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_{ref} = 238 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_{ref} = 185.5 mV (saturated KCl, immersed with the platinum electrode in ZoBell's at 25°C) is the measured potential of the calomel ($Hg:HgCl_2$) electrode;

E° = 430 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 combination electrode[3,4]
	3*M* KCl[1]	3.5*M* KCl[2]	Saturated KCl[2]	3*M* KCl[2]	3.5*M* KCl[2]	4*M* 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

[1]Modified from Langmuir (1971).
[2]Modified from Bates (1973).
[3]Nordstrom (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.
[4]Orion™ manufacturer recommends that for sample solutions with total ionic strength exceeding 0.2 molar (for example, seawater), use a 4*M* 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 ($\pm$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.

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

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 mV.

b. Check table 6.5–2. The interpolated reference potential = 202 mV for Ag:AgCl–saturated KCl at 22°C.

c. From $Eh = emf + E_{ref}$

$$Eh\ (ZoBell's) = 238\ mV + 202\ mV = 440\ mV.$$

d. Check table 6.5–3. The test value of 440 mV is within ± 5 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_{ref}=	____________	____________
4. Calculate Eh of ZoBell's: Eh = *emf*+E_{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)	ΔEh=	____________	____________
7. Check: is ΔEh within ± 5 mV?	Observations:	________________________	

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