Application Note

THORNTON
Leading Pure Water Analytics

pH Measurement
In Low Conductivity Samples

Care is needed in the selection and installation of sensors for obtaining reliable pH measurements in water samples.

Power plant cycle chemistry guidelines and standards specify narrow ranges of pH to minimize corrosion of highly valuable components. In addition, makeup water treatment systems using two-pass reverse osmosis optimize performance by careful control of pH between passes. In both of these applications, pH must be measured accurately under the difficult conditions of low conductivity.

Background

pH measurements in high purity water must be made on side-stream samples in conductive flow through housings with discharge to open drain at atmospheric pressure. This ensures a sample uncontaminated by contact with air and minimal, constant sample pressure at the reference electrode diaphragm or junction—the primary source of instability in this measurement.

A stainless steel housing is typically used to shield the measurement from electrical noise. The side stream sample line should have a very small diameter to minimize sample delays at the low flows needed for the measurement and to minimize waste of costly high purity water. Measurement becomes more difficult as sample water purity increases (as conductivity decreases below 50 µS/cm). Under these conditions the electrical resistance between the glass measuring membrane and the reference electrode rises and the potential at the reference junction/diaphragm can become more variable.

Streaming potentials or static charges generated at the surfaces of flow housings, electrodes, etc. increase. In general, the measurement becomes noisier.

In addition, a significant offset may occur between buffer calibration and high purity measurements due to the large difference of ionic strength between these two solutions and the effect it has on the reference junction/diaphragm potential.

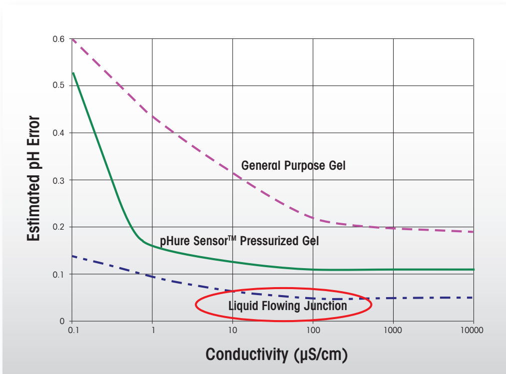
A further consideration is the sample flowrate vs. flow housing volume. With a relatively large volume housing (as needed to hold separate measuring, reference and temperature compensator elements), any corrosion product or ion exchange resin particles in the sample tend to settle and accumulate in the flow housing where they can absorb and desorb ionic materials. The resulting delayed response can be detrimental to performance and accuracy.

Alternatively, an electrode system that has measuring, reference and temperature compensator elements built into a single probe can be used with a very low volume housing that prevents particles from accumulating because they are carried out with the sample flow. As a result, a much faster response is maintained without frequent cleaning.

METTLER TOLEDO

Options

In addition to the basics of a sealed, low volume, conductive flow housing and single probe electrode, there are a variety of reference electrode systems available. These include gel filled, pressurized gel filled and liquid electrolyte filled. The relative performance for each of these reference electrodes is illustrated in the graph below.

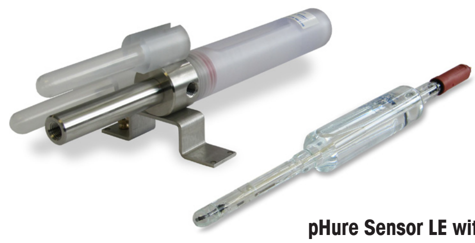


Gel-filled electrodes are not suitable for high purity water because the diaphragm/junction potential is so strongly influenced by the type of sample, resulting in an offset of 0.5 pH or more between calibration and measurement in high purity water.

Pressurized gel-filled electrodes provide more stability of the reference diaphragm/junction potential by forcing a small amount of potassium chloride gel through it. The METTLER TOLEDO Thornton pHure Sensor™ system offers this type of electrode. It requires no maintenance other than occasional calibration throughout its one-year life.

pHure Sensor with pressurized gel-filled reference system

Liquid electrolyte electrodes provide the highest accuracy of measurement by maintaining a steady flow of liquid electrolyte through the junction/diaphragm. It requires refilling the liquid electrolyte periodically and can have a life of several years. The METTLER TOLEDO Thornton pHure Sensor™ LE has this capability, plus it includes convenient buffer calibration containers built-in.



pHure Sensor LE with liquid electrolyte reference system

Intelligent Sensor Management

METTLER TOLEDO Thornton pHure Sensor electrodes are available with Intelligent Sensor Management (ISM®). This technology offers a number of valuable features including; fast error-free startup with Plug and Measure, embedded measurement circuitry for greater signal integrity, on-board storing of factory and user calibration data.

pHure Sensors conform to ASTM Standard D5128, Test Method for On-Line pH Measurement of Water of Low Conductivity.

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