

## MEASUREMENT 6.5.3

To obtain accurate results, it is necessary to prevent losses and gains of dissolved gases in solution. 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. 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.

Measure Eh in situ with a submersible instrument or use an airtight flowthrough system.

**First:**

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.**

***Next, 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 ( $\pm 5$  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 5–7 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).

<b>Eh Data Record</b>		
<b>Field Measurements</b>		
	Field Eh	Field Eh <sup>1</sup>
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: $E_{ref}$ = _____	_____	_____
5. Calculate sample Eh: $emf + E_{ref}$ (add step 3 + step 4): Eh = _____	_____	_____
6. Field measurements should agree within about 10 mV. Observations: _____		

<sup>1</sup>The second measurement is necessary for quality control.

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

## 7. Quality control—Repeat the measurement.

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).

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### 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, 1992).
- ▶ 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 electrode(s) contact with 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 a measurement of Eh 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 groundwater 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.