

"Flow Sensitivity of High Purity Water Measurements"



Guest Article - by David M. Gray

High purity pH and conductivity measurements are occasionally observed to show a flow sensitivity. This raises many questions and lowers confidence in on-line measurements. To answer such questions, there are at least three areas to consider: ionization, sampling and sensor effects.

Ionization. First of all, is pH or conductivity inherently dependent on flow rate? In theory, flow itself does not cause change in ionic concentration. Movement of a sample under moderate conditions has no effect on ionization - which determines these parameters. It only affects the turbulence of the sample. There is no inherent flow dependence. However, there can be secondary factors, for example, where flow affects sample temperature, which influences ionization. For this, proper temperature control and high purity temperature compensation can help.

Sampling. In real life sampling systems with numerous fittings, crevices and corrosion product deposits, flow rate changes can have a significant effect on the adsorption and desorption of ions at these complex surfaces. Thus the actual ionic content may be affected by flow changes, especially in dirty sample lines. Such lines can behave somewhat like ion chromatographs, with various ions adsorbing and desorbing along the length. Response times can be longer and more variable than simple volume divided by flow rate calculations would suggest. Flow rates will certainly affect the ion transport.

EPRI studies have cited the need for fairly high flow velocities near 6 ft/sec in sample lines to minimize deposition of solids. This corresponds to a flow of 1200 mL/min in typical 1/4" OD tubing. This scouring action can keep the sample lines clean and yield a more predictable response. While this high flow rate is needed for the length of the sample line, individual sensors and analyzers may have lower flow requirements and necessitate bypassing a portion of the sample.

Conductivity Cells. Conductivity sensors can be influenced by flow. In particular, exceeding flow rate specifications of the old glass and platinum leaf-type cells can bend the electrodes, change the cell constant and cause a permanent error in subsequent readings. This type of low constant cell has a high surface area with tight

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dimensions, and requires a great deal of rinsing to purge accumulated ionic contamination. Thus its down scale response is very slow and flow-dependent. Slow, flow-dependent down scale response can be true of other cell designs, but to a considerably lesser extent.

Extremely low flows are to be avoided since high purity water is quite aggressive at dissolving anything available. Maintaining sample integrity requires that it move fast enough that accumulation of dissolved anything available. Maintaining sample integrity requires that it move fast enough that accumulation of dissolved ions within the sampling system is insignificant. There is a preference for higher flow rates to conductivity cells, to several hundred mL/min, which is compatible with most modern cell designs.

pH Electrodes. pH sensors are susceptible to flow dependence from two basic sources: Streaming potentials and reference junction potentials. High purity water flowing along insulating surfaces builds up static charges called streaming potentials. When this occurs between pH measuring and reference electrodes, it causes flow-dependent interference since pH measurement is based on the millivolt signal between electrodes. Such streaming potentials are eliminated by using a conductive (stainless steel) flow housing and relatively low flow rates - near 100 mL/min. Greatest stability is usually obtained with the flow chamber earth grounded, although there are exceptions where the available ground actually contributes electrical noise. Concentric, symmetrical combination pH electrodes with the reference effects by reducing the distance over which potential gradients can develop.

Reference junction potentials occur where the reference electrode makes contact with the sample. The high concentration of electrolyte inside the electrode contacts the pure water sample and develops a small potential. The more consistent these conditions can be held, the more consistent the junction potential and the better the ability to eliminate it during calibration. Constant sample pressure (generally atmospheric) at the reference electrode junction is important. High flow rates or restrictions on the discharge of the flow chamber which would build up pressure should be avoided.

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Because of the high and variable resistance of the reference electrode in pure water, a measuring circuit using a solution ground or other means to boost reference input impedance can provide improved stability. Otherwise, replacing or rejuvenating the reference electrode at more frequent intervals may be necessary.

Following good sampling practices and using quality instrumentation can normally reduce the flow dependence of these measurements to negligible levels. This enables closer control of cycle chemistry with resultant increases in efficiency by reducing corrosion rates and corrosion product deposition in the plant.

Design Tips - Where to Locate Flowmeter

Legitimate analysis of steam or water samples requires that the flow rate in the main sample line be adequate to assure sample representivity. To set this rate, an easy method of measurement must be available to the user. Sentry suggests locating a total sample flowmeter downstream of the trim sample cooler or the pressure reducer if no trim cooler is used. This method allows the user to visually set the total flow required.

An alternate measurement of total flow can be accomplished by the summation of the individual in-line analyzer, grab sample, and/or back pressure regulator flowmeters; but is more cumbersome.

NOTE: For low level oxygen analysis, flowmeters may be located after sensors to eliminate the possibility of air inleakage.

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