pH Measurement in Low Ionic Waters

Many investigators have noticed errors as large as one pH unit when measuring the pH of waters under 200 micromhos/cm, even though their pH meters were successfully calibrated with standard (i.e. high ionic strength) buffers.

The situation gets worse with decreasing sample conductivity and temperature, and with increasing pressure, flow, and time between calibrations.

Most measurement circuitry and pH sensors operate normally in dilute samples. However, poor design or maintenance procedures can cause unstable potentials in the reference electrode junction. The usual result is too-low pH readings in acidic waters.

The Solution

The solution to the problem of pH measurement in waters of low ionic strength is in two parts: hardware and procedure.

Hardware: The porous Teflon™ junction of Hydrolab's standard reference electrode may not be as stable, over a period of five days or more, as the optional LISREF (Beckman© Red Label Lazaran™) reference electrode. The LISREF has been tested extensively by Hydrolab and many customers, and found to perform well.

Procedure: It has been shown both in theory and in practice that a pH system cannot be assumed to make accurate measurements of anything but solutions whose ionic strength is not greatly different from that of the calibrating buffers. Errors as high as one pH unit have been produced in "calibrated" pH meters that have not been checked (after calibration) with a solution approximating the ionic strength (and pH) of the anticipated sample.

It is Hydrolab's recommendation that anyone making field pH measurements of below-200 µmho waters use the LISREF reference electrode.

It is Hydrolab's recommendation that a pH system be calibrated with two conventional buffers and then check-pointed, before and after measurements, with a dilute standard. Orion© makes dilute buffers for this purpose.

It has also been demonstrated that some types of reference electrodes have a pressure-induced error of up to 0.5 pH unit. This error may show little instability with depth and so cannot be distinguished from legitimate pH readings. A pH system should be checked for pressure insensitivity if it is to be used at a depth of more than a few inches. This can be accomplished by placing the sensors and a dilute standard in a plastic bag. The assembly is then lowered through the water column to the desired depth; any changes in the pH reading are attributable to pressure effects (provided a large change in temperature has not occurred).

It is also strongly advised that the pH system is checked for errors in cold and flowing waters, as opposed to the warm, still solutions used for calibration. That the reference electrode be kept clean and soaking in a solution approximating its filling solution whenever the electrode is not in use. That field samples be grabbed, carefully transported to a laboratory pH meter (calibrated and tested in the same manner as the field unit, except for the pressure test), and checked for correlation with field readings.

Lazaran Electrode

The Lazaran electrode is manufactured from a polymer composite material with KCl crystals in the polymer itself, which gives the design a very low resistance. This design allows the electrode to be used in high purity waters as low as five micromhos. The wall thickness is much less than that of a typical wicking length and therefore response time is decreased. The tip and sides of the Lazaran are porous and compose the micro-junction. This large surface area reduces the problems with plugging and /or fouling.

The Lazaran electrode is capable of operating at pressures of up to 150 psig and

temperatures of 100 °C. It includes a silver/silver chloride internal half cell and is compatible with most conventional pH amplifiers.

Summary

A prudent investigator working with Specific Conductance less than 200 micromhos/cm will employ Hydrolab's LISREF reference electrode. he will, at minimum, check his buffer calibration with a dilute solution of known, pertinent pH, and use this same solution to run a depth profile as a pressure sensitivity test.

For more information on this or any Hydrolab application please contact Campbell Scientific (Canada) Corp. at (780) 454-2505.

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