Technical Note 112

HaloSense Free Chlorine Residual Tips and Tricks

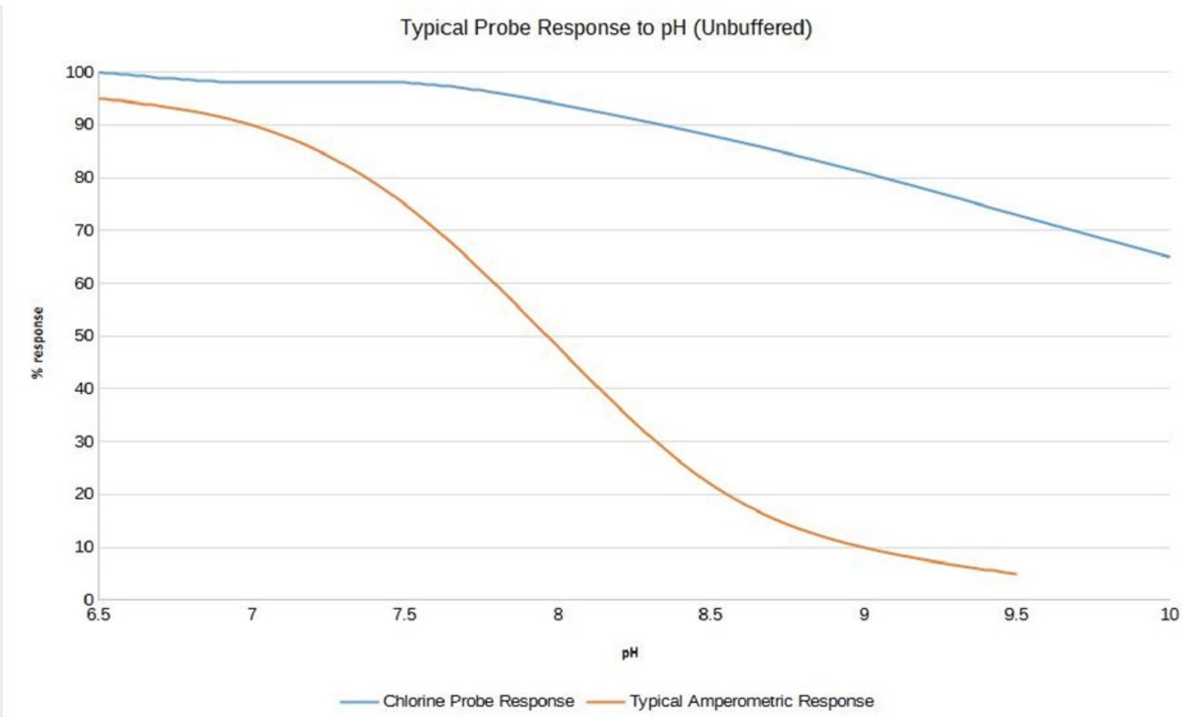
Principle of Operation

Free Chlorine

HaloSense sensor in a single flow cell

The HaloSense Free Chlorine sensor measures the concentration of dissolved free residual chlorine. In potable, process or swimming pool water this means HOCl (hypochlorous acid) plus OCl^- (hypochlorite ion). The relative amount of these two species is dependent on the pH of the sample water. At low pHs (pH 6 and below) all the free chlorine will be HOCl. At higher pHs most of the free chlorine will be present as OCl^-. Traditional amperometric measurement systems and some membraned sensors only measure the HOCl and need to be buffered to an exact pH in order that changes in the pH of the sample water do not affect the total Free Chlorine measurement. The probe supplied for Free Chlorine measurement with the HaloSense is not affected by changes in pH to the same degree. This means that on most plants (99.9%) it will not be necessary to buffer the sample water at all. On water supplies over about pH 8 it will only be necessary to correct for pH changes if the pH varies by a significant amount. The higher the pH the less it needs to vary to have a significant effect. If a plant does have high, variable pH it is possible to still use this sensor without acid buffering, however it will be necessary to use a pH sensor to compensate for varying pH. Please see Technical Note 02 pH Compensation for more information.

The HaloSense sensor is a three electrode chrono-amperometric potentiostatic sensor. The free chlorine molecules diffuse through the membrane and come into contact with the electrolyte. The electrolyte has a low pH which converts the majority of the OCl^- to HOCl. All the HOCl is reduced at the gold cathode and the resultant ions travel through the electrolyte where they are oxidised at the silver/ silver chloride anode. The current flow is proportional to the concentration of free chlorine in the sample. The anode and cathode are held at the potential difference that provides an optimum catalytic reduction of HOCl.



Technical Tips

- The sensor is designed to measure the chlorine when the sensor has reached a steady state. For a steady state to establish itself three things are required.
  - potential differences between the electrodes (i.e. power on)
  - free chlorine present at the membrane (free chlorine in the water)
  - the chlorine needs to be present and replaced faster than it is being consumed by the sensor (i.e. there needs to be a minimum flow rate (>200ml/min in the supplied flow cell)

The establishment of this 'steady state' is called polarisation. If any of these three requirements are removed the sensor will de-polarise.

- The first polarisation usually takes 2 hours but can take as much as 18 hours especially if chlorine levels are low (<0.2ppm). Subsequent polarisation times will vary from 30mins-120mins (after maintenance).
- The sensor is NOT SUITABLE for measuring 0ppm chlorine. (An analyser normally measuring low levels of free chlorine will measure '0' chlorine temporarily and rise again as the chlorine increases but a sensor habitually exposed to 0ppm chlorine will depolarise). To measure chlorine when there is often no chlorine, please use a HaloSense 'Zero'.
- Two analysers on the same source will track within 0.2ppm at the worst.
- Flow is needed because the diffusion rate across the membrane is greater than that through water. If there is no flow, chlorine would be depleted around the membrane and the value would go low.
- Below pH 4 you get gaseous chlorine and a very sensitive, unstable probe.
- The effective range of the analyser is pH 4.5 - pH 9. Any higher and we must buffer with CO_2 or acid.
- Zeroing is not normally required. To check zero you must use chlorine free, ozone free, cooled, boiled tap water. All other solutions give an invalid zero.
- Zero stability is excellent, due to the isolation of the electrodes from the water by the hydrophilic membrane, and by use of a reference electrode. As the device is polarographic, no current at 400mV = no chlorine.
- If manganese fouling is very, very high we will need to find a way to take it out before it gets to the sensor. Normal levels are no problem.
- Electrode life, normally >10 years.
- Rough guide to membrane changes; for both Free/Total in clean potable water, once a year.
- Rough guide to electrolyte changes; once a year.
- After loss of flow the recovery time is 2-3 minutes, unless it is for extended periods after which it can take up to 60 minutes to recover.
- Any fats or oils in the sample can block the membrane. Talk to Pi about any applications where Fats, Oils & Grease (FOG) are in the sample.
- If a sensor responds well for a short period and then drops to zero check that the cap is tightened up fully.
- Bubbles on the tip of the membrane will make the sensor read low. Push the sensor down dose to the inlet and increase the flow to displace the bubbles. If this doesn't work please contact Pi for advice.

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