# +GF+ SIGNET Analytical Technical Reference Section

## Simplified Analytical Sensing Technology

+GF+ SIGNET is committed to manufacturing products that simplify the installation, operation and maintenance of analytical measurement systems, and our creative solutions have offered customers the benefit of reduced cost of ownership for over 35 years. The growing line of +GF+ SIGNET analytical products today includes pH, ORP, Conductivity/Resistivity, Salinity, Pressure and Temperature.

Information in this section addresses frequently asked questions regarding pH & 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.gfsignet.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 (H2O). At pH 7, Hydrogen ions (H+) exist in equal concentration to Hydroxyl ions (OH-). A solution is considered to be acidic if the concentration of H+ exceeds that of OH-, and is indicated by pH values below 7. Conversely, a solution is considered to be basic if the concentration of H+ is less than that of OH-, and is indicated by pH values above 7.

## pH Scale

pH < 7 = Acidic (H+ > OH-) — pH = 7 = Neutral (H+ = OH-) — pH > 7 = Basic (H+ < OH-)

| 0 | 1 | 2 | 3 | 4 | 5 | 6 | **7** | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| +355 mV | | | | +177 mV | | | 0 mV | | | -177 mV | | | | -355 mV |

(Theoretical: 59.16 mV/pH @ 25°C)

| **Common Acids** | **Common Bases** |
|---|---|
| 1M HCl: 0.0 pH | Egg Whites: 7.5 pH |
| Sulfuric Acid: 0.3 pH | Seawater: 8.0 pH |
| Lemon Juice: 2.0 pH | Sodium Bicarbonate: 8.4 pH |
| Vinegar: 3.0 pH | Ammonia: 11.6 pH |
| Wine: 3.5 pH | Photo Developer: 12.0 pH |
| Beer: 4.5 pH | 0.1M Sodium Hydroxide: 13.0 pH |
| Milk: 6.0 pH | Lye: 14.0 pH |

## 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, +GF+ SIGNET’s included, are designed to produce 0 mV at pH 7, positive mV below pH 7 (associated with the charge of the Hydrogen ion, H+) and negative mV above pH 7 (associated with the charge of the Hydroxyl ion, OH-). 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.

# Installation & 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 sensor and preamplifier dry and clean at all times. Moisture in this area can also cause permanent damage.

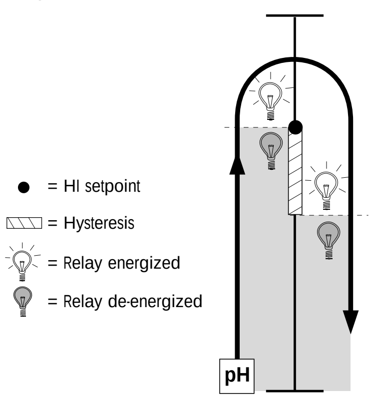
Most pH and ORP electrodes should be installed vertically, ±30°, so the internal solutions remain in contact with the sensing ends. Sensors are available from +GF+ SIGNET that allow horizontal or inverted installation. Consult the factory for details.

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.

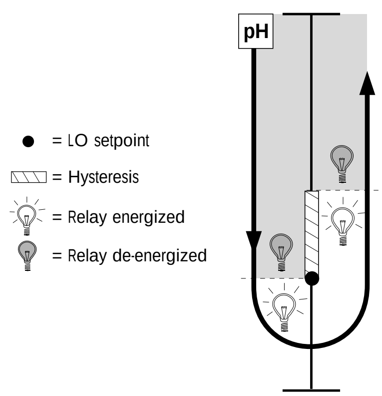
Proper electrode placement within a tank is also very important. Sensors should be mounted in well-mixed areas, away from reagent and waste introduction. It is usually advisable to position the sensor near the discharge outlet of the tank.

The two most common methods of controlling pH and ORP (and Conductivity) are “on/off” and “proportional” control. In on/off control, relay setpoints are defined as either high or low limits on the process variable. When the measurement value reaches a limit the relay is energized, typically for the purpose of opening a valve or starting a pump to introduce a chemical reagent to the process. This should cause the measurement value to change in the direction of the setpoint as shown in these on/off control diagrams:

**High limit on/off relay control**



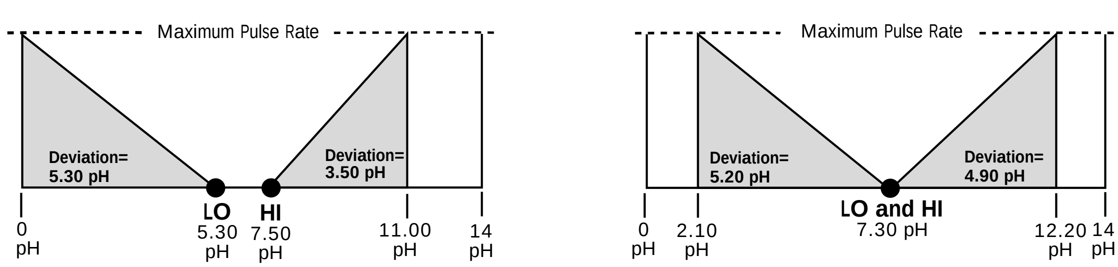

**Low limit on/off control**




Notice the relay will not de-energize until the setpoint is exceeded by the hysteresis value. This is a programmable value and is primarily used to prevent ”relay chatter”, which occurs if a relay is set to energize and de-energize at the same value. Because of hysteresis, and because reagent delivery is fairly constant while the relay is energized, a condition known as “overshoot” is inherent to the on/off control method. Overshoot refers to the introduction of more chemical reagent than is absolutely necessary for achieving a desired adjustment to the process value, and can be expensive over time.

Proportional control is a popular alternative to the on/off control method. This configuration controls variable-rate metering pumps to reduce overshoot and improve precision. Establishing a proportional control scenario requires the selection of setpoint(s), deviation range(s) and maximum pulse rates. The example shown here illustrates how two relays in ”pulse mode” can be used to proportionally control pH within a desired range, or to a single setpoint. Of course, a single relay in proportional pulse mode can be used to establish a high or low limit and will also reduce overshoot.

**Dual proportional pulse relay control**



Metering pumps are idle at and between setpoints. When a setpoint is exceeded, the pump begins delivering reagent at a rate proportional to the difference between the measurement value and the setpoint. The programmed deviation value defines how quickly the maximum pulse rate is reached. Depending on the input requirements of the metering pump, proportional control can also be accomplished with scaleable 4 to 20 mA outputs instead of pulsing relays or open collectors.

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.

Observe flow velocity limitations for in-line installations: 5 fps for flat-style and 4 fps for bulb-style electrodes. Fluctuating pH readings and reduced sensor life can occur at higher velocities.

Simply stated, 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. 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 +GF+ SIGNET 3-2714-HF sensor. This sensor 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, or 50 °F, use the 3-2716 bulb-style or 3-2714-HF flat-style electrodes in place of the 3-2714 electrode. This is a function of the electrical impedance of the glass that increases dramatically as temperature decreases.

## Maintenance Tips

Cleaning pH and ORP sensors 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 good for a start.

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 sensor’s materials of construction when selecting a cleanser.

The purpose of calibration is to compensate the system for the continual changes occurring within the sensors. Like batteries, all pH and ORP electrodes eventually deplete and must be replaced. A good time to determine the condition of a sensor 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 <u>Saturated</u> with Quinhydrone**

| | **pH4** | | | **pH7** | | |
|---|---|---|---|---|---|---|
| **Temperature (°C)** | 20 | **25** | 30 | 20 | **25** | 30 |
| **ORP Value (mV)** | 268 | **264** | 258 | 92 | **87** | 79 |

The typical shelf-life recommendation for pH and ORP sensors from +GF+ SIGNET is 12 months at 25 °C. 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 sensors into service is the possible disappointment of shorter than expected service-life. All +GF+ SIGNET pH and ORP electrodes are marked with date codes to identify the date they were manufactured.