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ProcessProbe® ORP Sensor

For use in all industrial, process ORP (redox) measurement applications.

Sensor Specifications

ORP Range:	± 5000 mV
Sensing Tip:	Platinum band, 99.99% pure, 0.25 in OD x 0.1 in L
Temperature Range:*	0–105° C
Pressure Range:*	Up to 150 psig
Cable:	Dual Shielded, Low Noise Coax

*Varies depending upon model selected

Preparation for Use

1. Remove protective cap containing the storage solution (3.8 M KCl).
2. Save the storage boot for future use as a storage container and bulb protector when sensor is not in service. We recommend 3.8 M KCl as the storage solution.
3. **For first-time use after removing the storage boot:** Inspect the sensor for any signs of breakage or shipping damage and start with calibration procedures.
4. **For sensors with replaceable o-ring seals:** All o-rings require proper lubrication. We recommend use of **PARKER O LUBE** or equal for this purpose. Follow the instructions provided with lubricant. For best results we recommend that all o-rings be replaced whenever sensor is removed for service or inspection.

Caution: Hand-tighten only. It is not necessary to apply excessive torque to achieve a liquid tight installation. Severe twisting of the sensor housing could cause internal damage. If necessary, use wrench for removal only. For valve retractable sensors, refer to the SA877/SA878 Service Manual for assembly, installation and complete service instructions.

Calibration Procedure

1. Unlike pH sensors, the measurement half-cell of the ORP (redox) sensors undergo no zero-point or slope changes. Nevertheless, incorrect redox potentials may be occasionally measured and the cause of these errors is usually a contaminated Pt surface.

In such cases, the sensor may be regenerated by cleaning as described in the next section. To test the redox ProcessProbe's accuracy proceed with the following quinhydrone tests.

Caution: Quinhydrone is very toxic and should be handled by qualified technicians only. Handle with care and avoid ingesting. Avoid contact with bare skin. Dispose of the quinhydrone solutions per your local waste water regulations.

2. The oxidation-reduction potential of a quinhydrone solution is pH dependent. By saturating pH buffers with quinhydrone you can make stable mV standard solutions to use in testing your redox ProcessProbe. Ideal values for some common buffers (saturated with quinhydrone) are listed below:

7.00 pH	+86 mV
<u>4.01 pH</u>	<u>+263 mV</u>
$\Delta = 2.99 \text{ pH}$	$\Delta = 177 \text{ mV}$

3. Sensor construction and prior usage will make the actual magnitude of the first two test readings vary. The actual readings in the buffers could vary by $\pm 20 \text{ mV}$.

However, a clean redox ProcessProbe will give reproducible Δ values of $\Delta 173 \pm 4 \text{ mV}$. It is this Δ value that provides an indication of the functional performance of the sensor.

Procedure

1. Place 50–100 ml of pH 7.00 and 4.01 buffers in suitably sized beakers, stir about 0.2g/100 ml of quinhydrone into each buffer.

Note: The quinhydrone will not all dissolve. The intention here is to prepare a saturated solution. There should be a little of the powder undissolved.

2. Prepare the redox ProcessProbe for testing by cleaning the platinum surface with a liquid hand soap and soft toothbrush (do not scar or scratch the platinum surface). Consult factory prior to use of solvents or other cleaning agents. Rinse thoroughly with clean tap water.
3. Connect the ProcessProbe to a suitable pH meter, set to the millivolt scale.
4. Immerse the sensor in the pH 7.00 quinhydrone mixture. The meter should read between +70 and +110 mV.
5. Rinse the sensor thoroughly with clean tap water, and immerse it in the pH 4.01 quinhydrone mixture. The meter should now read between +240 and +280 mV.

Notes: This test verifies the function of the platinum combination redox (ORP) sensor by actual measurement of a known oxidation-reduction potential change. If a sensor responds adequately in this test (e.g. $\Delta 169$ to $\Delta 177 \text{ mV}$ between the 7 and 4 buffer quinhydrone mixtures) but the values fall outside of these ranges, it indicates a plugged reference junction or a contaminated reference internal solution.

The buffer quinhydrone mixtures will not remain useful for more than two hours since the quinhydrone decomposes slowly in contact with air. Dispose of this solution per local waste water regulations.

Cleaning a ProcessProbe® with Impaired Response

Used sensors which are physically intact can sometimes be restored to an improved level of performance. All sensors have a given useful lifespan depending on the conditions of use. One of the following procedures may prove helpful in restoring a used sensor.

1. **Initial Cleaning:** Wash with a solution of liquid detergent or enzyme detergent and warm water by gently scrubbing with a soft toothbrush or tissue. Follow with thorough rinse in DI or clean tap water.
2. **Inorganic Scale Deposits:** Dissolve deposit by immersion of the sensor's measurement tip in dilute hydrochloric acid for a few minutes followed by a thorough rinse with DI or clean tap water. Platinum bands can be polished with a fine grade of alumina (Al_2O_3) or some similarly fine polishing compound.
3. **Organic Oil or Grease Films:** If film is known to be soluble in a particular organic solvent which is not harmful to platinum or glass, wash it with this solvent. Repeat step 1 above. Depending on the extent of and/or grease contamination, it should be noted that the reference half-cell's ceramic liquid junction may be damaged beyond recovery.

Cleaning a ProcessProbe® (Cont.)

3. **Plugged or Dry Liquid Junction:** Remove contaminant with one of the above procedures, then soak in 3.8 M KCl solution for 30–45 minutes.

Notes:

- Do not permit sensor to dehydrate or dry out. Always keep in a wetted environment especially when not in service.
- Cracked or broken sensors are not repairable.
- Inspect cable and connector to ensure that the insulation is intact and that there are no signs of corrosion or contaminants on the metal components.

Storage

1. **Short Term:** Immerse the sensor measurement tip and liquid junction surface areas in 3.8 M KCl. If this solution is not available, use 4.01 pH buffer, clean tap water, or a sample of the process being measured to keep the sensor hydrated.
2. **Long Term:** Fill protective cap that the sensor was originally shipped in with a freshly prepared 3.8 M KCl solution and insert sensor. The sensor should be stored in an upright vertical position.

Oxidation-Reduction Potential Measurements with Redox ProcessProbes®

The redox sensors are designed for the measurement of the oxidation-reduction potential of an aqueous process medium or waste water.

The sensor is used in conjunction with a pH meter or other electro analytical instrumentation that can be set to read millivolts.

The redox probe is a combination sensor with a reference half-cell and platinum band measurement half-cell built into one body. Essentially, the measured redox potential is the EMF difference between the potential on the platinum band and the potential of the built-in reference half-cell.

The potential measured with the redox probe is proportional to the ratio of the concentration of the oxidized and reduced states of the elements and compounds that make up the test sample. The potential of the redox probe can be expressed by the general form of the Nernst equation:

Equation 1.

$$E = E_o + \frac{E_N}{N} \text{Log} \frac{[\text{Oxidant}]}{[\text{Reductant}]} \text{ at } 25^\circ \text{ C}$$

Where:

- E = The voltage potential observed with the redox ProcessProbe
- E_o = A constant characteristic of the system in question (mV)
- E_N = Nernst potential (59.2 mV at 25° C)
- N = The number of electrons reacting in the redox equation

Some work requires that the measured potential E be converted to E_h . The value E_h is the observed potential difference between the platinum band and a normal hydrogen sensor as the reference; (the potential of which is zero by definition). Since the normal hydrogen sensor is rarely used as a reference in actual measurements, the measured potential E will not be equal to E_h .

However, E_h can be calculated by adding algebraically the measured potential E and the standard potential, $E_{R'}$, of the reference sensor that is used for the sample measurement. The standard potential E_R is the difference between the measuring reference sensor and the normal hydrogen sensor at 25° C. Therefore:

Equation 2.

$$E_h = E + E_R$$

Where:

E_R = standard potential of the reference sensor.

Please note that the reference sensors used in the ProcessProbe series of combination sensors are the Ag-AgCl type utilizing a 3.8 M KCl electrolyte salt bridge. The standard potential E_R of the ProcessProbe series reference is + 202 mV at 25° C (see Table 1 for other temperatures).

Example:

If the potential E is measured with the redox ProcessProbe and is found to be 400 mV at 25° C, then the E_h (at 25° C) of the test sample is calculated as follows:

$$\begin{aligned} E_h &= E + E_R \\ E_h &= 400 \text{ mV} + 202 \text{ mV} \\ E_h &= 602 \text{ mV} \end{aligned}$$

Please note that the values E and E_h , and E_R , are all temperature dependent.

Use Table 1 for values of E_R at temperatures other than 25° C. These values are necessary to calculate E_h at temperatures other than 25° C with Equation 2.

Table 1
 E_R Values for the Redox ProcessProbe®

Temp.(°C)	E_R (mV)
15°	209
20°	206
25°	202
30°	198
35°	195
38°	193
40°	191

Table 2
Nernst Potentials (E_N) from 15° to 40° C

Temp.(°C)	E_N (mV)
15°	57.2
20°	58.2
25°	59.2
30°	60.1
35°	61.1
38°	61.7
40°	62.1

The actual magnitude of the potentials E or E_h of any particular oxidation-reduction system will depend on three things:

1. The constants of that system, E_o and N.
2. The temperature dependent values, E_N and E_R (see Tables 1 and 2).
3. The ratio of concentrations of the oxidants and reductants in the system.

In any reversible oxidation-reduction system the measured potential E and the calculated potential E_h are both functions of the temperature and of the ratio of concentrations of the oxidants and the reductants. Please note that if all measurements are done at the same temperature, the temperature dependent values become constants. Regardless of the initial magnitude of the values E and E_h , both values will become more positive when the concentration of the oxidant increases relative to the reductant (oxidizing intensity becomes greater).

Conversely, the values of E and E_h will become more negative when the concentration of the reductant increases relative to the oxidant (reducing intensity becomes greater).