APPLICATION NOTE

Differential pH Design Overcomes Common pH Sensor Challenges

Conventional pH Measurement Methodology

All pH measurement systems operate on the principle of an electrochemical cell; that is, when two dissimilar conductors are placed in an electrolyte (a liquid capable of carrying a charge) they will develop a potential between them. The magnitude of this potential is dependent on the characteristics of the conductors and the electrolyte. The measurement of pH depends on a phenomenon associated with a particular kind of glass which responds to the hydrogen ions that are present. A conventional pH sensor is basically a high impedance battery. The high impedance results from one of the battery plates being "glass coated." A conventional pH measurement system, shown in Figure 1, is comprised of a pH glass electrode and a pH reference electrode.

The glass electrode, common to all systems, is designated E1. The other half cell, the reference electrode, is designated E2. The reference electrode is a closed cylinder, usually made of plastic that contains a silver wire coated with AgCI (silver chloride), and a filling solution, gel, or crystals of saturated potassium chloride (KCl). The electrical circuit to the process being measured is completed through a porous plug junction in the tip of the electrode. The junction may be ceramic, wood, Teflon, or a small hole. These liquid junctions provide an electrical path but prevent the reference electrode fill solution from flowing freely into the process. The output of the cell is:

$$(pH - pC1) = E1 - E2$$

The pH and pC1 components are the logarithms of hydrogen and chloride ion concentration, respectively. If pC1 is constant, then:

$$pH = K\ (E1 - E2)$$

Therefore, the output of the cell is proportional to a constant (K) times the potential of the glass electrode (E1), which is a function of the hydrogen ion concentration, less the potential of the reference electrode (E2), which is a function of its chloride ion concentration. Since pH measurement is the negative logarithm of hydrogen ion concentration, it becomes apparent that the accuracy of such a cell depends on the constancy of the potential of the reference electrode.

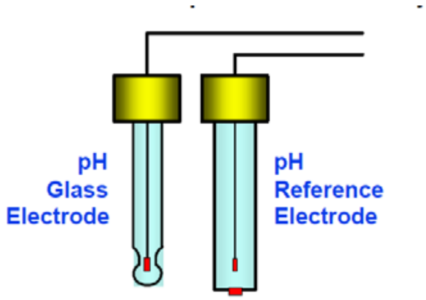

Figure 1: Conventional pH Measurement System

Conventional pH System Weaknesses

A conventional pH measurement system has several weaknesses. One shortcoming is due to the dependence of unbuffered chloride ion concentration in the reference electrode. Any contamination of this KCl fill solution will cause error. Consider the case of the reference electrode in clear water. Even in as mild an environment as water, chloride ions will migrate out of the reference electrode and water will migrate into the electrode, diluting the reference electrode fill solution. A dilution of 100 to 1 can cause a possible measurement shift of 2 full pH units! This infers that long before the reference electrode solution becomes diluted, the error becomes unacceptable. When an unbuffered solution is used in a conventional reference electrode, any dilution, no matter how slight, represents some error, and relatively minor dilutions represent substantial error.

The second shortcoming of a conventional pH measurement system is that, since chloride ion concentration cannot be kept constant, it is a practical necessity to provide the means to occasionally replenish the KCl fill solution. Such replenishment requires opening the sensor to add a gel, crystals, or a solution, or to replace a throwaway style reference electrode.

A pH sensor, which is always immersed in the process, contains electronics that must be kept dry, and requires a means for maintenance access. These requirements make the sensor very vulnerable to leakage. Mechanically, the sensor usually has machined surfaces and O-rings or other gasketed seals. Such construction is relatively expensive and does not positively preclude the possibility of leaks. When process fluid leaks into a sensor, it generally destroys the entire sensor which then must be replaced.

Understanding the third major weakness of a conventional pH measurement system requires an overview of the total system (sensor and analyzer). The sensor, normally used in a vessel or pipe, makes electrical contact through the vessel or pipe and its contents to an earth ground. The difference in the earth potential to which the vessel or pipe is connected and the earth potential to which the analyzer is connected can be represented as a ground loop voltage source. By Ohm's Law, most of that ground loop current will flow through the lowest impedance path of the sensor. Since the glass electrode has extremely high impedance, essentially all of the ground loop current flows through the reference electrode.

In practical applications, it is not uncommon to find that the chemical makeup of the solution being measured is such that it leaves some precipitate on the sensor elements. Any precipitate coating on the reference electrode creates a resistance in the path of the ground loop current. This is the fourth weakness of a conventional system. According to Ohm's Law, there will be a voltage drop across this resistance. The measurement system cannot distinguish this voltage change from a voltage change caused by a change in pH. Consequently, the voltage drop due to ground loop current causes a measurement error that is proportional to the magnitude of the ground loop current and the added resistance of the reference electrode coating.

Summary of Weaknesses

- Potassium chloride fill solution used in the reference electrode cannot be buffered. Thus, any contamination or dilution of this solution will result in relatively large measurement errors.

- Changes in the fill solution necessitate dismantling the sensor to replace the reference electrode. The result is more downtime and greater risk of glass breakage. Additionally, the need to access the reference electrode makes the sensor's mechanical design inherently more complex, resulting in higher initial cost and greater vulnerability to leakage.

- All ground loop current flows through the reference electrode, causing measurement error that is proportional to the magnitude of the current.

- Precipitate deposited from the process solution onto the reference electrode causes errors in measurement, due to ground loop voltage drop across the resistance of the precipitate.

Hach's Differential Electrode Technique, using our field-proven Standard Electrode, overcomes all of these shortcomings.

The Differential Electrode Technique

Rather than a reference electrode in KCl solution, the Hach Differential Electrode Technique uses two glass electrodes to make the measurement differentially with respect to a third metal electrode. The Standard Electrode consists of a glass electrode in a chamber which is filled with a concentrated, buffered solution of pH 7. This inner chamber makes electrical contact with the process through a double junction salt bridge. The second glass electrode is exposed to the process.

The Standard Electrode assembly is shown as E2 in Figure 2. The glass electrode in this assembly is kept in a constant pH environment. As the figure shows, the electrode is contained within a chamber filled with a 7 buffer (standard cell solution). The inner chamber makes electrochemical contact with a salt bridge chamber through a ceramic plug. The use of a second glass electrode to create a standard cell permits the use of a buffer solution which, by definition, resists pH change.

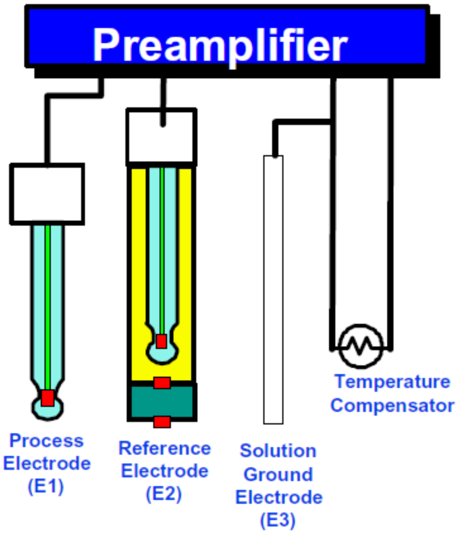

Figure 2: The Hach Differential Electrode Technique

A unity gain amplifier amplifies the output of each electrode to reduce the impedance of the system. The output of the first unity gain amplifier is the voltage of the process electrode (E1) minus the voltage of the metal, solution ground electrode (E3). The output of the second unity gain amplifier is the voltage of the Standard Electrode (E2) minus the voltage of the metal, solution ground electrode. The circuitry of the analyzer subtracts the outputs of the unity gain amplifiers, canceling the E3 term.

$$pH = K [(E1 - E3) - (E2 - E3)] = K [E1 - E2]$$

Benefits of Differential Electrode Technique

The Hach Differential Electrode Technique system does not depend on a reference electrode or KCl solution. The Hach Standard Electrode maintains its pH level regardless of substantial dilution. A dilution of the Hach Standard Electrode to 100 to 1 represents only a 0.05 pH shift! This is a very favorable comparison with the shift of 2 full pH units in the conventional pH measurement system example previously described.

The associated chambers contained in the Standard Electrode are sealed, and the only entrance from chamber to chamber is through the tight ceramic junctions which provide electrical contact to the solution being measured, thereby completing the circuit. Any contaminant that could find its way into the inner chamber of this assembly must first enter through the outer junction. It is apparent from this configuration that it is extremely unlikely that any appreciable amounts of contaminant could find its way to the inner chamber. If this were to occur, however, the inner chamber is filled with a buffer that could receive a dilution upwards of 100 to 1, with essentially no effect on the pH environment of the Standard Electrode.

Since the Hach Standard Electrode is comprised of a sealed glass measuring electrode, the silver/silver chloride wire cannot be contaminated. Also, the standard cell solution contained in the Standard Electrode usually lasts for a year or more in typical process and wastewater applications. The salt bridge and standard cell solution can be replaced periodically at a very low cost, making the Hach Differential sensor economical to maintain. Furthermore, the Hach sensor is constructed with a specially designed housing into which all of its components are inserted. Then the assembly is completely encapsulated. The combination of all of these features provides a vastly superior pH sensor, available at the lowest cost of ownership, with not only higher performance, but also unparalleled reliability due to its simplified construction.

Tests confirm that, due to the inherent stability of the Standard Electrode, the Hach Differential sensor is very stable over a wide spectrum of applications.

The Hach Differential Electrode Technique also provides a unique way to bypass ground loop currents that would otherwise cause measurement error. The Hach Differential sensor uses two glass electrodes to make the measurement differentially with respect to a third metal ground electrode, purposely eliminating the conventional reference electrode.

One of the shortcomings of conventional systems described earlier is the effect of ground loop currents. In a measurement system using a Hach sensor, ground loop currents flow through the path of least resistance, which is through the low impedance metal ground electrode. Any precipitate build-up on this electrode can be the source of a voltage drop. However, this voltage simply modifies E3, but as the earlier equation shows, E3 is mathematically cancelled, and does not cause an error in the pH measurement.

Furthermore, any resistance that occurs due to precipitate forming on the salt bridge of a Hach sensor is in series with a high impedance glass electrode. The effect of such precipitate resistance is minimal. On a conventional reference electrode, any precipitate resistance will affect the measurement because it is in series with a low impedance electrode. For these reasons, the Hach Differential sensor will provide measurements of undiminished accuracy over far longer periods of time than a conventional sensor.

By its defined function, the unity gain amplifier associated with each electrode (Figure 2) provides a millivolt output that is equal to the millivolt input. Its sole purpose is to reduce the impedance of the system. The 50 megohms impedance of a glass electrode appears as one-tenth ohm at the output of the unity gain amplifiers. These amplifiers are very reliable, enabling them to be imbedded in the sensor to provide a pH measurement system that acts as a relatively low impedance source. This allows for a separation distance between the analyzer and sensor of up to 3000 feet.

Summary of Benefits

The patented Hach Differential Electrode Technique is better by design:

Double-junction salt bridge of the Hach Standard Electrode makes it extremely unlikely that an appreciable amount of contaminant can find its way to the inner chamber. In addition, the nature of the Standard Electrode buffer is such that a 100 to 1 dilution would represent a change in the measurement of only 0.05 pH. With a conventional system, a similar level of dilution could cause a shift of two full pH units.

The Hach Differential sensor is a simple and economical encapsulated sensor with a removable salt bridge to provide access to the Standard Electrode buffer while sealing the sensor preamplifier from moisture.

Since ground loop currents do not pass through the Standard Electrode in the Hach Differential sensor, the reference signal is not affected by precipitate buildup on the reference components of the sensor.

The Hach Differential pH Sensor provides a definitive solution to the problems common with conventional systems: errors due to reference contamination, and errors due to precipitate build-up on the sensor. Also, the Hach Differential sensor provides a unique solution to the third shortcoming of conventional systems. That is, the need for a sensor which can be easily dismantled.

All Hach Differential pH sensors are manufactured so that the double junction salt bridge and the Standard Electrode buffer may be removed and replaced in the field.

Compared to conventional techniques, the patented Differential Electrode Technique provides measurements of greater stability over longer periods of time with less downtime and maintenance.

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