Technical Note 102

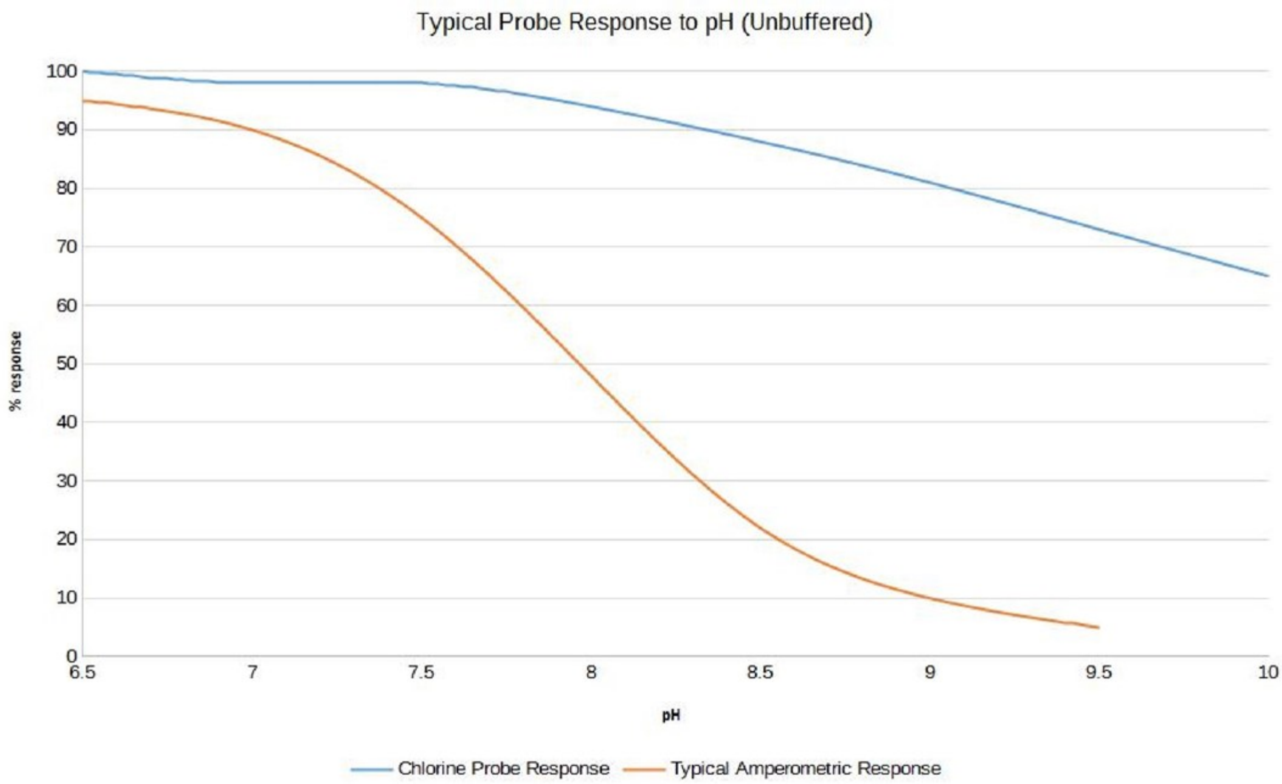
pH Compensation of a Residual Chlorine Measurement

Background

Many water companies want to measure free chlorine residuals without the need for chemical buffers traditionally associated with such measurements. Acetate and phosphate buffers are expensive and environmentally unfriendly. Buffer delivery systems are maintenance intensive and have fairly costly consumables and there are health and safety considerations to the handling of the acids, and disposal costs if the acid treated water is unable to be fed back into the water supply.

Amperometric cells and most polarographic probes only respond to hypochlorous acid (HOCl). HOCl dissociates into hypochlorite (OCl^-) in a pH dependent manner. This is why most monitors need acid buffers in most applications. The typical pH of the water measured on a water treatment works may range from 7 to 9.2. Chemical buffering reduces the pH to between 5 and 6 and ensures that the majority of the residual chlorine is present as HOCl (orange line on graph).

If an HOCl monitor is combined with a pH monitor, it is proposed by some manufacturers that the output of the HOCl monitor can be compensated for with reference to the HOCl vs pH dissociation curve.



pH correction as a solution

A solution to the problem used by some instrument suppliers is to measure the pH of the sample and use that measurement to apply a compensation to the HOCl measured signal to give a 'free chlorine' output. Before a customer purchases such an instrument, they should be aware of the issues surrounding it.

- **There is more than one dissociation curve for HOCl and OCl^-. The shape of the curve depends upon the ionic strength of the solution, and the temperature.**
- **The errors in measuring the pH are large and have a disproportionate effect on the calculated free chlorine.**
- **At higher pHs, the measured signals are low and the compensation errors are high.**

Errors

Although significant errors are introduced through the shift in dissociation through temperature and ionic strength changes, the largest errors are introduced through using pH as a correcting signal. For example, if an accuracy of +/-0.1pH is assumed (often not achievable in a real life situation) it is possible to look at the kind of errors that could occur.

At 25°C, pH 8.5, 40ppm total dissolved solids.

% HOCl at pH 8.5 = 10%

% HOCl at pH 8.4 = 11.5%

% HOCl at pH 8.6 = 8.5%

The correction factor applied to the HOCl measurement would be times 10 from the pH monitor. The actual factor needed could be between 8.7 and 11.8. The error in the chlorine measurement due purely to the error in the pH would be +/-18%. If we then introduce the errors on the HOCl measurement and the errors from temperature and ionic strength , we can see that the accuracy of these systems is severely compromised.

Solutions

The HaloSense free chlorine sensor measures all the HOCl and the majority of the OCl^- present (blue line on graph). This results in a vastly reduced pH effect and means that most monitoring application require no buffer and no pH compensation. It also means that when the pH is high and variable, it is possible to compensate with either a pH sensor integral to the unit or a separate (perhaps existing) pH meter without the same errors as an amperometric sensor or a membrane sensor that doesn't measure any of the OCl^-. Taking the same example, we can see how reduced the errors are:

At 25°C, pH 8.5, 40ppm dissolved solids

% signal at pH 8.5 = 80%

% signal at pH 8.4 = 83%

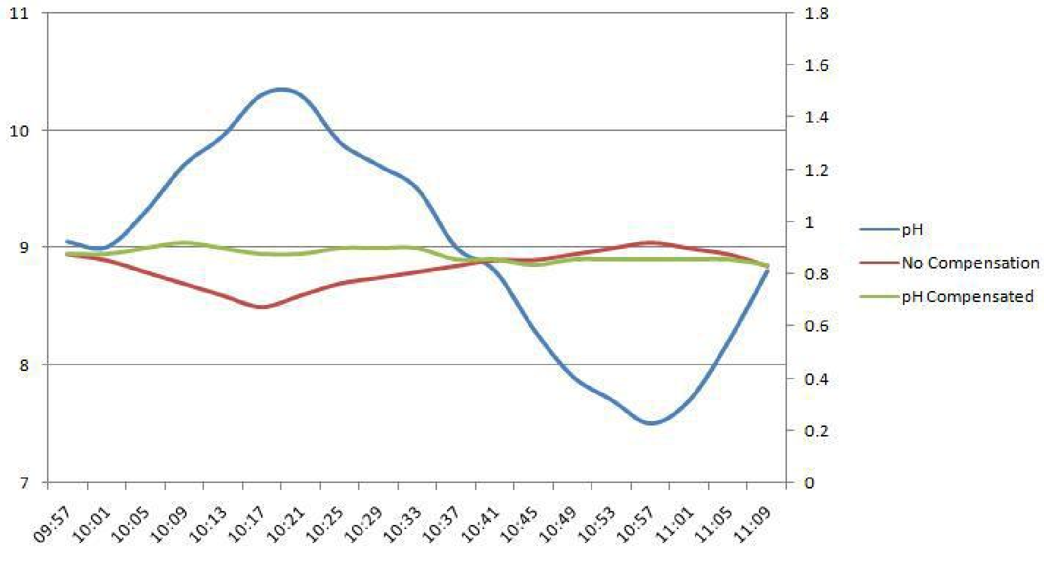
% signal at pH 8.6 = 78%

The correction factor applied to the signal would be 1.25. The actual factor needed would be between 1.28 and 1.20 so the error in the chlorine measurement, due to the pH compensation, is only + or—4%.

This is a mathematical consideration of the errors involved. A knowledge of signals will tell us that any signal that needs to be multiplied by a correction of x10 will also suffer from a low signal to noise ratio.

Conclusion

pH correction/compensation applied to a sensor that measures only HOCl produces very high errors and very poor signal to noise ratios. The same pH correction/compensation applied to a HaloSense free chlorine sensor results in far better results, with much higher signal to noise ratios.



The graph above shows the errors on a real HaloSense free chlorine sensor when a sample of 1ppm free chlorine has the pH changed from pH 9 to more than pH 10, down to pH 7.5 and back again. The graph shows that the vast majority of applications won't need pH compensation at all and, for those that do, the HaloSense free chlorine sensor is the most appropriate sensor available to have that compensation applied.