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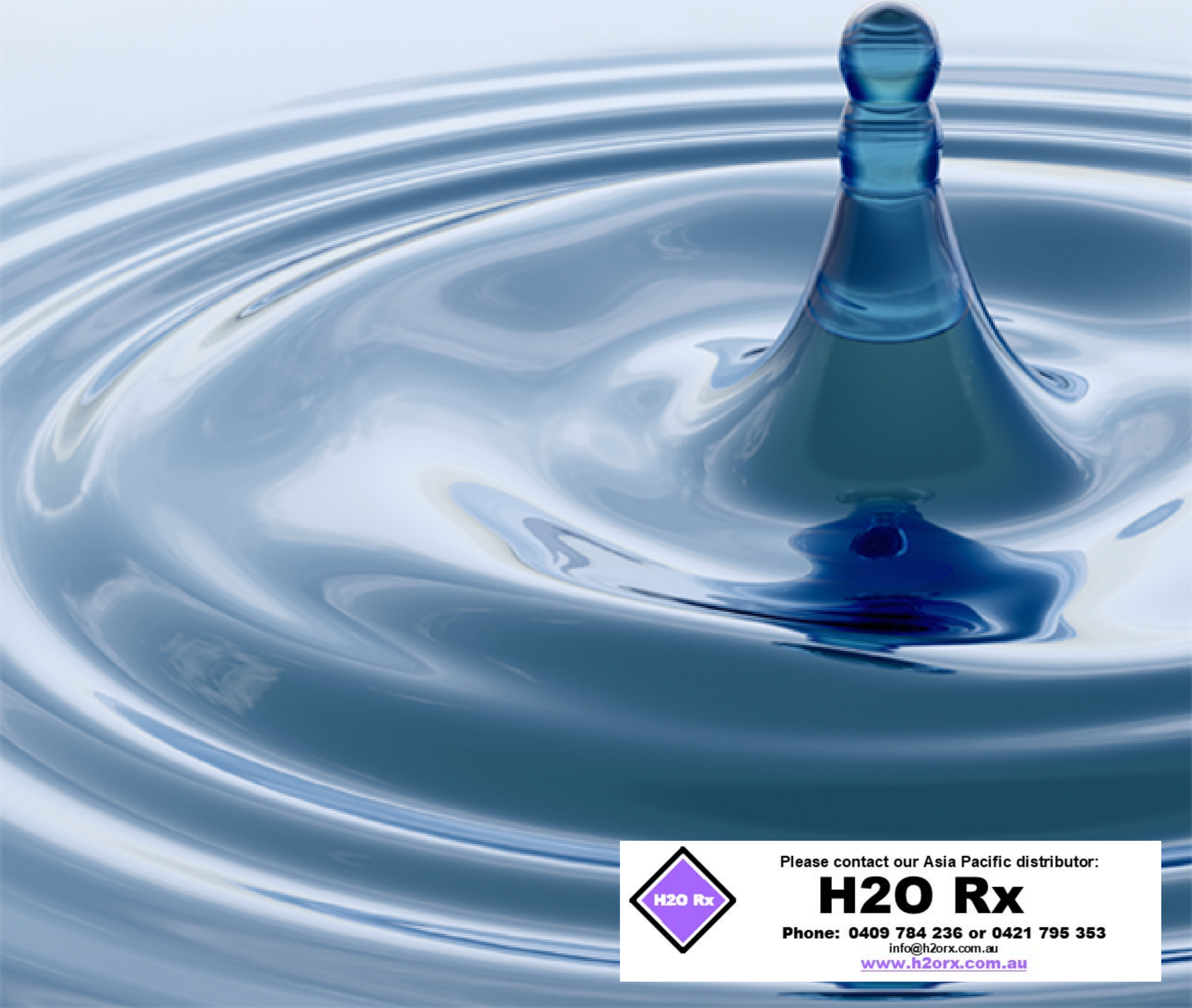
Education Series
The Chemistry of Chlorine



The Measurement of Chlorine

Introduction

The addition of chlorine into aqueous systems is used in many different industries for a variety of purposes. In the chemical processing, pharmaceutical, textile, and pulp & paper industries, chlorine is commonly used as a bleaching or oxidizing agent. The food and beverage processing industry, as well as municipal water plants, use chlorine as a disinfectant or sanitizer to control odors, improve the taste of drinking water and eliminate pathogens. Power plants and petrochemical refineries use chlorine to control the growth of microorganisms, algae, and biofilms in the cooling water used in their cooling towers, as these microorganisms and biofilms reduce the efficiency of the cooling towers. Chlorine is also a popular sanitizing agent used in the swimming pool industry to prevent health problems and keep the water sparkling and clear. This paper will focus on the measurement of chlorine in its use as a disinfectant, as this is the application in which chlorine is most widely used.

Chlorine is typically produced by the electrolysis of a sodium chloride solution, often referred to as “brine” solution. This process is a fairly expensive one, so proper measurement and control of chlorine levels is essential to keeping maintenance costs under control. If chlorine concentrations are too high, unnecessary costs are introduced into the process. If chlorine levels are too low, your disinfection process will be ineffective.

Terminology

Here is a quick list of some common industry terms and their concise definitions regarding chlorine measurement. The following terms will be discussed in further detail below.

Free available chlorine – The portion of total chlorine that has not yet reacted with contaminants, and is therefore “free”, or “available” to kill bacteria and other contaminants.

Combined available chlorine – The portion of chlorine in the water that has reacted and combined with ammonia, nitrogen-containing contaminants, or other organics.

Total residual chlorine – The sum of Free available chlorine and Combined available chlorine. This term is also sometimes referred to as *total chlorine*.

Chlorine Chemistry

Chlorine can be added to water as chlorine gas, aqueous sodium hypochlorite solution (liquid bleach), solid calcium hypochlorite (granular or tablets), lithium hypochlorite, or chlorinated isocyanurates (a family of compounds which add cyanuric acid – a stabilizer).

When chlorine is added to water in any of these forms, it creates hypochlorous acid, a very potent bactericide:

$Cl_2 + H_2O \rightarrow HOCl + HCl$

Hypochlorous acid (HOCl) is a weak acid that dissociates into hypochlorite ion (OCl^-) according to the following equation:

HOCl (Hypochlorous acid) ⇔ H^+ + OCL^- (hypochlorite ion)

Together, HOCl and OCl^- are referred to as *free chlorine*. These two species exist in an equilibrium which is both pH and temperature dependent. At 25 °C and a pH of 7.5, half of the chlorine is present as HOCl and the other half as OCl^-. At pH values below 7.5, HOCl is the dominant species. At pH values above 7.5, OCl^- is the dominant species. At pH 5, nearly all the chlorine is present as HOCl, while a pH value of 10 drives nearly all the chlorine to be present as OCl^-. See Figure 1 below:

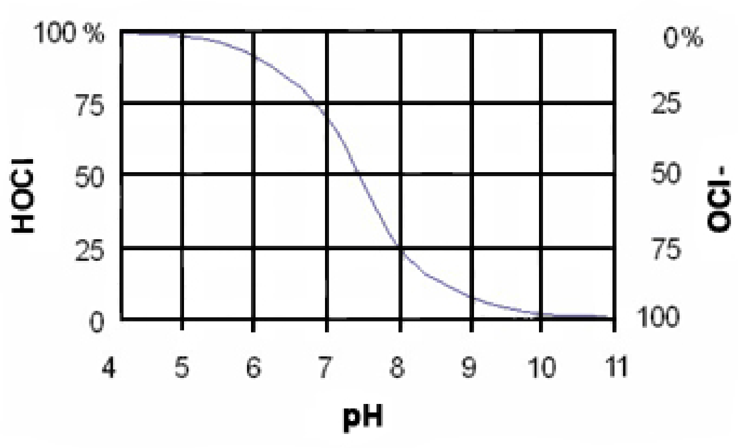


Figure 1. Ionization Curve of HOCl as a function of pH at 25 °C

As a disinfectant, hypochlorous acid (HOCl) is more effective than hypochlorite ion. By controlling the pH, we can ensure that the more effective bactericide, HOCl, remains the dominant species in solution.

Chloramination

Free chlorine readily reacts with Ammonia and other ammoniated compounds to form what are known as “chloramines”. These chloramines are known as monochloramine, dichloramine, and trichloramine. Chloramines are also referred to, in the industry, as *combined chlorine*. While chloramines do have some bactericidal properties, they are 80 to 100 times less effective than free chlorine. The rate of formation of chloramines is dependent on the ratio of free chlorine concentration to ammonia concentration. Optimum pH, temperature, and mixing conditions are also a factor.

When chlorine is added to water containing ammonia (NH_3), chlorine will replace one hydrogen ion on the ammonia molecule with a chloride ion, resulting in the formation of monochloramine:

$HOCl + NH_3 \rightarrow NH_2Cl$ (Monochloramine) + H_2O

If the free chlorine to ammonia ratio is allowed to fall below 5:1 by weight (either by chlorine loss or by the addition of ammonia to the sample), all free chlorine will be converted to monochloramine. Between the pH range of 7-8, this reactions takes place almost instantaneously.

If the chlorine to ammonia ratio is increased back above 5:1, the additional chlorine will displace a second hydrogen ion from the monochloramine molecule and replace it with another chloride ion, resulting in the formation of dichloramine:

$HOCl + NH_2Cl \rightarrow NHCl_2$ (Dichloramine) + H_2O

Dichloramines are notorious for their bad smell, and are usually the prime suspects for "chlorine smell" and eye irritation in the pool and spa industry.

The third member of the chloramines group, trichloramine, is similarly formed. Additional chlorine reacts with dichloramine to form the tri-substituted trichloramine (commonly referred to as Nitrogen trichloride):

$HOCl + NHCl_2 \rightarrow NCl_3$ (Trichloramine) + H_2O

(Trichloramine is both volatile and unstable and is usually not allowed to form in most industries).

At this point, if enough chlorine is added to bring the chlorine to ammonia ratio up to 10:1, the mono- and dichloramines are almost completely destroyed and converted back into less offensive nitrogen compounds and chloride salts:

$2\ NHCl_2 + 2\ HOCl \rightarrow N_2 + 6\ Cl^- + 2\ H_2O$

This last reaction is generally referred to as "*Breakpoint chlorination*". A constant state of breakpoint chlorination is required to prevent the formation of chloramines. This means maintaining the 10:1 chlorine to ammonia ratio in the water at all times.

Organic Chloramine Formation

Chlorine is not specific in reacting only with ammonia. Chlorine will also readily react with compounds containing carbon and nitrogen. These compounds are called organic nitrogen compounds and are generally described by the formula R-N, where R represents a carbon chain of some undefined length and contains at least one reactive nitrogen group. Chlorine reacts with these compounds in similar fashion as it does with ammonia, and the product of these reactions are referred to as organic chloramines, or *organochloramines*. They have little to no disinfectant properties. While these organochloramines are usually only present in low levels, it is important to realize that they can react as chloramines. This can lead to false readings in many tests used for controlling mono- and dichloramines.

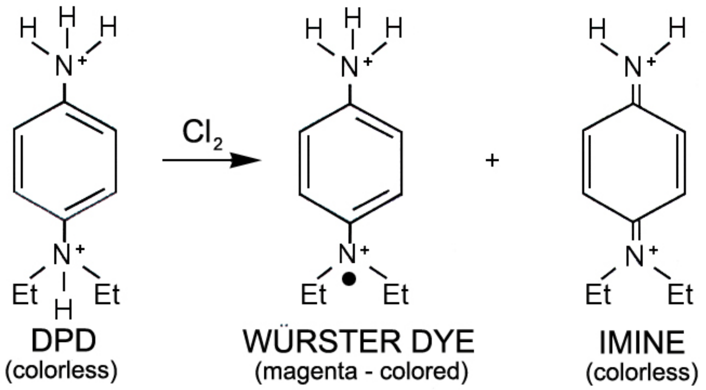
The Measurement of Free Chlorine

The methods for testing free chlorine levels in industry today fall into three distinct methodologies: colorimetric, potentiometric, and amperometric.

Colorimetric Method

This methodology uses chemical reagents added to the sample which react with chlorine to produce a color. The intensity of the color is directly proportional to the amount of chlorine present in the sample. The analytical instrument used in this method measures the intensity of the color and converts this measurement into a concentration reading, typically parts per million (ppm).

The most prevalent colorimetric method used in industry today is called the DPD Colorimetric Method. In this method, N,N-diethyl-p-phenyldiamine (DPD) is the reagent added to the sample. Chlorine oxidizes this DPD to form two possible oxidation products: a magenta colored compound known as Wϋrster Dye, and a colorless imine compound:



When small amounts of chlorine react with DPD, then the magenta colored Wϋrster Dye is the favored product. The colorless imine compound is favored when high levels of chlorine is present, which, unfortunately, leads to the apparent “fading” of the solution.

While this established method does indeed measure total free chlorine, the principle drawback of this method is that it does not differentiate between the two forms of free chlorine: HOCl, and OCl^-. Remember, that the amounts of HOCl and OCl^- present in solution are pH dependent. If the process pH is allowed to rise too high, all free chlorine in solution will be present as OCl^-, the less efficient sanitizer, yet the total free chlorine levels, as reported accurately by the DPD test, will remain the same.

Potentiometric Method

An ORP (Oxidation Reduction Potential) electrode is used in this methodology. When placed in a solution containing an oxidizer, such as chlorine, a measureable potential develops, which varies with the concentration of the oxidizer. This Oxidation Reduction Potential is dependent on the ratio of oxidized to reduced species of chlorine in solution.

The half-cell oxidation-reduction potential, E_0, for HOCl at 25°C is:

$HOCl + H^+ + 2e$ (electrons) $\rightarrow Cl^- + H_2O$ $E_0 = 1.49$ Volts

Assuming HOCl is the oxidized form of chlorine, with Cl^- being the reduced state of chlorine, the ORP value for HOCl can be expressed by the equation:

$ORP = E_0 + 0.059/N*\log[(HOCl)/(Cl^-)] - E_{ref}$

Where N = the number of electrons, and E_{ref} = the potential of the reference electrode of the ORP sensor.

The half-cell oxidation-reduction potential, E_0, for OCl^- at 25°C is:

$OCl^- + H_2O + 2e$ (electrons) $\rightarrow Cl^- + OH$ $E_0 = 0.90$ Volts

The ORP value for OCl^- is therefore expressed by the equation:

$ORP = E_0 + 0.059/N*\log[(OCl^-)/(Cl^-)] - E_{ref}$

Note that the E_0 value for OCl^- is much lower than that of HOCl. It is for this reason that ORP electrodes are said to read only the HOCl species of free chlorine – its higher ORP potential tends to mask the ORP potential of the OCl^- species in solution.

Let us now take a look at the Oxidation Reduction Potentials of solutions of varying free chlorine concentrations. Notice how the ORP value changes with changes in pH:

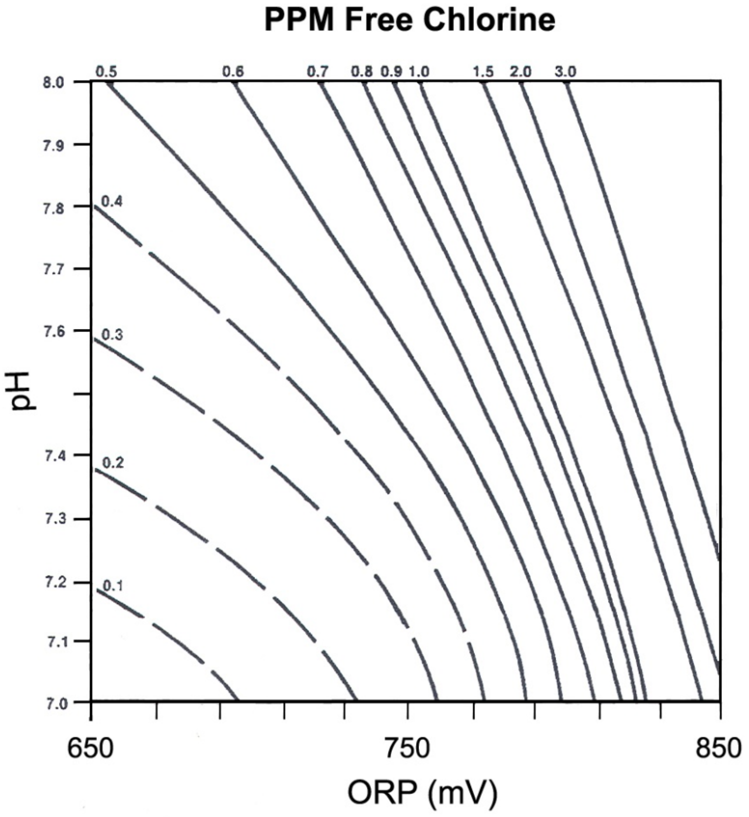


Figure 3. Variation of ORP for Varying Free Chlorine Concentrations as a function of pH

Figure 2 clearly shows that as pH levels rise, the ORP value decreases.

For further clarity, let us superimpose the Ionization curve of HOCl from Figure 1 (the dotted line) onto Figure 3:

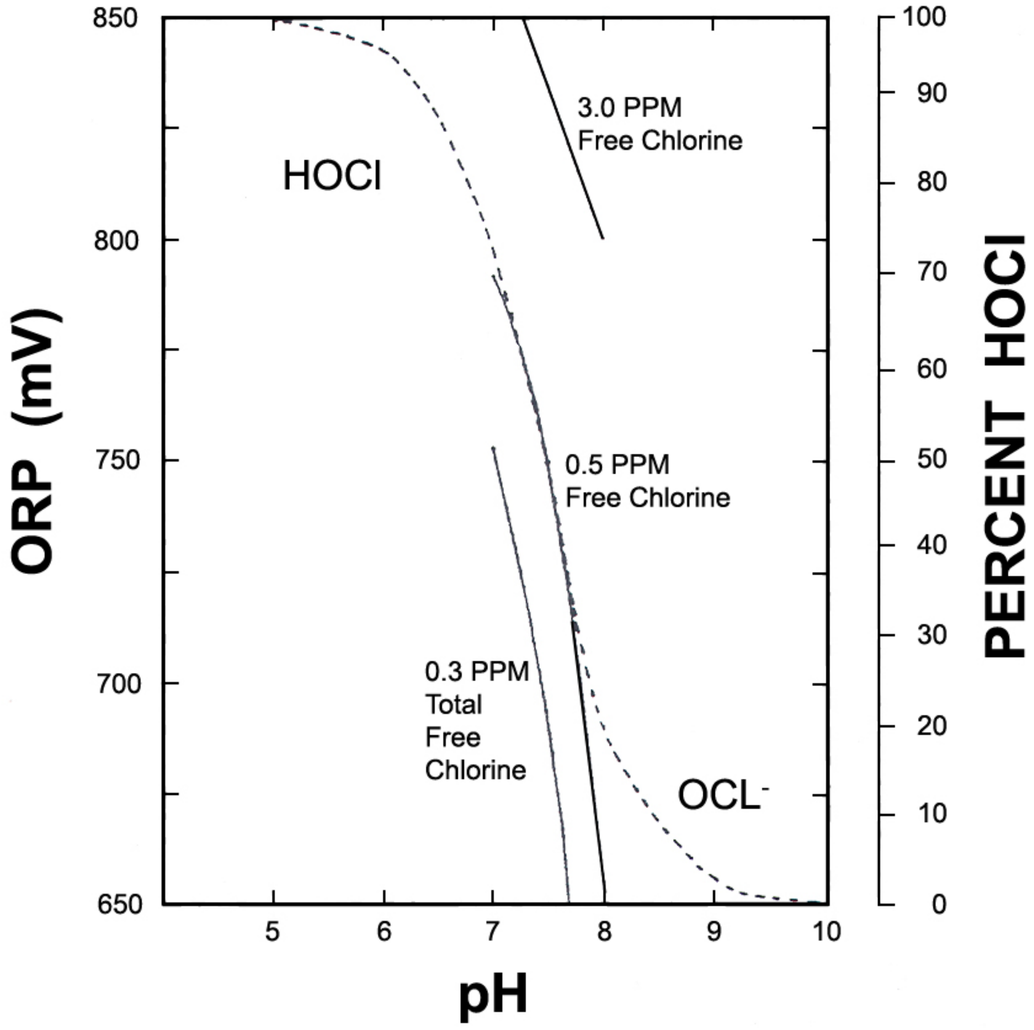


Figure 4. Comparison of ORP values and HOCl concentrations as a function of pH

The ionization curve of HOCl reminds us that as pH rises, the equilibrium of free chlorine shifts towards the formation of hypochorite ion (OCl^-). This equilibrium shift towards the formation of OCl^- causes the HOCl concentration to proportionately decrease. Thus, we see a decrease in ORP values from the ORP electrode. Proper understanding of these ORP and HOCl curves is what allows the use of ORP sensors to successfully monitor HOCl levels in water.

For adequate disinfection properties, it has recommended to maintain a minimum ORP level of 750 mV.

Amperometric Method

The amperometric method is electrochemical in nature. Chlorine diffuses across a hydrophobic membrane and is electrolytically reduced at the sensor's cathode. The current produced is directly proportional to the chlorine concentration. The analyzer measures this current and converts it into a concentration reading (typically ppm).

The main benefits of the traditional amperometric measurement are that no reagents need be added to the sample, and maintenance on the sensor itself is low. The only drawback to the typical amperometric method is its dependency on the pH of the sample. The amperometric sensor will only respond to the hypochlorous acid form of chlorine. If the sample's pH is allowed to change, this will cause a change in the sensor's current output, even if the total free chlorine levels have not actually changed.

There are two ways to handle the pH dependency. The first, is to add acid to the sample. Lowering the pH will ensure that all hypochlorite in the sample will be converted to hypochlorous acid. This may or may not be feasible, depending on the application. The second method is to measure the pH level of the sample with a pH sensor. Then, a pH-correction algorithm may be employed to calculate the actual free chlorine concentration.

Van London pHoenix Company has developed an amperometric chlorine sensor which retains all the advantages of the traditional amperometric sensor (no reagents + low maintenance) and eliminates the pH dependency of the sample!

By filling the sensor with an acidic fill solution behind the hydrophobic membrane, all chlorine which diffuses across the membrane will always be in the hypochlorous acid form, thereby making the sensor's response to chlorine independent of the sample's pH. The only regular maintenance required is the replacement of the membrane and fill solution, which can be done simultaneously.