

# APPLICATION NOTES

Issue 6-2

## PURE WATER pH MEASUREMENT IN LOW CONDUCTIVITY SAMPLES

Normally, pH measurements are made in water with 1,000 to 10,000  $\mu\text{S}/\text{cm}$  conductivity. The conductivity comes from dissolved solids, typically, salts plus net acid or base which explains the exhibited pH. These dissolved substances are in the solution in ion form, which makes such solutions conducting. With 1,000  $\mu\text{S}/\text{cm}$  conductivity of mobile ions pH electrodes have a good circuit and give fast, accurate pH readings.

In pure water, standard pH electrodes exhibit less reliable results. They respond more slowly, drift, and do not reproduce calibration results between buffers and grab sample. In highly pure water pH electrodes become jumpy, flow sensitive and inaccurate.

Pure Water is a relative term for low conductivity water of less than 500  $\mu\text{S}/\text{cm}$ . IC CONTROLS has observed these effects on waters between 50 and 500  $\mu\text{S}/\text{cm}$ , most likely due to pH Buffer carry-over on the pH electrode. IC CONTROLS considers water below 50  $\mu\text{S}/\text{cm}$  to be High Purity and recommends High Purity modification on all samples less than 15  $\mu\text{S}/\text{cm}$ . We consider water below 5  $\mu\text{S}/\text{cm}$  to be Ultra Pure and recommend Ultra Pure modification on all applications below 1  $\mu\text{S}/\text{cm}$ .

<i>Water Stream</i>	<i>Conductivity (<math>\mu\text{S}</math>)</i>
Purified effluent water	50 to 250
Surface water; high rain area	25 to 150
Well water; high rain area	50 to 100
Process water; purification plant	5 to 150
Process condensate water	5 to 100
Steam condensate	1 to 15
Boiler feed water	1 to 15
Reverse osmosis & Distilled water	0.5 to 10
Deionized water	0.1 to 2

Table 1: Conductivity of Typical Pure Water Streams

### LOW CONDUCTIVITY SYMPTOMS

Low conductivity effects can be traced to

- concentrated pH buffer carry-over into low conductivity sample;
- differences between reference junction potential in low sample conductivity versus high buffer conductivity;
- differences in apparent reference junction potential as rate of flow through the pH flow cell washes ions away from the reference;
- absorption of carbon dioxide by low conductivity sample when exposed to air for calibration;
- high resistance of the pure water producing a jumpy ungrounded “antenna” effect in the pH electrode.

The effects will become more noticeable as the conductivity falls from simply Pure to High

Purity and on to Ultra Pure, where they become predominant, below 1  $\mu\text{S}/\text{cm}$ . Also, the effects become more noticeable as greater accuracy is required.

### **Buffer Carry-Over**

Standardizing a pH electrode in a high conductivity buffer will increase the time required for the reading to stabilize in low conductivity samples. After a regular pH buffer was pumped through a general purpose pH flow-cell in laboratory tests, IC CONTROLS observed 3 hours of pH electrode drift before a 1  $\mu\text{S}/\text{cm}$  sample stabilized. Alternatively, grab sample calibration with regular pH buffers risks pH buffer contamination of the sample (carry-over). The best results will occur when pH buffers and sample are close to the same conductivity.

### **Reference Liquid Junction Potential**

A junction potential occurs when the reference electrolyte contacts the sample (much like the thermocouple potential that occurs when two different metallic conductors are in contact). The junction potential will vary with a difference in composition between the electrolyte and sample. Unlike metallic conductors, liquids are mobile and diffuse into each other until diffusion pressure equalizes. In an electrolyte, the charge carriers are ions which have different sizes and charges that affect their ability to move through the solution. Concentrations of various sizes and charges may tend to separate out at the liquid junction producing a junction potential. While a junction potential can be standardized, it must remain constant to fully disappear. With a big concentration differences between low conductivity sample and the reference electrolyte there will be a larger junction potential. Any sample flow variation will cause drift pH readings due to changes in the rate that ions are washed away. In the laboratory, steady readings can be achieved by measuring in samples and standards with conductivity similar to the reference electrolyte. For on-line samples, constant flow rates and attention to flow path are needed to

achieve steady junction potentials and readings.

### **Carbon Dioxide**

Since High Purity water contains little dissolved material, its resistance to pH change (its buffer capacity) is small. Absorption of carbon dioxide on exposure to air will result in carbonic acid formation and cause a change in pH, often between the original field reading and the same sample back in the laboratory. This fact can be readily demonstrated by taking a beaker of fresh demin water from a laboratory column, with pH electrode inserted and showing approximately 7 pH. Bubble compressed air through it and observe the pH reading quickly fall to between 5 to 5.5 as it reaches saturation. For on-line samples in a stainless steel line this is not a problem until a sample is drawn to take to the lab for comparison and it absorbs carbon dioxide along the way.

### **Laboratory Solutions**

Common laboratory remedies for these problems use a low-resistance pH electrode and a reference with a fast electrolyte flow. When placed in a low-conductivity water sample, the pH electrodes exhibit faster response and more stability due to the addition of salt from the reference raising the sample conductivity, and the dissolution of the low resistance glass into the sample at the glass surface (if the conductivity is low enough). While both raise the conductivity, they both may change the pH seen at the glass pH electrode. Stable pH readings are reached sooner at the cost of pH error dependent on the added ions.

A further step was introduced by Orion Research in the early 1980's. The addition used a research-quality glass pH electrode, plus a pH neutral additive to adjust conductivity, and special diluted pH buffers already containing the same background of pH neutral additive. Adding adjuster to samples increases the conductivity, reduces jumpiness and improves response time. Since the same

amount of adjuster is added to the buffers and the samples, any net pH effect is standardized out, and becomes negligible. Contamination due to carry-over from high conductivity buffers is minimized. Liquid junction potential variations are minimized because the buffers and adjusted sample have similar conductivity.

### ***On-Line Solutions***

IC CONTROLS has developed procedures to calibrate on-line pH flow-cells in use on low conductivity samples, which take the above problems into consideration. The flow-cells are specially constructed to deal with the effects of low conductivity on pH measurement. Also, dilute pH buffers and low conductivity sample handling procedures have been developed to ensure good calibrations.

Supplies for these procedures are available as:

A1100217	Low Conductivity 7.0 pH Buffer 500 mL
A1100217-6P	Low Conductivity 7.0 pH Buffer, 6-PAK
A1100216	Low Conductivity 4.1 pH Buffer 500 mL
A1100216-6P	Low Conductivity 4.1 pH Buffer, 6-PAK
A1100218	Low Conductivity 10.2 pH Buffer 500 mL
A1100218-6P	Low Conductivity 10.2 pH Buffer, 6-PAK
A1100219	pH Neutral Conductivity Adjustment Solution, 125 mL
A1100220-6P	pH Buffer mixed 6-PAK Low Cond
A7400017	5 cc Syringe
A1100020	Beakers, set of 4, 250 mL
A1601158	Ultra Pure pH Lab Cal Kit, air exclusion flow beaker type, Figure 1: Model 615-26 Ultra-Pure (< 1 $\mu$ S) pH System including research grade pH electrode.



615-25 for less than 1  $\mu$ S/cm