

# FREE CHLORINE RESIDUAL HINTS and TIPS

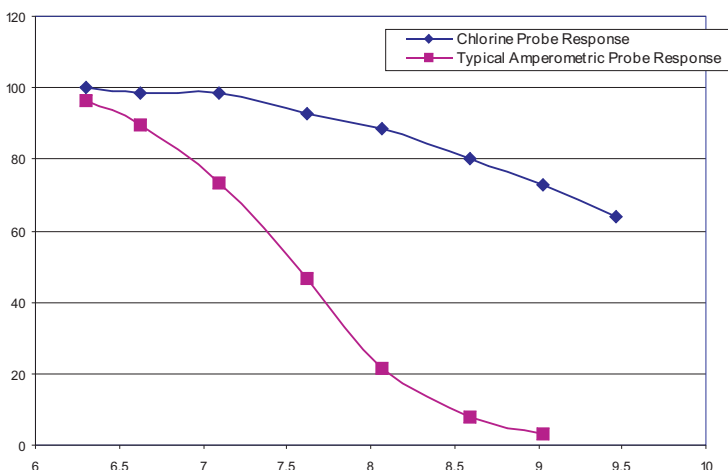
## PRINCIPLE OF OPERATION

### Free Chlorine

Chemtrac's Free Chlorine sensor measures the concentration of dissolved free residual chlorine. In potable, process or swimming pool water this means HOCl (hypochlorous acid) plus  $\text{OCl}^-$  (hypochlorite ion). The relative amount of these two species is dependent on the pH of the solution. 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  $\text{OCl}^-$ . 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 HydroACT is not affected by changes in pH to the same degree. This means that on most plants 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.



Typical Probe Response to pH (Unbuffered)



The Free Chlorine sensor is a three electrode chrono amperometric potentiastatic 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  $\text{OCl}^-$  to HOCl. All the HOCl is reduced at the gold cathode and the resultant ions travel through the electrolyte where they are oxidized 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

1. 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 (> 200 ml/min in the supplied flowcell))

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

2. The first polarization usually takes 4 or 5 hours but can take as much as 18 hours especially if chlorine levels are low (< 0.2 ppm). Subsequent polarization times will vary from 30 mins - 120 mins (after maintenance).
3. The sensor is NOT SUITABLE for measuring 0 ppm chlorine. (An analyzer normally measuring low levels of free chlorine will measure no chlorine temporarily and rise again as the chlorine increases but a sensor habitually exposed to 0 ppm chlorine will depolarize).
4. Two analyzers on the same source will track within 0.2 ppm at the worst.
5. Membrane cap must be screwed on all the way for probe to work properly. If readings are not accurate, try tightening cap.
6. Air bubbles on membrane tip can cause unstable readings. Increase flow rate to 700 ml/min or higher and lower the probe in the flow cell to prevent air bubbles from being able to form on membrane surface.
7. Flow is needed because the diffusion rate across the membrane is greater than the through water. If there is no flow chlorine would be depleted and the value would go low.
8. Below pH 4 you get gaseous chlorine and a very unstable reading.
9. Effective range of the analyzer is pH 4.5 - pH 10. Any higher and we must buffer with CO<sub>2</sub> or acid.
10. 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.
11. 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.

12. 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.
13. Electrode life, normally 7 to 10 years.
14. Rough guide to membrane changes; for both Free/Total in clean potable water, 12 to 18 months; electrolyte changes; 3 - 6 months.
15. Low level Cl readings (i.e. <0.05) can lead to biological buildup on the membrane which can reduce Cl reading if not cleaned routinely.
16. 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.
17. Any fats or oils in the sample can block the membrane. Think very carefully before the probe is used in waste streams.

