

REDUCTION- 6.5 OXIDATION POTENTIAL (ELECTRODE METHOD)

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	Page
Reduction-oxidation potential (electrode method)	REDOX-3
6.5.1 Equipment and supplies.....	4
6.5.1.A Electrode selection	5
6.5.1.B ZoBell's solution	5
6.5.1.C Equipment maintenance.....	6
6.5.2 Equipment test procedure	8
6.5.3 Measurement	13
6.5.3.A Interferences and limitations	16
6.5.3.B Interpretation.....	18
6.5.4 Troubleshooting.....	19
6.5.5 Reporting	20
Selected references	20

Illustrations

**6.5–1. Form showing Eh data record:
equipment test procedure 12**

**6.5–2. Form showing Eh data record:
field measurements..... 15**

Tables

6.5–1. Equipment and supplies used for Eh measurements.. 4

**6.5–2. Standard half-cell potentials of selected reference
electrodes as a function of temperature and
potassium chloride reference-solution
concentration, in volts 9**

**6.5–3. Eh of ZoBell’s solution as a function of
temperature 9**

6.5–4. Troubleshooting guide for Eh measurement 19

REDUCTION-OXIDATION POTENTIAL (ELECTRODE METHOD) 6.5

In contrast to other field measurements, the determination of the reduction-oxidation potential of water (referred to as redox) should not be considered a routine determination. Measurement of redox potential, described here as Eh measurement, is not recommended in general because of the difficulties inherent in its theoretical concept and its practical measurement (see “Interferences and Limitations,” section 6.5.3.A).

REDUCTION-OXIDATION POTENTIAL (*as Eh*)—A measure of the equilibrium potential, relative to the standard hydrogen electrode, developed at the interface between a noble metal electrode and an aqueous solution containing electroactive redox species.

- ▶ Eh measurement may show qualitative trends but generally cannot be interpreted as equilibrium values.
- ▶ Determinations of redox using the platinum (or other noble metal) electrode method (Eh) are valid only when redox species are (a) electroactive, and (b) present in the solution at concentrations of about 10^{-5} molal and higher. Redox species in natural waters generally do not reach equilibrium with metal electrodes.

Procedures for equipment calibration (test procedures) and Eh measurement are described in this section for the platinum electrode only. Although the general guidance given here applies to other types of redox electrodes (such as gold and glassy carbon electrodes), it is necessary to consult the manufacturer’s instructions for correct use of the specific electrode selected. Concentrations of redox species can be determined by direct chemical analysis instead of using the electrode method (Baedecker and Cozzarelli, 1992).

6.5.1 EQUIPMENT AND SUPPLIES

The equipment and supplies needed for making Eh measurements using the platinum electrode method and stand-alone millivolt or pH meter are listed in table 6.5–1.

Table 6.5–1. Equipment and supplies used for Eh measurements¹

[mV, millivolt; \pm , plus or minus; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius]

- ✓ Millivolt meter or pH meter with millivolt reading capability, preferably with automatic temperature compensator; 0.1-mV sensitivity; scale to at least $\pm 1,400$ mV; BNC connector (see instrument specifications for pH meters, 6.4.1 in NFM 6.4)
- ✓ Redox electrodes, either (a) platinum and reference electrode (calomel or silver:silver-chloride) or (b) combination electrode
- ✓ Electrode filling solutions (refer to manufacturer's specifications)
- ✓ Thermometer (liquid-in-glass or thermistor type), calibrated (see NFM 6.1 for selection and calibration criteria)—for use with millivolt meters without temperature compensator
- ✓ Flowthrough cell with valves, tubing, and accessories impermeable to air (for use with pump system)
- ✓ Sampling system: (1) in situ (downhole) measurement instrument, or (2) submersible pump (used with closed-system flowthrough cell). Pump tubing must be "impermeable" to oxygen.
- ✓ ZoBell's solution
- ✓ Aqua regia or manufacturer's recommended electrode-cleaning solution
- ✓ Liquid nonphosphate laboratory-grade detergent
- ✓ Mild abrasive: crocus cloth or 400- to 600-grit wet/dry Carborundum™ paper
- ✓ Deionized water (maximum conductivity of 1.0 $\mu\text{S}/\text{cm}$)
- ✓ Bottle, squeeze dispenser for deionized water
- ✓ Safety equipment: gloves, glasses, apron, chemical spill kit
- ✓ Paper tissues, disposable, lint free
- ✓ Waste-disposal container

¹Modify this list to meet specific needs of the field effort.

This report does not provide guidance or instructions for redox determination using an oxidation-reduction-potential (ORP) sensor connected to a multiparameter instrument. Eh equipment must be tested before each field trip and cleaned soon after use. Every instrument system used for Eh measurement must have a log book in which all the equipment repairs and calibrations or equipment tests are recorded, along with the manufacturer make and model numbers and serial or property number.

ELECTRODE SELECTION 6.5.1.A

Select either a redox-sensing combination electrode or an electrode pair (a platinum and reference electrode). **Use of the correct electrolyte filling solution is essential to proper measurement and is specified by the electrode manufacturer.** Orion Company, for example, recommends selection of a filling solution to best match the ionic strength of the sample solution, in order to minimize junction potentials.

- ▶ Silver:silver-chloride or calomel reference electrodes are the redox electrodes in common use.
- ▶ The Orion™ combination electrodes are platinum redox and silver:silver-chloride reference electrodes in one body (the Orion™ brand is used for purposes of illustration only).

CAUTION: The standard hydrogen reference electrode (SHE) can be dangerous and is not recommended for field use.

ZOBELL'S SOLUTION 6.5.1.B

ZoBell's is the standard solution for testing redox instruments. ZoBell's solution can be obtained from a commercial supplier or it can be prepared fresh (see below). Quinhydrone solution is sometimes used but is not recommended because it is significantly less stable above 30°C and its temperature dependence is not as well defined as that of ZoBell's.

ZoBell's solution consists of a 0.1 molal KCl solution containing equimolal amounts of $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$. ZoBell's is reported stable for at least 90 days if kept chilled at 4°C.

To prepare ZoBell's solution:

1. Weigh the chemicals (dry chemicals should be stored overnight in a desiccator before use).
 - 1.4080 g $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (Potassium ferrocyanide)
 - 1.0975 g $\text{K}_3\text{Fe}(\text{CN})_6$ (Potassium ferricyanide)
 - 7.4557 g KCl (Potassium chloride)

2. Dissolve these chemicals in deionized water and dilute solution to 1,000 mL.
3. Store the solution in a dark bottle, clearly labeled with its chemical contents, preparation date, and expiration date. Keep the solution chilled.

CAUTION: ZoBell's solution is toxic—handle with care.

6.5.1.C EQUIPMENT MAINTENANCE

Refer to 6.4.1 of NFM 6.4 on pH for general guidelines on meter and electrode maintenance, cleaning, and storage. Follow the manufacturer's guidelines on the operation and maintenance of the meters and electrodes, and keep a copy of the instruction manual with each instrument system. Keep the meters and electrodes clean of dust and chemical spills, and handle them with care.

Maintenance

Keep the surface of noble electrodes clean of coatings or mineral deposits. A brightly polished metal surface prevents deterioration of electrode response. The billet tip is more easily cleaned than the wire tip on the platinum electrode. Condition and maintain the Eh electrodes as recommended by the manufacturer.

Electrode Cleaning

Keep the O-ring on electrodes moist during cleaning procedures.

- ▶ To remove precipitate that forms on the outside wall or tip of the reference or combination electrode, rinse the outside of the electrode with deionized water.
- ▶ If particulates or precipitates lodge in the space between the electrode sleeve and the inner cone of sleeve-type electrode junctions, clean the chamber by flushing out the filling solution (the precise procedure to be followed must come from the electrode manufacturer).

- ▶ To remove oily residues, use a liquid nonphosphate detergent solution and polish the surface with mild abrasive such as coarse cloth, a hard eraser, or 400- to 600-grit wet/dry Carborundum™ paper (Bricker, 1982).
- ▶ To recondition the Eh electrode, immerse the electrode in warm aqua regia (70°C) for about 1 minute. **Do not immerse the electrode for longer than 1 minute** because aqua regia dissolves the noble metal as well as foreign matter and leads to an erratic electrode response (Bricker, 1982). Soak the electrode several hours in tap water before use.

TECHNICAL NOTE: Disassembly of the electrode is not recommended for routine cleaning and should only be used when absolutely needed. Additional cleaning and reconditioning procedures are discussed in NFM 6.4 and in American Public Health Association and others (1992), American Society for Testing and Materials (1990), Edmunds (1973), Adams (1969), and Callame (1968).

Aqua regia

Aqua regia can be used for cleaning the Eh electrode (check the electrode manufacturer's recommendations). Prepare the aqua regia at the time of use—do not store it. To prepare the aqua regia, mix 1 volume concentrated nitric acid with 3 volumes of concentrated hydrochloric acid.

Electrode storage

For short-term storage, immerse the electrode in deionized water to above the electrode junction and keep the fill hole plugged to reduce evaporation of the filling solution. The recommended procedures for long-term storage of electrodes vary with the type of electrode and by manufacturer. The Orion™ combination electrodes are stored dry after rinsing precipitates from outside of the electrode, draining the filling solution from the chamber, and flushing it with water (consult the manufacturer's cleaning instructions). The ends of the electrode connector must be kept clean. Clean them with alcohol, if necessary. Store the connector ends in a plastic bag when not in use.

Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer's instructions.

6.5.2 EQUIPMENT TEST PROCEDURE

Eh measuring systems can be tested for accuracy but they cannot be adjusted. Eh equipment must be tested, either in the laboratory or in the field, against a ZoBell's standard solution before making field measurements. In general, field testing with ZoBell's is not required, but the protocol used will depend on study needs.

- ▶ Before using, check that the ZoBell's solution has not exceeded its shelf life.
- ▶ Test the Eh equipment using the ZoBell's solution **before and after** field use.
- ▶ Be aware that:
 - ZoBell's is toxic and needs to be handled with care.
 - ZoBell's reacts readily with minute particles of iron, dust, and other substances, making field use potentially difficult and messy.

The Eh measurements are made by inserting a platinum electrode coupled with a reference electrode into the solution to be measured. The resulting potential, read directly in millivolts from a potentiometer (such as a pH meter), is corrected for the difference between the standard potential of the reference electrode being used at the solution temperature and the potential of the standard hydrogen electrode (table 6.5–2).

TECHNICAL NOTE: E_{ref} is the whole-cell potential of the reference electrode in ZoBell's solution.

$E_{\text{ref}} = 238 \text{ mV}$ (saturated KCl, immersed with the platinum electrode in ZoBell's at 25°C) is the measured potential of the silver:silver-chloride (Ag:AgCl) electrode;

$E_{\text{ref}} = 185.5 \text{ mV}$ (saturated KCl, immersed with the platinum electrode in ZoBell's at 25°C) is the measured potential of the calomel (Hg:HgCl₂) electrode;

$E^\circ = 430 \text{ mV}$ is the standard electrode potential of ZoBell's solution measured against the hydrogen electrode at 25°C.

Half-cell potentials for the calomel, silver:silver chloride, and combination electrodes are shown in table 6.5–2. Table 6.5–3 provides the theoretical Eh of ZoBell's solution as a function of temperature. For those temperatures not shown on tables 6.5–2 and 6.5–3, interpolate the values. Add the value corresponding to the solution temperature to the measured potential electromotive force (emf measurement).

Table 6.5–2. Standard half-cell potentials of selected reference electrodes as a function of temperature and potassium chloride reference-solution concentration, in volts

[Liquid-junction potential included—multiply volts by 1,000 to convert to millivolts; KCl, potassium chloride; Temp °C, temperature in degrees Celsius; M, molar; —, value not provided in reference]

Temp °C	Silver:silver chloride			Calomel ¹				Orion™ 96-78 combina- tion electrode ^{3,4}
	3M KCl ¹	3.5M KCl ²	Saturated KCl ²	3M KCl ²	3.5M KCl ²	4M KCl ²	KCl saturated ²	
10	0.220	0.215	0.214	0.260	0.256	—	0.254	0.256
15	0.216	0.212	0.209	—	—	—	0.251	0.253
20	0.213	0.208	0.204	0.257	0.252	—	0.248	0.249
25	0.209	0.205	0.199	0.255	0.250	0.246	0.244	0.246
30	0.205	0.201	0.194	0.253	0.248	0.244	0.241	0.242
35	0.202	0.197	0.189	—	—	—	0.238	0.238
40	0.198	0.193	0.184	0.249	0.244	0.239	0.234	0.234

¹Modified from Langmuir (1971).

²Modified from Bates (1973).

³Nordstrom (1977) and D.K. Nordstrom, U.S. Geological Survey, written commun., 1995; the half-cell potentials calculated from Nordstrom (1977) are recommended rather than the values from Chateau (1954) cited in the instrument manual provided by the Orion Company because Nordstrom's values were developed specifically for the Orion™ 96-78 redox electrode and provide greater accuracy and precision.

⁴Orion™ manufacturer recommends that for sample solutions with total ionic strength exceeding 0.2 molar (for example, seawater), use a 4M KCl-saturated filling solution (usually supplied with the Orion™ model 97-78 electrode) and the half-cell potentials shown above for the silver:silver chloride saturated KCl reference electrode.

Table 6.5–3. Eh of ZoBell's solution as a function of temperature

[From Nordstrom (1977); °C, degrees Celsius; mV, millivolts]

Temperature °C	Eh(mV)	Temperature °C, (continued)	Eh(mV), (continued)
10	467	26	428
12	462	28	423
14	457	30	418
16	453	32	416
18	448	34	407
20	443	36	402
22	438	38	397
24	433	40	393
25	430		

To test Eh equipment, complete the following 7 steps and record results on the Eh data record form for the equipment test procedure (fig. 6.5–1):

1. Follow the manufacturers' recommendations for instrument warm up and operation.
 - Set the scale to the desired millivolt range.
 - Record the type of reference electrode being used.
2. Unplug the fill hole. Shake the electrode gently to remove air bubbles from the sensing tip of the electrode. Check the level of the filling solution and replenish to the bottom of the fill hole.
 - The filling solution level must be at least 1 in. above the level of solution being measured.
 - Use only the filling solution specified by the manufacturer.
3. Rinse the electrode, thermometer, and measurement beaker with deionized water. **Blot (do not wipe) excess moisture from the electrode.**
4. Pour ZoBell's solution into a measurement beaker containing the electrode and temperature sensor.
 - The Eh electrode must not touch the bottom or side of the container.
 - Add enough solution to cover the reference junction.
 - Allow 15 to 30 minutes for the solution and sensors to equilibrate to ambient temperature.
5. Stir slowly with a magnetic stirrer (or swirl manually) to establish equilibrium between the electrode(s) and solution. Switch the meter to the millivolt function, allow the reading to stabilize (± 5 mV), and record the temperature and millivolt value.
6. Look up the half-cell reference potential for the electrode being used (table 6.5–2). Add this value to the measured potential to obtain the Eh of ZoBell's at ambient temperature.
 - If the value is within 5 mV of the ZoBell Eh given on table 6.5–3, the equipment is ready for field use. (See the example below.)
 - Refer to section 6.5.4 if the value is not within 5 mV of the ZoBell Eh.
7. Rinse off the electrodes and the thermometer thoroughly with deionized water. Store the test solution temporarily for possible verification.

EXAMPLE:

Example of the equipment test procedure using a silver:silver chloride-saturated KCl (Ag:AgCl) electrode.

$$Eh = emf + E_{\text{ref}}$$

where:

Eh is the potential (in millivolts) of the sample solution relative to the standard hydrogen electrode,

emf or E_{measured} is the electromotive force or potential (in millivolts) of the water measured at the sample temperature,

E_{ref} is the reference electrode potential of the ZoBell's solution corrected for the sample temperature (table 6.5–2).

- a. Follow steps 1–5 (above). For this example,
 - Measured temperature = 22°C
 - $emf = 238 \text{ mV}$.
- b. Check table 6.5–2. The interpolated reference potential = 202 mV for Ag:AgCl-saturated KCl at 22°C.
- c. From $Eh = emf + E_{\text{ref}}$

$$Eh (\text{ZoBell's}) = 238 \text{ mV} + 202 \text{ mV} = 440 \text{ mV}.$$
- d. Check table 6.5–3. The test value of 440 mV is within $\pm 5 \text{ mV}$ of 438 mV from table 6.5–3. Thus, the equipment is functioning well and ready for field use.

Check the date on Zobell's solution—do not use solution past its expiration date.

Eh Data Record**Equipment Test Procedure**

Equipment description and identification (model and serial and/or W number):

Meter _____

Eh electrode _____ Reference electrode _____

ZoBell's solution: Lot # _____ Date: prepared _____ expired _____

- | | Before sample Eh: | After sample Eh: |
|---|----------------------------|------------------|
| 1. Temperature of ZoBell's solution:
(after equilibration to ambient temperature) | T = _____ | _____ |
| 2. Observed potential (in millivolts) of ZoBell's
relative to measuring electrode, at
ambient temperature (E_{measured} or emf): | $emf =$ _____ | _____ |
| 3. Reference electrode potential (in millivolts)
at ambient temperature from table 6.5-2
(E_{ref}): | $E_{\text{ref}} =$ _____ | _____ |
| 4. Calculate Eh of ZoBell's: $Eh = emf + E_{\text{ref}}$ | $Eh =$ _____ | _____ |
| 5. Theoretical potential (in millivolts)
of ZoBell's at ambient temperature
from table 6.5-3: | Eh (theoretical) = _____ | _____ |
| 6. Subtract calculated Eh from Eh theoretical
(ZoBell's)(step 4 minus step 5) | $\Delta Eh =$ _____ | _____ |
| 7. Check: is ΔEh within ± 5 mV? | Observations: _____ | _____ |

Figure 6.5-1. Eh data record: equipment test procedure.

MEASUREMENT 6.5.3

To obtain accurate results, it is necessary to prevent losses and gains of gases dissolved in the sample. Consult NFM 6.0 for information on precautions and general procedures used in sample collection and NFM 6.2 for a description of the flowthrough cell used in dissolved-oxygen determination (the spectrophotometric method).

- ▶ Chemical, physical, and biological reactions can cause the Eh of water to change significantly within minutes or even seconds after the collection of a sample.
- ▶ Water samples cannot be preserved and stored for the Eh measurement.
- ▶ Use equipment that eliminates sample aeration and operate the equipment to meet this goal. Measure Eh in situ with a submersible instrument or use an airtight flowthrough system.
- ▶ If using a flowthrough chamber or cell:
 - Use tubing that is impermeable (relatively) to oxygen.
 - Channel the sample flow through an airtight cell (closed system) constructed specifically to accommodate redox or ion-specific electrodes, temperature, and other sensors.
 - Connections and fittings must be airtight
 - Purge atmospheric oxygen from the sample tubing and associated flow channels before measuring Eh.

Do not use pumping systems in which inert gas contacts and lifts the sample to the surface: the gas could strip gaseous redox species from the water.

Before measuring Eh:

1. Record the type of reference-electrode system being used (fig. 6.5–1).
2. Check for the correct electrode filling solution. If working in very hot or boiling waters, change the reference electrode filling solution daily.
3. Keep the electrode surface brightly polished.

TECHNICAL NOTE: Temperature determines the Eh reference potential for a particular solution and electrode pair, and may affect the reversibility of the redox reactions, the magnitude of the exchange current, and the stability of the apparent redox potential reading. The observed potential of the system will drift until thermal equilibrium is established. **Thermal equilibrium can take longer than 30 minutes but it is essential before beginning the measurements.**

Measure the Eh and complete the field form (fig. 6.5–2):

1. Select an in situ or closed-system sampling method. Immerse the electrodes and temperature sensors in the sample water.
 - **In situ (or downhole)**—Lower the sensors to the depth desired and follow the manufacturer’s recommendations.
 - **Closed-system flow cell**—Check that the connections and sensor grommets do not leak, and that the water being pumped fills the flowthrough cell.
2. Allow the sensors to reach thermal equilibrium with the aqueous system being measured and record the time lapsed.
 - It is essential that platinum electrodes be flushed with large volumes of sample water to obtain reproducible values.
 - Record the pH and temperature of the sample water.
3. Switch the meter to the millivolt function.
 - Allow the reading to stabilize (± 5 mV).
 - Record the value and temperature (see the **TECHNICAL NOTE** that follows step 7, below).
 - **Stabilization should occur within 30 minutes.**
4. Take readings of the sample temperature and potential (in millivolts) every few minutes for the first 15 to 20 minutes.
 - It is best to stop the flow of the sample while the reading is being taken to prevent streaming-potential effects.
 - After 15 to 20 minutes, begin to record the time, temperature, and potential in plus or minus millivolts about every 10 minutes. Continue until 30 minutes have passed from the initial measurement and until the measurements indicate a constant potential.

5. After the measurements have been completed for the day, rinse the electrode(s) thoroughly with deionized water.

If field calibration is required for a study,

- a. Place the electrode(s) and other sensors in ZoBell's solution that has been equilibrated to the temperature of the aqueous system to be measured. The electrode(s) must not touch the container, and the solution must cover the reference junction.
 - b. Allow the electrode to reach thermal equilibrium (15 to 30 minutes).
 - c. Record the potential reading.
 - d. Follow steps 5 through 7 of the equipment test procedure in section 6.5.2.
6. Record all data and calculate Eh (see **EXAMPLE**, section 6.5.2). Fill out the Eh data record form for field measurements fig. 6.5–2).

7. **Quality control**—Repeat the measurement.

Eh Data Record		
Field Measurements		
	Field Eh	Field Eh ¹
1. Temperature and pH of system measured: T =	_____	_____
pH=	_____	_____
2. Time to thermal equilibration:		
Measurement began at	_____	_____
Measurement ended at	_____	_____
3. Measured potential of water system (mV): <i>emf</i> =	_____	_____
4. Reference electrode potential mV of ZoBell's		
at sample temperature: <i>E</i> _{ref} =	_____	_____
5. Calculate sample Eh: <i>emf</i> + <i>E</i> _{ref}		
(add step 3 + step 4):	Eh = _____	_____
6. Field measurements should agree within about 10 mV.		
Observations: _____		

¹The second measurement is necessary for quality control.

Figure 6.5–2. Eh data record: field measurements.

TECHNICAL NOTE: The response of the Eh measurement system may be considerably slower than that of the pH system and that response also may be asymmetrical: the time required for stabilization may be longer when moving from an oxidizing to reducing environment or vice versa. If the readings do not stabilize within about 30 minutes, record the potential and its drift; assume a single quantitative value is not possible. If an estimate of an asymptotic final (hypothetical) potential in such a drifting measurement is desired, refer to the method used by Whitfield (1974) and Thorstenson and others (1979).

6.5.3.A INTERFERENCES AND LIMITATIONS

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).

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.

6.5.3.B INTERPRETATION

A rigorous quantitative interpretation of an Eh measurement requires interactive access to an aqueous speciation code. Exercise caution when interpreting a measured Eh using the Nernst equation. The Nernst equation for the simple half-cell reaction ($M^I_{(aq)} = M^{II}_{(aq)} + e^-$) is

$$Eh = E^0 + 2.303RT/nF \log (a^{II}_{M(aq)} / a^I_{M(aq)})$$

where:

R = gas constant;

T = temperature, in degrees kelvin;

n = number of electrons in the half-cell reaction;

F = Faraday constant; and

$a^I_{M(aq)}$ and $a^{II}_{M(aq)}$ = thermodynamic activities of the free ions $M^I_{(aq)}$ and $M^{II}_{(aq)}$ and not simply the analytical concentrations of total M in oxidation states I and II, respectively.

Measurements of Eh are used to test and evaluate geochemical speciation models, particularly for suboxic and anoxic ground-water systems. Eh data can be useful for gaining insights on the evolution of water chemistry and for estimating the equilibrium behavior of multivalent elements relative to pH for an aqueous system. Eh can delineate qualitatively strong redox gradients; for example, those found in stratified lakes and rivers with an anaerobic zone, in an oxidized surface flow that becomes anaerobic after passing through stagnant organic-rich systems, and in mine-drainage discharges.

TROUBLESHOOTING 6.5.4

Contact the instrument manufacturer if the suggestions in table 6.5–4 fail to resolve the problem.

- ▶ Check the voltage of the batteries.
- ▶ Always start with good batteries in the instruments and carry spares.

Table 6.5–4. Troubleshooting guide for Eh measurement

[\pm , plus or minus; mV, millivolts; *emf*, electromotive force]

Symptom	Possible corrective action
Eh of ZoBell's solution exceeds theoretical by ± 5 mV	<p><u>Check meter operation:</u></p> <ul style="list-style-type: none"> • Use shorting lead to establish meter reading at zero mV. • Check/replace batteries. • Check against backup meter.
Excessive drift	
Erratic performance	
Poor response when using paired electrodes	<p><u>Check electrode operation:</u></p> <ul style="list-style-type: none"> • Check that electrode reference solution level is to the fill hole. • Plug questionable reference electrode into reference electrode jack and another reference electrode in good working order of the same type into the indicator electrode jack of the meter; immerse electrodes in a potassium chloride solution, record mV, rinse off and immerse electrodes in ZoBell's solution. The two mV readings should be 0 ± 5 mV. If using different electrodes (Ag:AgCl and Hg:HgCl₂), reading should be 44 ± 5 mV for a good reference electrode. • Polish platinum tip with mild abrasive (crocus cloth, hard eraser, or a 400–600-grit wet/dry Carborundum™ paper), rinse thoroughly with deionized water. Use a Kimwipe™ if these abrasives are not available. • Drain and refill reference electrolyte chamber. • Disconnect reference electrode. Drain and refill electrolyte chamber with correct filling solution. Wipe off connectors on electrode and meter. Use backup electrode to check the <i>emf</i>. • Read <i>emf</i> with fresh aliquot of ZoBell's solution; prepare fresh ZoBell's solution if possible. • Recondition electrode by cleaning with aqua regia and renewing filling solution—this is a last resort.

6.5.5 REPORTING


Report the calculated Eh in mV to two significant figures.

Potentials are reported to the nearest 10 mV, along with the temperature at which the measurement was made, the electrode system employed, and the pH at time of measurement.

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