask, and Cl₂ was slowly added under constant mixing conditions. The ClO₂ was made using method 4500-ClO₂ (Standard Methods, 1995). The ZoBell’s solution was prepared by adding 1.41 g K₄Fe(CN)₆ + 3 H₂O, 1.01 g K₃Fe(CN)₆, and 7.46 g KCl (American Chemical Society grade) to 1 L of deionized water.

**Analytical methods.** The pH of the test water was measured with a pH/ion-selective electrode meter² and a combination pH electrode.³ The instruments were standardized daily using a two-point calibration with pH 7 and 10 standard solutions. DO was measured with a DO meter and probe.⁴ ORP was measured with a pH/ion meter⁵ equipped with platinum combination redox electrodes.⁶ The solid chemicals were weighed on an analytical balance.

The concentrations of free and total chlorine were measured with a portable spectrophotometer,⁷ using method 4500-Cl G DPD (Standard Methods, 1995). ClO₂ was measured using a chloridoximeter⁸ and 10-mL glass cuvettes. MCA and ammonia (NH₃) concentrations were measured using a pocket colorimeter⁹ (as milligrams Cl₂ per litre or milligrams NH₄ as N per litre). KMnO₄ concentrations were not measured. The ORP electrodes were stored in ZoBell’s reference solution when not in use and were rinsed thoroughly with deionized water before each use. Additional cleanings were performed when needed and in accordance with the manufacturer’s instructions.

**ORP measurement experiments.** To obtain the ORP measurements, simple bench-scale tests were performed in a 1-L glass reactor with a clear acrylic paddle (one blade with a 0.75-in. radius) continuously stirring the test solutions at 20 rpm (G = 3.5/s; see the photograph on page E15). The tests were conducted in a weak carbonate buffer (dissolved inorganic carbon [DIC] = 5 mg/L C) prepared in double deionized water, which was made by passing distilled water through a deionized water system with a resistivity ≥ 18.2 MΩ-cm. The pH was regulated and maintained at 7, 8, or 9 using a computerized acid and base titration system.¹⁰ The pH was adjusted with 0.6M HCl and 0.5N NaOH. The calculated alkalinites for 5-mg/L C DIC water are 17, 21, and 22 mg/L calcium carbonate at pH 7, 8, and 9, respectively.

The ORP measurements of free chlorine, MCA, KMnO₄, ClO₂, and O₂ solutions were determined at each pH value using two platinum Ag–AgCl ORP electrodes and were recorded every 100 s. In addition, every 200 s, a small amount (0.1–2 mL) of oxidant was added to the water until the electrodes were stabilized. For the experiments using O₂, the test water was purged of O₂ and then stirred until the water was saturated with air (DO ≈ 8 mg/L). Each test was run until the ORP stabilized. All ORP measurements were made with two electrodes to allow measurement reliability and reproducibility to be examined. Measured ORP was converted to $E_b$ by adding $E_{ref}$ of 241 mV according to manufacturer specifications. Measurements were made at room temperature (23 ± 0.1°C).

**RESULTS**

**DO.** The effect of DO concentration on the $E_b$ (calculated from the measured ORP) of carbonate-buffered water (DIC = 5 mg/L C, temperature = 23°C) was determined at pH 7, 8, and 9 (Figure 2). The initial $E_b$ of the pH 7 water was approximately 421 mV (0.46 mg/L O₂), and it increased steadily with increasing DO concentration to 582 mV (Table 2) as the DO concentration reached saturation (approximately 8 mg/L). Similar $E_b$ trends with increasing DO concentration were observed in water at pH 8 and 9; however, the magnitude of the $E_b$ decreased with increasing pH. Final maximum $E_b$ values were 552 mV (7.83 mg/L O₂) and 508 mV (8.07 mg/L O₂) for water at pH 8 and 9, respectively (Table 2). $E_b$ values calculated from the Nernst equation were within 0.30, 5.2, and 9% in water at pH 7, 8, and 9, respectively (not shown). The discrepancies in measured
and calculated $E_h$ values increased with increasing pH, and the Nernst equation underpredicted measured values.

Relatively 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 59 mV at pH 7 to 24 mV at pH 8 (Table 3). Maximum variability was observed in water with low DO concentrations (< 1 mg/L), and maximum differences were 94, 48, and 33 mV in water at pH 7, 8, and 9, respectively. These variations may not seem significant; however, the problems associated with measuring water with high DO concentrations have been documented extensively in the literature (Sigg, 2000).

MCA. Chloramines include MCA, dichloramine, and trichloramine. These compounds, formed by reacting chlorine with NH$_3$, are used to disinfect finished drinking water, and their distribution depends heavily on pH and the ratio of NH$_3$ to chlorine. With a chlorine-to-NH$_3$ weight ratio of 3:1 at pH 7, MCA will be the dominant chloramine form, with the dichloramine fraction making up < 10% of the total chloramine concentration (calculations based on Jafvert & Valentine, 1992). At pH 8 and 9, MCA is the only form present. Because chloramines are weaker oxidants than chlorine (Table 1), they are generally used only for disinfection purposes (White, 1999; Glaze, 1990). Many utilities have started using MCA rather than chlorine to reduce trihalomethane (THM) concentrations in treated water. Reducing THMs is advantageous because they are carcinogens and are strictly regulated in drinking water (White, 1999; Glaze, 1990). Furthermore, chloramines have been shown to be more effective at penetrating biofilms (Pressman et al, 2012; Lee et al, 2011). However, biofilm control by either free chlorine or chloramines is limited and in some cases has been shown to be comparable in capability, particularly at similar $C \times T$ values (the disinfectant concentration, $C$, multiplied by time, $T$; Baribeau et al, 2005).

The effect of MCA concentration on $E_h$ as a function of pH is shown in Figure 3. The initial $E_h$ of the pH 7 water was approximately 445 mV before MCA was added (close to the saturated DO concentration). $E_h$ increased rapidly with increasing MCA dose up to approximately 1.5 mg/L Cl$_2$. Increasing the MCA concentration beyond 1.5 mg/L Cl$_2$ had little additional effect on $E_h$, which approached a maximum value of approximately 806 mV by a concentration of 3.5 mg/L Cl$_2$ (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 $E_h$ and maximum stabilization values decreased with increasing pH to 716 mV and 660 mV at pH 8 and 9, respectively (Table 2). $E_h$ values calculated from the Nernst equation were within 4.2, 8.5, and 9.4% at pH 7, 8, and 9, respectively (not shown). The discrepancies in measured and calculated $E_h$ values increased with increasing pH, and the Nernst equation overpredicted measured values.

The average variability in replicate ORP measurements increased from 11 to 48 and 47 mV at pH 7, 8, and 9, respectively (Table 3). The maximum variation between the two electrode measurements increased to 18, 72, and 71 mV at pH 7, 8, and 9, respectively.

Cl$_2$. Cl$_2$ is the most commonly used disinfectant in water treatment because of its ability to kill a variety of bacteria, protozoa, and viruses. It also has the ability to oxidize manganese, remove color, and provide a residual in the drinking water distribution system to prevent biofouling (White, 1999; Glaze, 1990). The speciation and the oxidizing power of Cl$_2$ are highly dependent on pH, concentration, and temperature. Under normal drinking water treatment conditions and neutral pH, chlorine disproportion-

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>pH 7</th>
<th>pH 8</th>
<th>pH 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>582</td>
<td>552</td>
<td>508</td>
</tr>
<tr>
<td>Monochloramine</td>
<td>806</td>
<td>716</td>
<td>660</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>812</td>
<td>795</td>
<td>672</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>980</td>
<td>943</td>
<td>912</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1020</td>
<td>922</td>
<td>769</td>
</tr>
</tbody>
</table>

$E_h$—half-reaction electrode potential (measured in millivolts)
Dissolved inorganic carbon = 5 mg/L C; temperature = 23°C

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>pH 7</th>
<th>pH 8</th>
<th>pH 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>59</td>
<td>38</td>
<td>23</td>
</tr>
<tr>
<td>Monochloramine</td>
<td>11</td>
<td>48</td>
<td>47</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>68</td>
<td>50</td>
<td>73</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>50</td>
<td>78</td>
<td>112</td>
</tr>
<tr>
<td>Chlorine</td>
<td>25</td>
<td>24</td>
<td>55</td>
</tr>
</tbody>
</table>

$E_h$—half-reaction electrode potential (measured in millivolts)
Dissolved inorganic carbon = 5 mg/L C; temperature = 23°C

To obtain the oxidation–reduction potential measurements, simple bench-scale tests were performed in a 1-litre glass reactor with a plexiglass paddle that continuously stirred the test solutions.
tionates to form HOCl, which partly dissociates to OCl\(^-\). This dissociation is important because HOCl has a much higher redox potential than OCl\(^-\) (1.49 versus 0.90). Despite its versatility, one of the major disadvantages of Cl\(_2\) is that it reacts with organic material to form THMs.

The effect of chlorine concentration and pH on \(E_h\) is shown in Figure 4. \(E_h\) increased rapidly with increasing free chlorine concentration up to approximately 0.6 mg/L Cl\(_2\) at pH 7. Additional increases in \(E_h\) beyond a concentration of 0.6 mg/L Cl\(_2\) were relatively small and approached a maximum value of approximately 1,020 mV at a concentration of 3.2 mg/L Cl\(_2\) (Table 2). The \(E_h\) trends as a function of chlorine concentration were nearly parallel at pH 7, 8, and 9. The magnitude of the trends and stabilization values decreased as pH increased to 922 and 769 mV at pH 8 and 9, respectively (Table 2). \(E_h\) values calculated from the Nernst equation were within 1.8, 7.3, and 18% at pH 7, 8, and 9, respectively (not shown). The discrepancies in measured and calculated \(E_h\) values increased with increasing pH, and the Nernst equation overpredicted measured values.

The average variability in duplicate ORP measurements increased with pH from 25, 24, and 55 mV at pH 7, 8, and 9, respectively (Table 3). The maximum variation between the two electrode measurements increased to 67, 72, and 94 mV at pH 7, 8, and 9, respectively.

**FIGURE 4** Effect of chlorine concentration and pH on \(E_h\)

\(E_h\) = half-reaction electrode potential (measured in millivolts), SHE = standard hydrogen electrode

Dissolved inorganic carbon = 5 mg/L C; temperature = 23°C

**FIGURE 3** Effect of monochloramine and pH and \(E_h\)

\(E_h\) = half-reaction electrode potential (measured in millivolts), SHE = standard hydrogen electrode

Dissolved inorganic carbon = 5 mg/L C; temperature = 23°C

**KMnO\(_4\)** KMnO\(_4\) is typically used in conjunction with some form of granular media because in combination they can remove a variety of inorganic materials including iron, manganese, and arsenic. Although considered a strong oxidant, KMnO\(_4\) is a poor disinfectant and when present imparts a pink-to-purple color to the water. It is typically used to reduce tastes and odors and biological growth within treatment plants, as well as to remove color, iron, and manganese (Glaze, 1990). The dose must be monitored to ensure that the water’s aesthetic quality is not compromised by a pink hue (Glaze, 1990). KMnO\(_4\) can also cause precipitation problems such as buildup on filters and formation of unknown by-products (Glaze, 1990).

The \(E_h\) trend for KMnO\(_4\) was similar to the \(E_h\) trends for MCA in terms of magnitude. The initial \(E_h\) of the pH 7 water was approximately 619 mV before KMnO\(_4\) was added (close to the saturated DO concentration). \(E_h\) increased rapidly with increasing KMnO\(_4\) concentration up to approximately 0.6 mg/L KMnO\(_4\). Increasing KMnO\(_4\) concentration beyond 0.6 mg/L had little additional effect on \(E_h\) (Figure 5). The maximum \(E_h\) value reached approximately 812 mV with a concentration of 3.2 mg/L KMnO\(_4\). The \(E_h\) trends in water at pH 8 and 9 as a function of KMnO\(_4\) concentration were nearly parallel to the trends in pH 7 water. The magnitude of the trends and ultimate stabilization values decreased as pH increased to 795 mV at pH 8 and 672 mV at pH 9 (Table 2). \(E_h\) values calculated from the Nernst equation were
within 0.91, 7.3, and 1.4% at pH 7, 8, and 9, respectively (not shown). The discrepancies in measured and calculated \( E_h \) values were not affected by pH, and the Nernst equation slightly underpredicted measured values.

The average variability in replicate ORP measurements increased with pH from 68, 50, and 73 mV at pH 7, 8, and 9, respectively (Table 3). The maximum variation between the two electrode measurements increased to 83, 81, and 121 mV at pH 7, 8, and 9, respectively.

\( \text{ClO}_2 \). Despite higher chemical costs and required on-site generation because of safety issues, \( \text{ClO}_2 \) can be used as a disinfectant to kill chlorine-resistant pathogens such as \textit{Giardia} and \textit{Cryptosporidium}. It is also able to oxidize iron and manganese and remove color. One major advantage of \( \text{ClO}_2 \) is that it rarely forms THMs (White, 1999; Glaze, 1990).

The effect of \( \text{ClO}_2 \) dose on the \( E_h \) of carbonate-buffered water (DIC = 5 mg/L C; temperature = 23°C) was determined in duplicate at pH 7, 8, and 9 (Figure 6). The initial \( E_h \) of the pH 7 water was approximately 445 mV before \( \text{ClO}_2 \) was added (at the saturated DO concentration). \( E_h \) increased rapidly with increasing \( \text{ClO}_2 \) concentration, up to approximately 0.3 mg/L \( \text{ClO}_2 \). Increasing the concentration beyond 0.3 mg/L \( \text{ClO}_2 \) had little additional effect on \( E_h \). The \( E_h \) approached a maximum value of approximately 1,000 mV with a concentration of 0.6 mg/L \( \text{ClO}_2 \). The \( E_h \) trends at pH 8 and 9 as a function of \( \text{ClO}_2 \) dose were nearly parallel to the trends in pH 7 water. The magnitude of the trends and ultimate stabilization values decreased with increasing pH to 943 mV and 912 mV at pH 8 and 9, respectively.

The average variability in replicate ORP measurements increased with pH from 50, 78, and 112 mV at pH 7, 8, and 9, respectively (Table 3). The maximum variation between the two electrode measurements increased to 79, 114, and 218 mV at pH 7, 8, and 9, respectively.

\textbf{Comparison of all oxidants.} Figure 7, which compares the \( E_h \) measurements for all studied oxidants at pH 8, shows that different oxidants produced different ORP readings, and Table 2 summarizes the maximum \( E_h \) values achieved. \( E_h \) observations were in agreement with expectations (Table 1). Oxidant strength in water decreased in order from highest to lowest with the use of \( \text{Cl}_2 \) (highest), \( \text{ClO}_2 \), \( \text{KMnO}_4 \), MCA, and DO (lowest) at pH 7. The order remained the same in water at pH 8 and 9, with the exception that \( \text{ClO}_2 \) and \( \text{Cl}_2 \) shifted positions because of the shift in chlorine species. For example, the maximum \( E_h \) values for \( \text{ClO}_2 \), \( \text{Cl}_2 \), \( \text{KMnO}_4 \), MCA, and DO at pH 8 were 943, 922, 795, 716, and 552 mV, respectively. The strength of all oxidants decreased with increasing pH, with \( \text{ClO}_2 \) and DO being least affected. Trends at pH 7 and 9 (not shown) were similar but shifted in magnitude, reflecting the pH effect already discussed. As noted, differences in measured ORP were in reasonable agreement with predictions based on the Nernst equation (Table 1).
Electrode measurement variability. Electrode consistency is an important factor for obtaining accurate, reproducible, and comparable measurements. During this study, the readings of both electrodes were within 0.1 mV of one another when they were placed in the standard ZoBell’s solution, suggesting that they responded in a similar manner. However, when readings were taken during the experiments, the two electrodes often differed significantly (by as much as 218 mV). These differences could possibly be explained by the redox chemistry of each system (i.e., reversible redox couples and inert couples), slow kinetics, electrode contamination, and other limitations. Additional maintenance and cleaning of the probes might be able to reduce the large variation in the readings.

Tables 3 and 4 show the variation between the measurements of two electrodes reported as the average variation (Eq 3) and percent difference (Eq 4) in $E_h$ values as a function of pH and oxidant type.

$$A_v = \frac{\sum (M_{ORP1} + M_{ORP2})}{N_{ORP}} \tag{3}$$

$$\%D = \frac{A_v}{A_R} \times 100 \tag{4}$$

in which $A_v$ = the average variation in $E_h$ for a given pH, $A_R$ = the average final $E_h$ of the two electrodes at stabilization, $M_{ORP1}$ = the $E_h$

![Figure 7: Effect of oxidant type on $E_h$](image)

**Legend:**
- Cl₂ electrode 1
- Cl₂ electrode 2
- ClO₂ electrode 1
- ClO₂ electrode 2
- MCA, electrode 1
- MCA, electrode 2
- KMnO₄, electrode 1
- KMnO₄, electrode 2
- DO, electrode 1
- DO, electrode 2

**Notes:**
- Cl₂—chlorine, ClO₂—chlorine dioxide, DO—dissolved oxygen,
- $E_h$—half-reaction electrode potential (measured in millivolts),
- KMnO₄—potassium permanganate, MCA—monochloramine,
- SHE—standard hydrogen electrode
- Dissolved inorganic carbon = 5 mg/L C; pH = 8; temperature = 23°C
determined from electrode 1, $M_{\text{ORP}2} = E_b$ determined from electrode 2, $N_{\text{ORP}} = \text{the number of measurements taken for a given pH range, and } \%D = \text{the percent difference in } E_b$ values.

Although this analysis is based on measurements from only two electrodes and is not a rigorous statistical assessment of ORP electrode variability, it provides a sense of the differences that can exist between electrodes presumed to be identical. Several trends were observed. With the exception of O$_2$ and KMnO$_4$, the variability of replicate electrode measurements increased with increasing pH or decreasing $E_b$. The reverse trend was observed in the O$_2$ system (i.e., variability decreased with increasing pH), and the lowest variability in the KMnO$_4$ system was at pH 8. The greatest variability was observed in the ClO$_2$ system.

Additionally, probe contamination or precipitation formation (see the photograph above) may have caused variation in the measurements. The red circle points out a possible example of probe interference.

This study could not determine whether the apparent clogging or precipitation formation was contributing to the variation in the readings. Clogging of the electrodes can cause kinetic issues and reading interferences. Additional measurements were taken in various natural water systems to compare the bench readings with field readings to verify that the $E_b$ readings were comparable.

**Recommendations for electrode maintenance and use.** Many problems can arise when ORP is measured. There are a variety of troubleshooting methods, ranging from electrode cleaning (minor to aggressive) to electrode replacement options. During this study, the electrodes were cleaned once by flushing the filling solution out of the electrodes (according to manufacturer’s instructions) and replacing it with new filling solution. The probes were allowed to stabilize for 24 h after the cleaning. Despite the new filling solution, variations in measurements were observed. No alternative aggressive cleaning methods were undertaken. Recommendations for electrode cleaning can be found in *Standard Methods* (1995), and manufacturers also provide recommended procedures for cleaning electrodes. Other troubleshooting options, such as checking faulty connections between the meter and the electrodes and frequent refilling of the reference electrode solution, are also recommended (Standard Methods, 1995). The rule of thumb is that the functionality of the electrodes can be restored so long as there is no physical or chemical contamination of the reference solution and no electrical problem with the system as a whole.

**CONCLUSIONS**

This research provides an important step toward understanding and interpreting ORP measurements in drinking water. The results may eventually lead to greater recognition and application of ORP as a tool to monitor drinking water processes such as the effectiveness of disinfection in water distribution systems. This study suggests that redox electrodes can produce relatively similar $E_b$ values (calculated from measured ORP readings) in different types of water when a strong oxidant like chlorine is present. These readings could aid in monitoring disinfection or distinguishing among different oxidant formations that are present, such as verifying the presence of Cl$_2$ versus MCA. Relative oxidant strength, measured ORP values, and the effect of pH and oxidant concentration on ORP were in reasonable agreement with theory (i.e., the Nernst equation). Because the test water was simple in makeup, additional investigation is recommended to establish correlations between the theoretical $E_b$ values and the actual $E_b$ values measured in natural water systems containing the oxidants used in this study. ORP will vary to some extent with different water supplies because it reflects total water quality composition. Finally, good maintenance of ORP electrodes is necessary to ensure reliable and proper interpretation of measurements.

**ACKNOWLEDGMENT**

The authors thank US Environmental Protection Agency (USEPA) colleagues Christy Muhlen, Daniel Williams, and Nicholas Dugan for laboratory support; Cheryl James and Victoria (Blackschleger) Berry, formerly with the University of Cincinnati, for laboratory support; Andrew Alleman with Texas Tech University for data analysis support; and Dorie Wheeler and Kyle Hawkins with Miami University and Emily Nauman with Pegasus Technical Services for editing and providing helpful comments during the development of this article.

The USEPA, through its Office of Research and Development, funded and managed, or partially funded and collaborated in, the
research described in this article. The article has been subjected to the agency’s administrative review and has been approved for external publication. Any opinions expressed in the article are those of the authors and do not necessarily reflect the views of the agency; therefore, no official endorsement should be inferred. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABOUT THE AUTHORS

Ari Copeland is an operational specialist with Black & Veatch, Centennial, Colo. A certified water professional in the state of Colorado, he has a Water A operator’s license and a Wastewater C operator’s license. He has 10 years of experience in water and wastewater operations and four years of experience training water and wastewater plant operators. He holds an MS degree in environmental engineering from the University of Cincinnati, Cincinnati, Ohio, and a BS degree in civil engineering from Worcester Polytechnic Institute, Worcester, Mass. He currently chairs AWWA’s Treatment Plant Operations and Maintenance Committee and teaches water- and wastewater-related classes part-time at Red Rocks Community College, Lakewood, Colo. Darren A. Lytle (to whom correspondence should be addressed) is an environmental engineer with the US Environmental Protection Agency, 26 West Martin Luther King Dr., Cincinnati, OH 45268; Lytle.Darren@epa.gov.

FOOTNOTES

1EMD Millipore, Billerica, Mass.
2EC 40 meter, Hach Co., Loveland, Colo.
3Hach Co., Loveland, Colo.
4Hach Co., Loveland, Colo.
5Model 450, Corning Inc., Corning, N.Y.
7DR/2010, Hach Company, Loveland, Colo.
8Micro 1000 chlormeter, Paimestry USA, Erlanger, Ky.
9Hach Co., Loveland, Colo.
10Multi_T® v2.0 computer software-driven (Jenson Systems, Hamburg, Germany) acid and base titration system (Schott Geräte, Mainz, Germany).

REFERENCES


