Region 4 U.S. Environmental Protection Agency Laboratory Services and Applied Science Division Athens, Georgia	
Operating Procedure	
Title: Field Measurement of Oxidation-Reduction Potential	**ID: FSBPROC-113-R5**
Issuing Authority: Field Services Branch Chief	
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Method Reference: N/A	**SOP Author: Michael Roberts**

Purpose

This document describes procedures, methods and considerations to be used and observed when conducting field Oxidation-Reduction Potential (ORP) measurements in aqueous environmental media, including groundwater, surface water and certain wastewater. The measurement of soil ORP is a non-standard measurement and procedures should be developed on a project-specific basis. While this SOP may be informative for other businesses, it is not intended for and may not be directly applicable to operations in other organizations. Mention of trade names or commercial products in this operating procedure does not constitute endorsement or recommendation for use.

Scope/Application

This document describes procedures generic to all ORP measurement methods to be used by Laboratory Services and Applied Science Division (LSASD) field personnel when collecting and handling samples in the field. On the occasion LSASD personnel determine that any of the procedures described in this section are inappropriate, inadequate, or impractical and that another procedure must be used to obtain an ORP measurement, the variant procedure will be documented in the field logbook, along with a description of the circumstances requiring its use.

Note: LSASD is currently migrating to a paperless organization. As a result, this SOP will allow for the use of electronic logbooks, checklists, signatures, SOPs, and forms as they are developed, which will also be housed on the Local Area Network (LAN) and traceable to each project.

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Procedural Section

1. General Information

1.1. Documentation/Verification

    1.1.1.   This procedure was prepared by persons deemed technically competent by LSASD management, based on their knowledge, skills and abilities and has been tested in practice and reviewed in print by a subject matter expert. The official copy of this procedure resides on the LSASD local area network (LAN). The Document Control Coordinator (DCC) is responsible for ensuring the most recent version of the procedure is placed on the LSASD LAN and for maintaining records of review conducted prior to its issuance.

1.2. General Considerations

    1.2.1.   Safety

        1.2.1.1.   Proper safety precautions must be observed when verifying or calibrating instruments for measurement of Oxidation-Reduction Potential. Refer to the EPA Region 4. Region 4 Safety & Occupational Health SharePoint Site:

https://usepa.sharepoint.com/sites/r4-safety-occup-health

        and any pertinent site-specific Health and Safety Plans (HASP) for guidelines on safety precautions. These guidelines should be used to complement the judgment of an experienced professional.

        1.2.1.2.   Reagents commonly used in the preparation of ORP calibration standards are toxic and require care when handling. When using this procedure, avoid exposure to these materials through the use of protective clothing, eye wear and gloves. Safety precautions when handling and preparing verification solutions should include gloves and eyewear to prevent dermal and eye contact, and a mask to avoid inhaling dust particles when handling dry materials. Vigorous flushing should be used if the reagents or solutions come in contact with skin or eyes. Following is specific information on commonly used solutions. The application of the solutions is described in detail in Section 3.1, Standard Solutions, of this procedure.

- Quinhydrone (CAS# 106-34-3) is a skin and respiratory irritant and is poisonous if ingested. Safety precautions when handling quinhydrone should include gloves to prevent dermal contact and a mask to avoid inhaling dust particles when mixing dry material to prepare calibration standards. Vigorous flushing should be used if concentrated material comes in contact with skin or eyes.

- Zobell's solution is also an irritant and toxic if ingested. The same handling precautions apply when mixing and using Zobell's solution as when using quinhydrone. Zobell's reacts with acid to form harmful byproducts, including hydrocyanide gas.

- Light's solution contains ferro- and ferric-cyanide compounds in sulfuric acid. The components are toxic and burns are possible from contact with this solution.

- Potassium iodide solutions have lower toxicity than most calibration solution options. General ingestion, skin contact, and eye contact precautions apply.

1.2.1.3.   Unused quinhydrone, Zobell's, Light's or other calibration reagents and solutions should be returned to LSASD for disposal in accordance with the LSASD Safety, Health, and Environmental Management Plan (SHEMP).

1.2.2. Records

1.2.2.1.   Documentation of field activities is done in a bound logbook. All records, including a unique, traceable identifier for the instrument, should be entered according to the procedures outlined in the Sample and Evidence Management (LSASDPROC-005-R5) and the LSASD Operating Procedure for Equipment Inventory and Management, (LSASDPROC-108, most recent version).

1.2.2.2.   All field ORP measurements pertinent to the sampling event should be recorded in the field logbook for the event as outlined in the Sample and Evidence Management (LSASDPROC-005-R5) or managed electronically with appropriate backups as described in LSASD Operating Procedure for Control of Records (LSASDPROC-002, most recent version).

1.2.3. Shipping

1.2.3.1.   Shipped material shall conform to all U.S. Department of Transportation (DOT) rules of shipment found in Title 49 of the Code of Federal Regulations (49 CFR parts 171 to 179), and/or International Air Transportation Association (IATA) hazardous materials shipping requirements found in the current edition of IATA's Dangerous Goods Regulations.

1.2.3.2.   All shipping documents, such as bills of lading, will be retained by the project leader and stored in a secure place.

2. Background

2.1. General

    2.1.1.   Oxidation is the process of liberating electrons or gaining oxygen. Examples of oxidation include conversion of elemental iron to rust, elemental sulfur to sulfate, and elemental hydrogen to water (Pankow 1991). Reduction is the process of gaining electrons resulting in the charge on some atomic unit in the species to be reduced. Oxidation-reduction potential (ORP) or redox potential (hereafter, referred to as redox) is a measure of the intensity or activity of an aqueous environment or soil to mediate reactions of important elements in biological systems (e.g., O, N, Mn, Fe, S, and C) and other metallic elements.

    2.1.2.   Considerable confusion arises on the use of the terms oxidation and reduction as they apply to the media under study. The following introduction reproduced from an online 'Wikipedia' article on the topic lucidly explains their relationship in ORP measurement:

        2.1.2.1.   **Reduction potential** (also known as **redox potential, oxidation / reduction potential** or **ORP**) is the tendency of a <u>chemical species</u> to acquire <u>electrons</u> and thereby be <u>reduced</u>. Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced.

        2.1.2.2.   In aqueous solutions, the reduction potential is the tendency of the solution to either gain or lose electrons when it is subject to change by introduction of a new species. A solution with a higher (more positive) reduction potential than the new species will have a tendency to gain electrons from the new species (i.e., to be reduced by oxidizing the new species) and a solution with a lower (more negative) reduction potential will have a tendency to lose electrons to the new species (i.e., to be oxidized by reducing the new species). Just as the transfer of hydrogen ions between chemical species determines the pH of an aqueous solution, the transfer of electrons between chemical species determines the reduction potential of an aqueous solution. Like pH, the reduction potential represents an intensity factor. It does not characterize the capacity of the system for oxidation or reduction, in much the same way that pH does not characterize the buffering capacity.

    2.1.3.   In short, a numerically positive redox potential or ORP represents an environment conducive to the oxidation of an introduced substance by reduction of the original media.
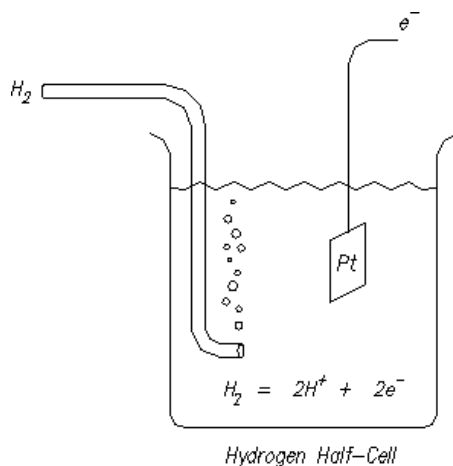
2.2. Instrumentation

2.2.1. ORP measurement systems are a practical implementation of electrochemical cells, which use metal electrodes in a solution to generate an electric current or voltage. If a platinum electrode is immersed in water with hydrogen bubbled into the solution, the H2 is oxidized as follows:
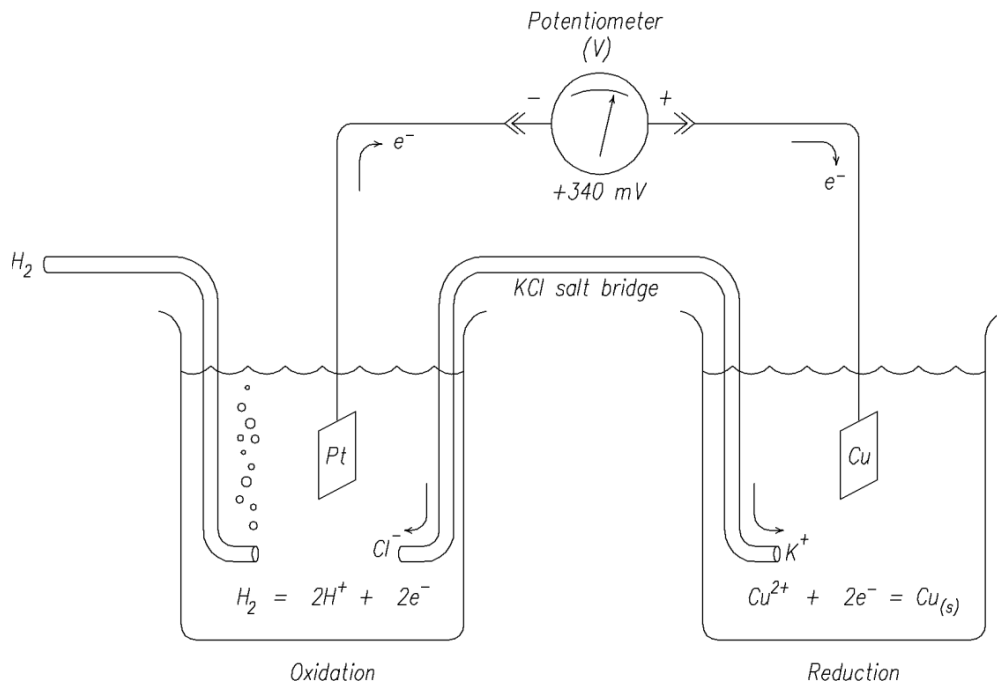
$$H^2 = 2H^+ + 2e^-$$

2.2.2. In the electrochemical half-cell illustrated below in Fig.1, hydrogen gas oxidizes to hydrogen ions and free electrons, comprising an oxidation-reduction couple. This couple reaches an equilibrium state that maintains the reference potential of the electrode. The electric potential develops on the wire connected to the platinum electrode but is difficult to measure in practice in the isolated half-cell. However, when used in a complete electrochemical cell, the cell illustrated is used as a reference to measure other half-cells against and is called a Standard Hydrogen Electrode (SHE).

Figure 1: Hydrogen Half-Cell

Hydrogen Half-Cell

2.2.3. If, as shown in Figure 2, a SHE is connected with a salt bridge to a second half-cell in which a reduction reaction is taking place, the electric potential between the two cells can be measured. In the case shown, the potential of the right cell will be +0.34 Volts in reference to the standard hydrogen electrode on the left. This would be represented as an Oxidation Reduction Potential (ORP) of +340mV on the hydrogen scale, or simply as Eh = +340mV.
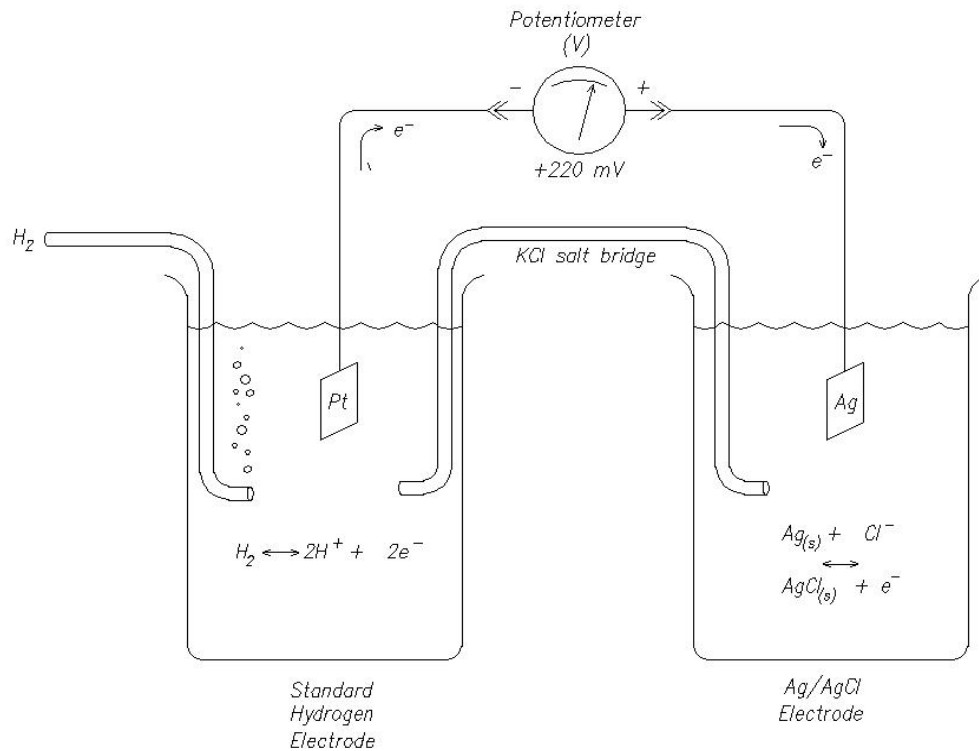
Figure 2: SHE connected with a salt bridge to a second half-cell

Potentiometer
(V)

$-$ $+$

$+340\ mV$

e^- e^-

H_2

KCl salt bridge

Pt

Cu

Cl^-

K^+

$H_2\ =\ 2H^+\ +\ 2e^-$

$Cu^{2+}\ +\ 2e^-\ =\ Cu_{(s)}$

Oxidation

Reduction

2.2.4. In field practice, the hydrogen electrode is difficult to reproduce. To conduct field measurements, a reference electrode is needed that is simple to maintain and will generate a potential that can be referenced to the standard hydrogen electrode. These requirements are met by the Saturated Calomel Electrode (SCE) and the Silver/Silver Chloride Electrode (SSCE - the SSCE is also commonly identified as an Ag/AgCl electrode). The SCE contains a small amount of elemental mercury, and while useful for certain applications, would rarely be used at LSASD. The SSCE or Ag/AgCl electrode is generally used as the reference cell in LSASD instrumentation.

2.2.5. In Figure 3 below, a SHE is connected to an Ag/AgCl electrode. In this example of an electrochemical cell, both cells reach an equilibrium potential. At that equilibrium state, the potential of the Ag/AgCl cell is 220mV more positive than the standard hydrogen electrode.

Figure 3: SHE is connected to an Ag/AgCl electrode

2.2.6.   This half-cell potential of the Ag/AgCl electrode in reference to the SHE is used to convert measurements taken with an Ag/AgCl reference back to the hydrogen scale. While the laboratory Ag/AgCl half-cell shown has a potential of +220mV, practical reference cells have varying potentials based on temperature and filling solutions as shown in Table 1 below.

Table 1: Half-cell Potential of Ag/AgCl Reference

T(°C)	Molarity of KCl filling solution			
	3M	3.3M*	3.5M	Sat/4M
10	220	217	215	214
15	216	214	212	209
20	213	210	208	204
25	209	207	205	199
30	205	203	201	194
35	202	199	197	189
40	198	195	193	184

*interpolated value
derived from USGS NFM, Table 6.5.2 (9/2005)

Note: YSI sondes and Thermo electrodes typically use 4M KCl filling solutions. Eureka sondes typically use 3.3M KCl filling solutions.

2.2.7. In Figure 4, below, the relationship between a hydrogen electrode, a reference electrode, and a platinum sensing electrode in an arbi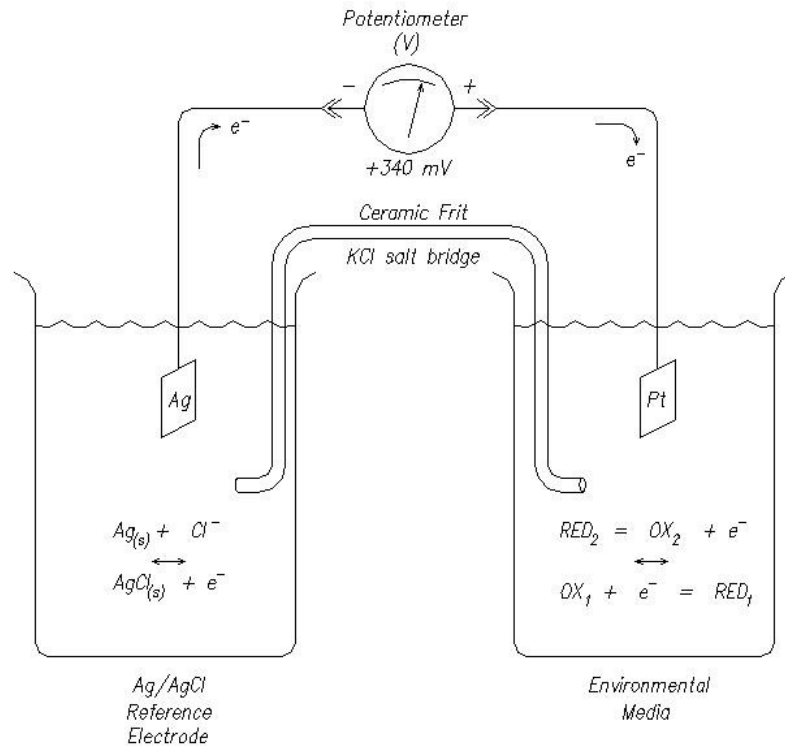trary media is shown. In this case, the ORP of the media in reference to the silver/silver chloride electrode is 150mV. To obtain Eh, the potential of the reference electrode in relation to a hydrogen electrode is added to the potential of the sensing electrode in relation to the reference electrode. In practice, the potential of the reference electrode in relation to a hydrogen electrode is not measured but obtained from Table 1 above.

Figure 4: Relationship between a hydrogen electrode, a reference electrode, and a platinum sensing electrode

In Figure 5 below, a field instrument is represented as separate electrochemical cells. The Ag/AgCl reference electrode uses a ceramic frit or other means to provide the essential salt bridge to the environmental media. The platinum sensing electrode is immersed in the environmental media and connected internally in the instrument to measure the potential (voltage) between the two electrodes.

Figure 5: Separate Electrochemical Cells

In this illustration, the ORP is measured as 340 mV. This measurement is made in reference to the Ag/AgCl reference electrode and would be reported as such, or as $E_{Ag/AgCl} = 340mV$.
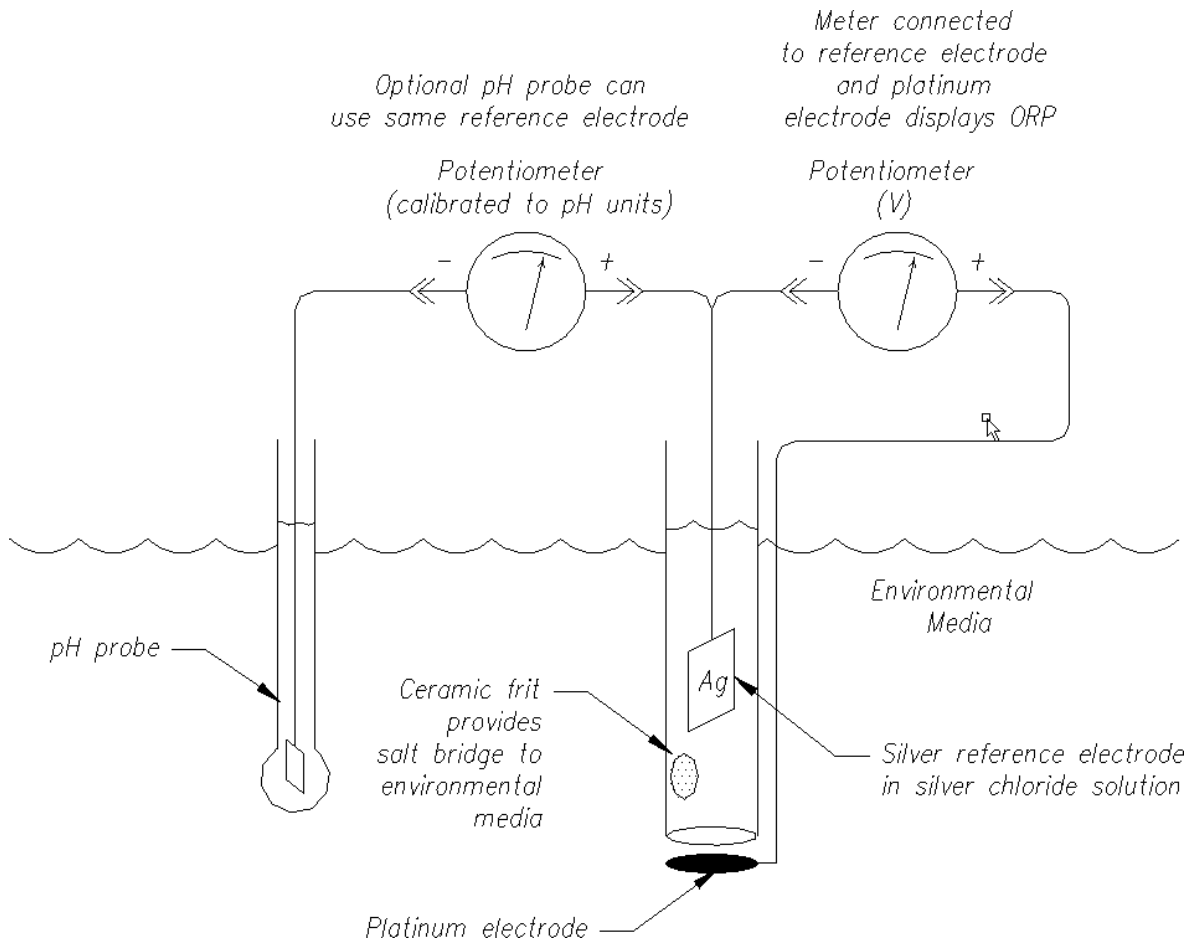
2.2.8. In some cases it will be desirable to report the reading on the hydrogen scale, or Eh. To do so, the potential of the reference electrode against the SHE, obtained from Table 1, is added to EAg/AgCl. For our example:

    340 mV Measured ORP ($E_{Ag/AgCl}$) of sample

+   <u>204 mV</u> Eh of Ag/AgCl electrode (ORP of Ag/AgCl electrode referenced to SHE)

    544 mV   Eh of sample

2.2.9. Both the +340 mV field reading and the adjusted +544 mV Eh can properly be referred to as ORP results. It is only through specifying the reference scale that the ambiguity can be eliminated.

2.2.10. In Figure 6, below, the theoretical cells shown above have been configured as a practical field instrument. The salt bridge is commonly provided by a ceramic frit connecting the environmental media to the reference electrode. In multi-parameter sondes, the pH probe commonly uses the same reference electrode as the ORP probe.

Figure 6: Practical Field Instrument

Optional pH probe can use same reference electrode

Meter connected to reference electrode and platinum electrode displays ORP

Potentiometer (calibrated to pH units)

Potentiometer (V)

Environmental Media

pH probe

Ceramic frit provides salt bridge to environmental media

Ag

Silver reference electrode in silver chloride solution

Platinum electrode

2.3. Redox Chemistry

2.3.1.   In acid-base chemistry, the pH of a system is defined as the negative logarithm of the hydrogen ion activity (simplified in practice to the hydrogen ion concentration):

$$pH = -\log \{H^+\}$$

2.3.2.   Similarly, Pankow (1991) described the negative logarithm of the electron activity (pe) as the master variable for describing the equilibrium position for all redox couples in a given system:

$$pe \ / \ -\log \{e^-\}$$

2.3.3.   It can be shown (Pankow) that pe is related to Eh by

$$Eh = pe*(2.303*R*T)/F$$

Where:
 R = gas constant = 8.314 J K^{-1} mol^{-1}
 T = temperature, $^{\circ}$K
 F = Faraday constant = 96.485*10^3 C mol^{-1}

At 25°C (298°K) this simplifies to:

$$E_H = pe * 0.05916$$

and,

$$pe = E_H / 0.05916$$

2.3.4.   According to Faulkner et al. (1989) redox is a quantitative measure of electron availability and is indicative of the intensity of oxidation or reduction in both chemical and biological systems. When based on a hydrogen scale, redox (E_H) is derived from the Nernst Equation (Stumm and Morgan 1981):

$$E_H = E_H^{\circ} + 2.3 \ H \ (R \ H \ T)/nF \ H \log (\vartheta_i \{ox\}^{ni}/\vartheta_j \{red\}^{nj})$$

 Where:
 E_H° = potential of reference, mV
 R = gas constant = 81.987 cal deg^{-1} mole^{-1}
 T = temperature, $^{\circ}$K
 n = number of moles of electrons transferred
 F = Faraday constant = 23.061 cal/mole-mv
 $\{ox\}$ and $\{red\}$ = activity of the oxidants and reductants, respectively

2.4. Applications

  2.4.1. When interpreted properly, redox combined with other conventional water quality parameters is useful in developing a more complete understanding of water chemistry. Several applications of redox are identified below:

1. Redox could be viewed as an extension of the oxygen scale. In this model, the DO probe spans the aerobic scale and the redox probe extends that scale to measure anaerobic conditions. Inferences to geochemistry and chemical speciation can be made from the oxidative state of the system. Application to metal sequestration, metal-iron, -sulfide, -methane complexation, and the subsequent bioaccumulation potential is possible.
2. Redox can be used to identify anaerobiosis at or near the water column and sediment interface in streams, lakes, and estuaries.
3. Redox may be useful in determination of stream jurisdiction and wetland delineation in that it can indicate conditions of soil saturation.
4. Based on redox, a pe (or EH) vs. pH stability diagram can be developed to aid in nutrient exchange studies including the timing, release, and partitioning of important water and sediment quality pollutants such as nitrogen and phosphorus species. Most importantly, redox can be used to address error associated with chamber-effect during closed chamber measurements of the water-sediment interface. Redox probes placed inside the contact chamber and inserted approximately ten centimeters into the underlying sediment can be used to monitor changes in sediment redox caused by the chamber, and steps can be taken to reduce chamber-effect.
5. Redox may be useful in establishing water and sediment quality standards applicable to wetlands.
6. Redox is used to assess the potential of a groundwater system to support various in situ reactions with contaminants, such as reductive dechlorination of chlorinated solvents.
7. Redox can provide a useful indicator of conditions that might compromise the performance of Clark-type dissolved oxygen (DO) probes. In general, anaerobic conditions occur at a redox range of +150 mV to +300 mV (pH-dependent and adjusted to hydrogen reference electrode). When redox drops below this level, DO measurements as determined with a Clarke-type probe are highly suspect as the semi-permeable membrane does not discriminate between partial O_2 and sulfides. Consequently, the meter may be reading sulfides.

2.5. Limitations

2.5.1.   In most environmental media, redox reactions will not reach equilibrium due to low concentrations or multiple redox species. Consequently, redox measurements can generally be considered semi-quantitative in environmental media, unless certain conditions exist.

2.5.2.   The USGS in the Interferences and Limitations Section 6.5.3A of their National Field Manual succinctly describe some of the issues encountered in the application of ORP measurements. This section is reproduced here, unedited:

2.5.2.1.   INTERFERENCES AND LIMITATIONS

2.5.2.1.1.   *Measurements should not be carried out without an awareness of the interferences and limitations inherent in the method.*

- *Organic matter and sulfide may cause contamination of the electrode surface, salt bridge, or internal electrolyte, which can cause drift or erratic performance when reference electrodes are used (American Public Health Association and others, 2001).*

- *Hydrogen sulfide can produce a coating on the platinum electrode that interferes with the measurement if the electrode is left in sulfide-rich water for several hours (Whitfield, 1974; Sato, 1960).*

- *The platinum single and combination redox electrodes may yield unstable readings in solutions containing chromium, uranium, vanadium, or titanium ions and other ions that are stronger reducing agents than hydrogen or platinum (Orion Research Instruction Manual, written commun., 1991).*

- *Do not insert redox electrodes into iron-rich waters directly after the electrode(s) contact ZoBell's. An insoluble blue precipitate coats the electrode surface because of an immediate reaction between ferro- and ferricyanide ions in ZoBell's with ferrous and ferric ions in the sample water, causing erratic readings.*

- *Many elements with more than one oxidation state do not exhibit reversible behavior at the platinum electrode surface and some systems will give mixed potentials, depending on the presence of several different couples (Barcelona and others, 1989; Bricker, 1982, p. 59–65; Stumm and Morgan, 1981, p. 490–495; Bricker, 1965, p. 65). Methane, bicarbonate, nitrogen gas, sulfate, and dissolved oxygen generally are not in equilibrium with platinum electrodes (Berner, 1981).*

2.5.2.2.   Technical Note:

Misconceptions regarding the analogy between Eh (pe) and pH as master variables and limitations on the interpretation of Eh measurements are explained in Hostettler (1984), Lindberg and Runnells (1984), Thorstenson (1984), and Berner (1981). To summarize:

(1) Hydrated electrons do not exist in meaningful concentrations in most aqueous systems—in contrast, pH represents real activities of hydrated protons. Eh may be expressed as pe (the negative logarithm of the electron activity), but conversion to pe offers no advantage when dealing with measured potentials.
(2) Do not assume that redox species coexist in equilibrium. Many situations have been documented in which dissolved oxygen coexists with hydrogen sulfide, methane, and ferrous iron.
  - *The practicality of Eh measurements is limited to iron in acidic mine waters and sulfide in waters undergoing sulfate reduction.*
  - *Other redox species are not sufficiently electroactive to establish an equilibrium potential at the surface of the conducting electrode.*
(3) A single redox potential cannot be assigned to a disequilibrium system, nor can it be assigned to a water sample without specifying the particular redox species to which it refers. Different redox elements (iron, manganese, sulfur, selenium, arsenic) tend not to reach overall equilibrium in most natural water systems; therefore, a single Eh measurement generally does not represent the system.

3. Methodology

3.1. Standard Solutions

3.1.1.   Care should be taken not to contaminate standards and samples and to verify the expiration date of all standards prior to use. All meters should be verified or calibrated according to the manufacturer's procedures.

3.1.2.   Standard solutions for calibration and verification should be selected to meet project requirements. LSASD generally maintains a stock of Zobell's solution suitable for most projects. The characteristics and use of the common standard solutions are described below.

  - Zobell's solution contains potassium ferri- and ferro- cyanide compounds. The solution is available as prepared solutions or premeasured reagents for mixing by the user. Zobell's has moderate toxicity but will react with acid to form harmful byproducts, including hydrocyanide gas. It has a shelf life

ranging from several days to several months depending on the manufacturer. Stock and working solutions of Zobell's should be stored in dark bottles due to its light sensitivity.

- Quinhydrone solutions are mixed at the time of use by adding quinhydrone to pH 4 or pH 7 buffers. At 25°C, the Eh of quinhydrone pH 4 and pH 7 verification solutions are 462mV and 285mV respectively. An advantage of quinhydrone solutions is that they offer a span of calibration points that may be appropriate for particular applications. Quinhydrone is a lightly 'poised' solution in that it offers less driving force towards the calibration point: a compromised instrument is more likely to be revealed in a quinhydrone calibration. A quinhydrone calibration/verification solution is created by adding 10g of quinhydrone to 1L of pH 4 or pH 7 buffer solution (ASTM D1498). The solutions are mixed on a magnetic mixing plate for a minimum of 15 minutes to create a saturated solution with undissolved crystals remaining. Quinhydrone solutions are usable for 8 hrs from the time of mixing.

- Light's solution consists of ferrous and ferric ammonium sulphate in sulphuric acid. The solution would rarely be used at LSASD due to its high acidity and associated handling difficulty. Spent solutions with a pH<2 would be regulated as a hazardous waste. Light's is a highly poised solution that may allow a marginally functioning electrode to pass calibration.

- A prepared potassium iodide solution is available which has low toxicity and a long shelf life. The solution may stain clothing or surfaces if spilled.

3.2. Verification and Calibration

3.2.1. ORP instruments may be **verified** or **calibrated**, depending on the application. The approach chosen should be selected based on project needs and information presented in Section 2.4., Limitations. Standard laboratory practice in making ORP measurements is to **verify** the accuracy of the instrument prior to use, and this practice should be followed when true quantitative results are required. In a **verification**, the instrument in its direct-reading mode is checked against a standard solution in a pass/no-pass test, and no corrections are applied to subsequent measurements. In most applications, the ORP information is used semi-quantitatively and for these applications, the instruments may be **calibrated** to the standard solutions. In an instrument **calibration**, the instrument probe is placed in the standard solution and the difference between the standard measurement and the known ORP value of the standard is used by the instrument to make adjustments to the subsequent measurements.

3.2.2. In **verification** of an ORP instrument, the instrument is set to absolute mV reading mode or the internal calibration offset is zeroed out. The instrument probe should then be placed in the standard solution and the reading verified to fall within +/-10mV of the predicted reading for the standard. Instruments with single-purpose electrodes are most suitable for this approach. If the instrument fails the verification, standard solution quality should be considered and instrument maintenance performed per the manufacturer's procedures.

3.2.3. In most LSASD field practice, the end data use is semi-quantitative. In this case, the instruments can be **calibrated** to standard solutions appropriate for the project using the manufacturer's recommended procedure. One minute after the calibration, the instrument should display a stable reading within +/-10mV of the predicted reading. An instrument failing this test should be recalibrated to determine if the problem is inadequate equilibration time. In the event of continued instrument failure, aging or contamination of the standard solution should be considered. Subsequently the electrode should be serviced according to the manufacturer's procedures. Common service procedures include cleaning the platinum electrode with mild abrasives or acids and refilling or replacing the reference electrode.

3.2.4. Prior to a mobilization, all ORP instruments will be checked for proper operation and verified or calibrated against standard solutions. During the field mobilization, each instrument will be calibrated or verified prior to, and verified after, each day's use or deployment.

3.2.5. Even though it is not necessary to re-calibrate ORP instrument at regular intervals during the day, it may be appropriate to occasionally perform operational checks to determine if site conditions, such as an extreme temperature change or submersion of a filling solution port have impacted the instrument's performance. If an operational check is warranted, the field operator should follow the appropriate verification/calibration steps as described above.

3.2.6. The predicted ORP values of standard solutions will be obtained from the manufacturer of prepared solutions, literature, or appropriate values listed in this procedure. Care is in order, as the predicted ORP value is specific for the type of reference electrode used by the probe (either Ag/AgCl or calomel) and the molarity of the filling solution in the reference electrode. To use the solution with another electrode or filling solution, the expected ORP readings for the solution should be converted to Eh for the probes intended for the solution as per the Reporting section of this procedure. Then a table can be compiled for the electrode in use by subtracting the Eh,ref for the electrode and filling solution in use. This will be done at the Field Equipment Center (FEC) for the solutions stocked.

3.2.7. Verification solutions should be managed per the manufacturer's directions regarding storage and handling. After instrument verification or calibration, the solution cannot be returned to the stock solution container, although a separate container of working solution can be maintained.

3.2.8. Spent solutions and working solutions should be returned from the field to the LSASD laboratory for proper disposal by the SHEMP or handled as directed by the SHEMP. Properly handled stock solutions may be returned to the FEC for use at that facility.

3.3. Measurement

3.3.1. ORP measurements should be conducted in a fashion that prevents the addition or loss of any potential oxidants or reductants. Results could be compromised by exposing the sample to air or allowing H_2S to off-gas from anoxic samples. Like dissolved oxygen measurements, ORP measurements should be conducted in situ or by using a flow-through cell evacuated of air (see the LSASD Operating Procedure for Field Measurement of Dissolved Oxygen (LSASDPROC-106-R5). Good results are commonly obtained with the use of an overtopping cell where the environmental media is pumped into the bottom of a narrow cup (generally field fabricated from a sample container) containing the instrument sensors. The sensors are continually flushed with fresh media as the cup is allowed to overflow. Caution should be exercised at very low flow rates where the media in the cup could potentially re-oxygenate.

3.3.2. When using multi-parameter probes for ORP measurements, the general guidelines for probe deployment described in the LSASD Operating Procedure for Field Measurement of Dissolved Oxygen ((LSASDPROC-106-R5) and the LSASD Operating Procedure for In-situ Water Quality Monitoring (LSASDPROC-111, most recent version) apply.

3.3.3. ORP probes must be operated and maintained in accordance with the manufacturer's instructions. Reference electrodes in multi-parameter probes may require regular filling or replacement. Single parameter ORP electrodes may require regular filling and operation in an upright position to assure that proper salt bridge flow is maintained. Platinum electrode surfaces are easily contaminated and polishing, or cleaning of the electrodes should be performed as recommended by the manufacturer.

3.3.4. Measurements in field logbooks should be recorded to the nearest mV. The type of reference electrode in use and its filling solution should be recorded in at least one logbook as part of the field project records.

3.3.5.   ORP is a temperature sensitive measurement, but ORP instruments are not temperature compensated. Consequently, the media temperature should always be recorded at the same time as the ORP is recorded. Likewise, as ORP is often pH dependent, pH should also be recorded at the time of ORP measurement.

3.4. Reporting

3.4.1.   In the absence of a specified reference scale, ORP data has no meaning. Therefore, the reference scale used should always be specified in reporting or discussing the ORP data. ORP measurements converted to a hydrogen scale can be reported as "Eh". Data reported as the direct field measurement without correction might be described as "ORP referenced to Ag/AgCl electrode" or "EAg/AgCl". The expectations of the data user should be ascertained, or the measurements should be reported in both systems.

3.4.2.   To apply corrections to obtain Eh from the direct field measurement, the known half-cell potential of the reference electrode is added to the recorded field ORP value:

$$E_{h,sample} = ORP_{sample} + \text{half-cell potential of reference electrode}$$

3.4.3.   The following table presents the half-cell potential of a silver/silver chloride reference electrode at various temperatures and with various molarities of KCl filling solutions.

Table 1: Half-Cell Potential of Ag/AgCl Reference

T(°C)	Molarity of KCl filling solution			
	3M	**3.3M***	**3.5M**	**Sat/4M**
10	220	217	215	214
15	216	214	212	209
20	213	210	208	204
25	209	207	205	199
30	205	203	201	194
35	202	199	197	189
40	198	195	193	184

Derived from USGS NFM, Table 6.5.2 (9/2005)
*interpolated value

Note: YSI sondes and Thermo electrodes typically use 4M KCl filling solutions. Eureka sondes typically use 3.3M KCl filling solutions

3.4.3.1.   Example:

3.4.3.1.1.   A multi-parameter probe with a silver/silver chloride reference electrode and 4M KCl filling solution is used to record a stream ORP measurement of 146mV. The stream temperature is recorded as 15°C.

3.4.3.1.2.   From the above table, the half-cell potential of an Ag/AgCl reference electrode filled with 4M KCl is 209mV at 15°C. Then:

$E_{h,sample} = ORP_{Ag/AgCl,sample}$+ half-cell potential of Ag/AgCl reference electrode

$E_{h,sample}$ = 146mV + 209mV

$E_{h,sample}$ = 355mV

3.4.3.1.3.   As noted in Section 3.3, Measurement, ORP measurements are sensitive to temperature, and may be sensitive to pH. As the instruments do not compensate for these parameters, ORP data should always be reported with the temperature and pH of the media at the time of measurement.

3.4.3.1.4.   Final reporting values of Eh or ORP should be rounded to the nearest 10mV. The following spreadsheet formula can perform the rounding of an interim result located in spreadsheet cell 'A1':

=INT(A1/10+0.5)*10

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Revision History

History	Effective Date
FSBPROC-113-R5, *Field Measurement of Oxidation-Reduction Potential*, replaces LSASDPROC-113-R4 Administrative Changes Only (Updated formulae formatting, Table of Contents, references to other LSASD SOPs, and Region 4 Safety & Occupational Health SharePoint site link)	March 4, 2024
Replaced Chief with Supervisor; General formatting revisions.	April 22, 2023
SESDPROC-113-R3, *Field Measurement of Oxidation-Reduction Potential*, replaces SESDPROC-013-R2 SOP was put in the new SOP format. Replace SESD with LSASD and updated SOP reference numbers throughout the document. Updated the reference section.	December 17, 2021
SESDPROC-113-R2, *Field Measurement of Oxidation-Reduction Potential (ORP)*, replaces SESDPROC-013-R1 **General:** Corrected any typographical, grammatical, and/or editorial errors. **Title Page:** Changed the EIB Supervisor from Danny France to the Field Services Branch Supervisor John Deatrick, and the Field Quality Manager from Bobby Lewis to Hunter Johnson. **Section 2.2**: Figure 6 modified for clarity. **Section 3.3**: Use of overtopping cell described consistent with current practice.	April 26, 2017
SESDPROC-113-R1, *Field Measurement of Oxidation-Reduction Potential (ORP)*, replaces SESDPROC-013-R0	January 29, 2013
SESDPROC-113-R0, *Field Measurement of Oxidation-Reduction Potential (ORP)*, Original Issue	August 7, 2009