

# Technical Reference Section: pH/ORP

Information in this section addresses frequently asked questions regarding pH and ORP and is provided as REFERENCE ONLY to supplement procedures and recommendations specifically outlined in individual product instruction manuals. All manuals, data sheets, and additional helpful information are available at [www.gfpiping.com](http://www.gfpiping.com).

## Definition of pH

pH is defined as the negative logarithm of the Hydrogen ion concentration in aqueous solutions. The common pH scale ranges from 0 to 14, with 7 being neutral water (H<sub>2</sub>O). At pH 7, Hydrogen ions (H<sup>+</sup>) exist in equal concentration to Hydroxyl ions (OH<sup>-</sup>). A solution is considered to be acidic if the

concentration of H<sup>+</sup> exceeds that of OH<sup>-</sup>, and is indicated by pH values below 7. Conversely, a solution is considered to be basic if the concentration of H<sup>+</sup> is less than that of OH<sup>-</sup>, and is indicated by pH values above 7.

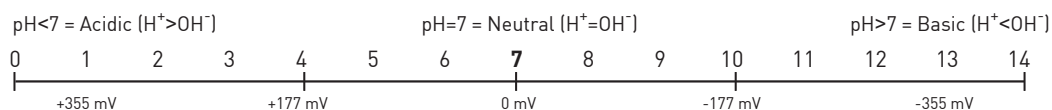
### Common Acids

1M HCl: 0.0 pH  
Sulfuric Acid: 0.3 pH  
Lemon Juice: 2.0 pH  
Vinegar: 3.0 pH  
Wine: 3.5 pH  
Beer: 4.5 pH  
Milk: 6.0 pH

### Common Bases

Egg Whites: 7.5 pH  
Seawater: 8.0 pH  
Sodium Bicarbonate: 8.4 pH  
Ammonia: 11.6 pH  
Photo Developer: 12.0 pH  
0.1M NaOH: 13.0 pH  
Lye: 14.0 pH

## pH Scale



(Theoretical: 59.16 mV/pH @ 25 °C)

## Definition of ORP

ORP is an abbreviation for **O**xidation-**R**eduction **P**otential. Oxidation is a term used to denote the occurrence of a molecule losing an electron. Reduction occurs as a molecule gains an electron. The "potential" is simply an indication of a solution's propensity to contribute or accept electrons. ORP reactions (sometimes referred to as REDOX) always take place simultaneously. There is never oxidation without reduction, and ORP electrodes are used to detect electrons exchanged by molecules as these reactions occur.

Both pH and ORP electrodes produce voltages that depend on the solutions in contact with their sensing ends. Most pH electrodes, including the Signet brand, are designed to produce 0 mV at pH 7, positive mV below pH 7 (associated with the charge of the Hydrogen ion, H<sup>+</sup>) and negative mV above pH 7 (associated with the charge of the Hydroxyl ion, OH<sup>-</sup>). According to the Nernst Equation, the interval between each pH unit is approximately 59.16 mV at 25 °C. This "raw" output is converted to a pH value by the display instrument.

The ORP scale is typically -1000 mV to +1000 mV, and the electrodes produce these values directly.

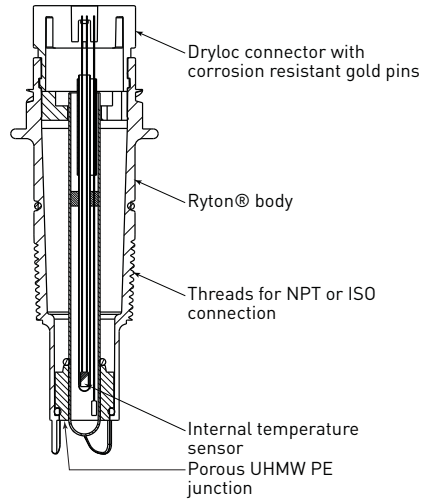
Whereas pH is a specific measure of the Hydrogen ion concentration in solution, ORP only provides relative measures of chemicals and cannot discriminate one from another. Although non-specific, it is a very useful and inexpensive method of monitoring and controlling the activity of such compounds as chlorine, ozone, bromine, cyanide, chromate, and many other chemical reactions.

It is worth noting that Temperature Compensation, very important for accurate pH measurement, is NOT used in ORP measurements. Temperature does indeed affect the reactionary potential of all chemicals, some to a greater extent than others. But even if the affects of temperature could be precisely known in all of the many different REDOX reactions, it would not be desirable to remove them from the measurement. True ORP is the direct measurement of electrons in transit during Oxidation-Reduction reactions, regardless of temperature.

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## Principle of Operation

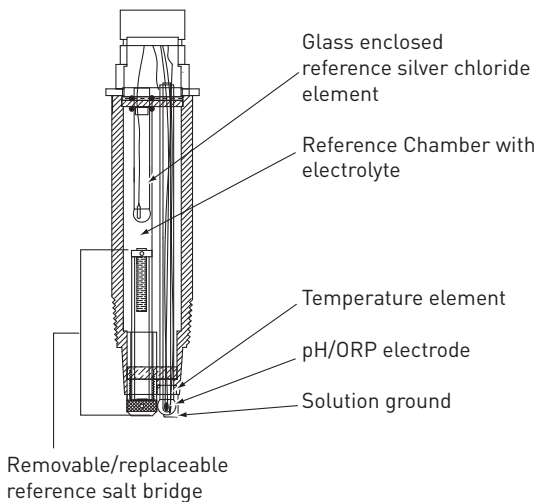
Cutaway of 2724 pH electrode



Signet offers two different groups of Standard pH/ORP Electrode Models: Models 2724-2726 and 2774-2777

- **Standard pH/ORP** electrodes are also commonly called combination electrodes; a pH/ORP measuring electrode and a reference measuring electrode are combined in a single body. The pH/ORP sensor measures the amount of hydrogen ions in the liquid. The pH signal is measured against the steady reference signal. Various chemical elements leaching through the porous reference junction can react with the reference electrolyte, dilute the electrolyte solution, or attack the silver chloride element; in either case, it will disturb the steady reference signal. Stray electrical currents will also affect the steady reference signal. A temperature element is also built into the pH combination electrode. Instruments interpret the temperature compensated pH signal into a pH reading at 25 °C (77 °F). ORP values are not temperature dependent; Signet ORP sensors do not have temperature compensation.

Cutaway of 2766 pH electrode



Signet offers one group of Differential pH/ORP Electrodes: Models 2764-2767

- **Differential pH/ORP** electrodes function similar to the standard (combination) electrodes, but the reference design is modified and there is a third electrode, the solution ground. The pH and reference electrodes are measured against the solution ground. The solution ground drains stray currents away from the reference element, hence maintaining a steady signal at all times. The reference salt bridge slows or stops various chemical elements from leaching into the reference chamber. Chemicals that leach in may dilute the electrolyte but will not react with the glass-encased reference silver chloride element. The reference electrolyte can be refreshed if it is diluted or depleted. The temperature element is embedded in the pH/ORP electrode for an extremely quick response.

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## Standard versus Differential pH/ORP Electrodes:

Signet offers what is called combination pH/ORP electrodes; a combination of three or four electrodes built into one common body that measures the pH or ORP of the solutions. These electrodes are the pH/ORP sensing element, temperature sensing element (pH only), the reference, and sometimes a solution ground. An electrical path between the process solution, reference electrode, and the pH/ORP sensing electrode must always be present to complete the measuring circuit. When the circuit is broken or interrupted, the result is a faulty reading. There are only a few things in a chemical process that would affect the glass-sensing element. These include concentrations of HF, constant high temperatures, and particles that can break the glass.

On the other hand, there are many problems that can occur with the reference electrode. The reference silver chloride sensing element (wire) is exposed to the process liquid via the primary porous reference junction, which is in constant contact with the process and allows liquid to pass through to the reference electrolyte. Because of the direct contact with the process liquid, the reference electrolyte and reference silver chloride sensing element can react with chemicals in the process. Many application liquids do not chemically react with the reference and therefore a standard electrode will perform well in this scenario. However, there are other process chemicals that will easily attack the reference and therefore, a differential style electrode should be used. There are three advantages of the differential electrode:

1. If the process chemicals attack the KCl electrolyte, the reference electrolyte chamber is refillable.
2. If the reference junction becomes clogged by chemical reactions between the KCl and the process chemicals, the reference salt bridge is replaceable.
3. If there are stray currents or if there are process chemicals that attack the silver chloride wire in the standard electrodes, it will not attack it in the differential electrode because the wire is encased in a glass electrode.

A general rule of thumb is to use a differential electrode if you have mercury, copper, lead, chlorate, bromine, iodine, cyanide, or sulfide compounds in the process liquid. Differential electrodes may also be useful in processes where oil, grease, and dirt build up on the reference junction because it is easily replaced.

See Model 2764-2767 Differential pH/ORP catalog pages for more information on standard versus differential electrodes.

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## Important Application Tips

- It is important that the sensing end of pH and ORP electrodes remain wet, for they may be permanently damaged if allowed to dehydrate. This is true for both in-line and submersible installation configurations. However, be careful to keep the electrical interconnection between electrode and preamplifier dry and clean at all times. Moisture in this area can also cause permanent damage.
- pH control is best when performed in a tank. This is especially true in neutralization applications since it is very important for reagents to mix thoroughly with waste fluids, and to be allowed adequate time for the reactions to occur. Limiting adjustments to fewer than 3 pH units per stage, and sizing tanks to provide at least 10 minutes retention time, will increase the probability of producing safe effluents.
- For bulb-style pH and ORP electrodes, significant natural self-cleaning by turbulent eddies is achieved at velocities of 1.5 m/s or more (5 ft/s). Flat surface electrodes get adequate self-cleaning at velocities of 0.3 to 0.6 m/s (1 to 2 ft/s). In all cases, exposure to velocities greater than 3 m/s (10 ft/s) can cause excessive measurement noise and electrode wear and should be avoided.
- The aging of pH and ORP electrodes (i.e., reference depletion and decreased glass sensitivity) results from a series of chemical reactions. And as a general rule, the rates of chemical reactions double with every increase of 10 °C (50 °F). This means shorter life expectancy for all pH and ORP electrodes as application temperatures increase.
- HF acid and strong caustics etch pH glass. High concentrations, especially at high temperatures, destroy electrodes quickly. For applications containing trace quantities of HF (<2%), use the Signet 2726-HF electrode. This electrode has a polymeric constituent in the pH glass that resists attack by HF and extends the service life considerably over “normal” electrodes.
- In applications where process temperatures will drop below 10 °C (50 °F), use the bulb-style electrodes in place of the Flat style electrode. This is a function of the electrical impedance of the glass that increases dramatically as temperature decreases.
- Proper electrode placement within a tank is also very important. Electrodes should be mounted in well-mixed areas, away from reagent and waste introduction. It is usually advisable to position the electrode near the discharge outlet of the tank.
- In-line pH control is not recommended because it is very difficult to determine the amounts of reagent necessary to achieve a desired reaction if both pH and flow are variables. However, in-line pH monitoring is very common and useful.

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## Maintenance Tips

- Cleaning pH and ORP electrodes and calibrating the systems should be done regularly. The required frequency is application-dependent, but once/week for cleaning, and twice/month for calibration is recommended.
- Isopropyl alcohol may be used for removing mild grease and oils from the pH sensitive glass or from the metallic tips of ORP electrodes. Use 5% HCl on porous reference junctions clogged with hard water deposits, or other solvents/detergents as necessary. Always consider the electrode's materials of construction when selecting a cleanser.
- The purpose of calibration is to compensate the system for the continual changes occurring within the electrodes. Like batteries, all pH and ORP electrodes eventually deplete and must be replaced. A good time to determine the condition of an electrode is after cleaning and during calibration. Note the mV readings in pH buffers and replace the electrode if its actual mV output differs more than 50 mV from these theoretical values: pH 7 = 0 mV, pH 4 = +177 mV, pH 10 = -177 mV. Replace an ORP electrode if its actual mV output differs more than 50 mV from the theoretical values in the table below:

### ORP Values of Standard pH Buffers Saturated with Quinhydrone

	pH4			pH7		
Temperature (°C)	20	<b>25</b>	30	20	<b>25</b>	30
ORP Value (mV)	268	<b>264</b>	258	92	<b>87</b>	79

- The typical shelf-life recommendation for Signet pH and ORP electrodes is 12 months at 25 °C (77 °F).
- Refrigeration will extend this period, but do not allow them to freeze! Expansion of internal solutions during freezing can cause permanent damage to the electrodes.
- The risk of putting older electrodes into service is the possible disappointment of shorter than expected service-life. All Signet pH and ORP electrodes are marked with date codes to identify the date of manufacture.