TECHNICAL NOTES

Issue 8-2

# CHLORINE THEORY & MEASUREMENT

## Introduction

Chlorine, dissolved in liquid, is one of the most effective and economical germ-killers for the treatment of water to make it potable or safe to drink. Chlorine's powerful disinfectant qualities come from its ability to bond with and destroy the outer surfaces of bacteria and viruses. Drinking water chlorination is one of the most widely used methods to safeguard drinking water supplies. In addition to water disinfection, chlorine and its derivatives are used to treat sewage and industrial effluent, and as household and industrial bleaches (eg., to control biological agent growth in water filled industrial systems) to maintain and improve hygiene standards.

### *What is chlorine?*

Chlorine (Cl) is among the most abundant of nature's elements, and combines with other elements to sustain life and the natural processes that make up our environment. Chlorine is found in the Earth and, in the oceans.

Chlorine is highly reactive and, as such, is typically found in nature bonded to other elements like sodium, potassium, and magnesium. When isolated as a free element, chlorine is a greenish yellow gas, which is 2.5 times heavier than air. It turns to a liquid state at -34°C (-29°F), and it becomes a yellowish crystalline solid at -103°C (-153°F).

## Chlorine Chemistry

The different forms of chlorine are named as follows:

$Cl_2$ = chlorine

HOCl = hypochlorous acid

$OCl^-$ = hypochlorite ion

NOTE: *At atmospheric pressure and 20 °C, the maximum solubility of chlorine is about 7,395 mg/L or 7.395 ppm (parts per million).*

When chlorine gas is dissolved in water, it hydrolyzes rapidly according to equation (1). This reaction occurs very rapidly, in only a few tenths of a second at 18°C (64.4 °F).

(1) $Cl_2 + H_2O \longrightarrow HOCl + HCl$

Since HCl, hydrochloric acid, is a strong acid, addition of gaseous chlorine to water results in a lowering of the pH from the acidic HCl by-product. The important product of reaction (1) is HOCl or hypochlorous acid. Hypochlorous acid is the killing form of chlorine in water. Hypochlorous acid is unstable because the chlorine molecule is lightly bound and therefore will react quickly. Free available chlorine, or free chlorine, is hypochlorous acid and is taste free and aggressive against germs and organic compounds.
Chlorine supplied as sodium hypochlorite, calcium hypochlorite, or bleach is in alkaline or basic form. When a base is present, a different reaction sequence occurs:

(2) $NaOCl + H_2O \longrightarrow HOCl + Na^+ + OH^-$

(3) $Ca(OCl)_2 + 2H_2O \longrightarrow 2HOCl + Ca^{++} + 2OH^-$

In any hypochlorite solution, the active ingredient is always hypochlorous acid. Then once HOCl and $OH^-$ are formed an additional reaction occurs:

(4) $HOCl + OH^- \longleftrightarrow OCl^- + H_2O$

The proportion of chlorine, hypochlorous acid, and hypochlorite ion in solution depends primarily on pH and somewhat on temperature.

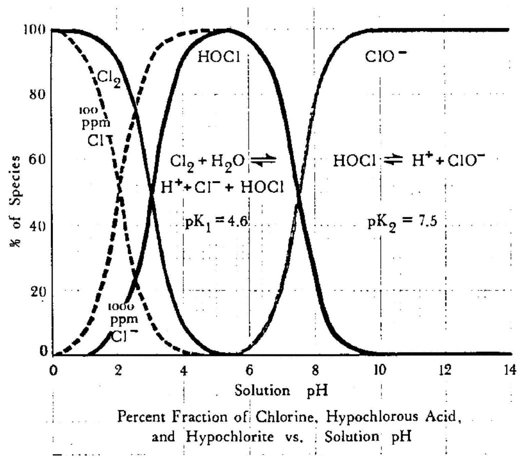


Figure 1: Chlorine Species Change vs. pH

## Chlorine and the Effect of pH

The most important reaction in the chlorination of an aqueous solution is the formation of hypochlorous acid, a form of chlorine very effective for killing germs. Hypochlorous acid is a 'weak' acid, meaning that it tends to undergo partial dissociation to form a hydrogen ion ($H^+$) and a hypochlorite ion ($OCl^-$) in a water environment HOCl tends to dissociate into these ions.

(5) $HOCl \longleftrightarrow H^+ + OCl^-$

In water between 5 pH and 8.5 pH, the reaction is incomplete and both species are present to some degree. Since $H^+$ is one of the ions formed and its concentration is expressed as pH, changing pH levels will influence the balance of this reaction and with it, the availability of hypochlorous acid for reaction. Therefore, in an aqueous environment, the water pH will affect the chemistry of chlorine through its pH sensitivity; this is important as the pH value increases.

(6) $H_2O \longleftarrow H^+ + OH^-$

Three things follow from this form of ionization:

1. Since the tendency of these two ions to react and form $H_2O$ is much stronger than the tendency of water to break down into the ions, as the pH increases there are fewer $H^+$ ions and more $OH^-$ ions.

2. The $H^+$, released by the breakdown of HOCl (equation 5), react to form water (equation 6) and leave behind residual $OCl^-$ ions. Hypochlorite does not react readily so the chlorine is weaker.

3. If the pH goes down and H+ ions become readily available again, the $OCl^-$ ions revert to HOCl, which is the killing form of chlorine.

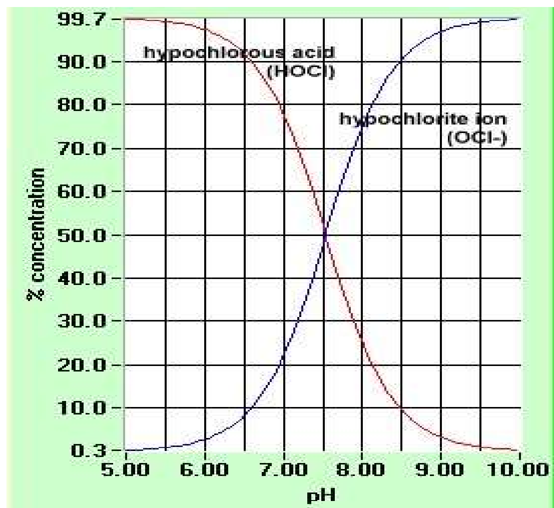


Figure 2: % Chlorine Concentration vs. pH

## Terminology

In the industry, there are a number of terms used to indicate the various forms of chlorine that are of interest. These terms tend to be used rather loosely and not necessarily consistently. For that reason, the following terms are defined:

**Free Available Chlorine** refers to the hypochlorous acid (HOCl) form of chlorine only. It is the free, uncombined form of chlorine that is effective for disinfection.

**Total Free Chlorine** refers to the sum of hypochlorous acid (HOCl) and hypochlorite ion

($OCl^-$). The hypochlorite ion is not effective for disinfection, but it is in a free form. All of the total free chlorine would be in the form of hypochlorous acid if the pH was low enough.

**Combined Chlorine** refers to chlorine which is not readily available. For example, chlorine combined as chloramines or organic nitrogen is not an effective disinfectant and will not readily convert to hypochlorous acid or hypochlorite ion.

**Total Residual Chlorine** refers to the sum of total free chlorine and combined chlorine. Low total residual chlorine is of particular interest to ensure there are no downstream consequences for aquatic life.

### Disinfectant Properties of Chlorine

Chlorine is known to be a good disinfectant; it is able to kill living matter in water such as bacteria, cysts, and spores. Studies show that certain forms of chlorine are more effective than others. Whatever the chemical reaction, the relative efficiency of various disinfecting compounds is a function of the rate of diffusion of the active agent through the cell wall. Factors which affect the efficiency of destruction are:

- ➔ Nature of disinfectant (type of chlorine residual fraction)
- ➔ Concentration of disinfectant
- ➔ Length of contact time with disinfectant
- ➔ Temperature
- ➔ Type and concentration of organisms
- ➔ pH

Hypochlorous acid is the most effective of all the chlorine forms, similar in structure to water. The germicidal efficiency of HOCl is due to the relative ease with which it can penetrate cell walls. This penetration is comparable to that of water, and can be attributed to both its modest size and to its electrical neutrality. The concentration of hypochlorous acid is dependent on the pH, which establishes the amount of dissociation of HOCl to $H^+$ and $OCl^-$ ions. Lowering the temperature of the reacting solution suppresses the dissociation; conversely, raising the temperature increases the amount of dissociation. The rate of dissociation of HOCl is so rapid that equilibrium between HOCl and the $OCl^-$ ion is maintained, even though the HOCl is being continuously used up. The $OCl^-$ ion form of chlorine is a relatively poor disinfectant because of its inability to diffuse through the cell wall of microorganisms; the obstacle being the negative electrical charge.

## *GALVANIC MEASUREMENT*

### Principle of Operation

A flow cell house a galvanic sensor. The water flows across the permeable membrane and produces a galvanic current proportional to the concentration of chlorine present. The microprocessor in the analyzer computes this value relative to the input temperature and pH to display the chlorine reading.

### Galvanic Measuring Cell

The model 832 and model 835 chlorine sensors are electrochemical cells similar to a battery that produce a current when chlorine is present. By using electrodes, in contact with an appropriate electrolyte, a chemical reaction occurs that uses electrons gained from chlorine molecules to produce a galvanic current directly proportional to the concentration of chlorine present. Also, unlike an electrolytic cell in which a flow of current produces the chemical reaction, there is no zero-current as galvanic current is naturally zero when zero chlorine is present. Simply put, no chlorine present equals no current produced.

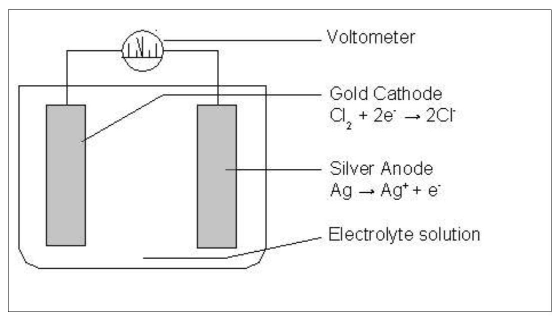


Figure 3: Basic Galvanic Cell

The IC Controls chlorine sensors use a galvanic cell separated from the sample by a chlorine permeable PTFE membrane. The cell has a gold cathode in close contact with the PTFE membrane where chlorine gains electrons (is reduced) to become chloride ions and a silver anode that produces a fixed potential and completes the reaction with the chloride to form silver chloride.

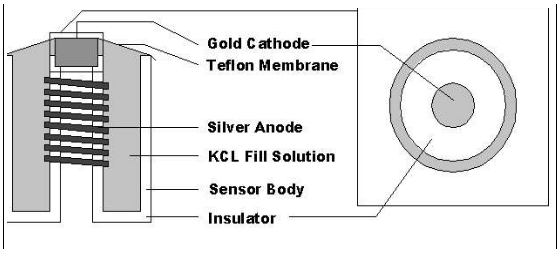


Figure 4: Galvanic Chlorine Sensor

The chemical reactions within the cell are:

At the cathode: $Cl_2 + 2e^- = 2Cl^-$

At the anode: $2Ag = 2Ag^+ + 2e^-$

Overall: $Cl_2 + 2Ag = 2AgCl$

*The measurement of the chlorine concentration is done by the galvanic HOCl sensing electrode.* However, the chlorine chemistry of the sample will change with temperature and pH. Figure 2 shows how the relative concentrations of hypochlorous acid and hypochlorite ion shift with changes in pH and temperature.

### Advantages of Galvanic Method

1. Measures the chlorine directly
2. Continuous measurement
3. No reagents or buffers added
4. No mechanical parts
5. pH and temperature compensated
6. Provides a true zero chlorine reading
7. Easy to set up and calibrate
8. Dedicated relay control for chlorine

## *pH/ORP MEASUREMENT*

### Operating Principle

Water flows through a dual flow cell consisting of an ORP and a pH sensor. A microprocessor calculates the free residual chlorine ($HOCl + OCl^-$) concentration by using a polynomial formula requiring the measured ORP, pH, and temperature values.

### Relation of ORP and Chlorine

The measurement of ORP is the reading of a voltage potential between the reference electrode and the platinum ORP sensing electrode. The voltage generated by the sample is proportional to the concentration of free available chlorine. The 877 uses a polynomial formula to calculate the total free chlorine value, which adds the hypochlorite ion concentration. This calculation requires the pH and temperature of the sample. The following graph illustrates the logarithmic relationship between ORP and chlorine.

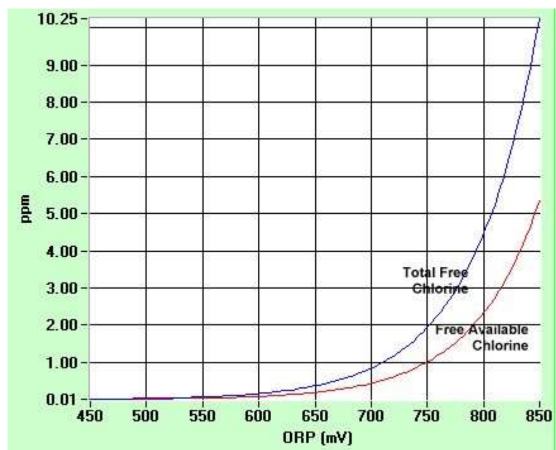


Figure 5: Relationship between ORP and Chlorine

### Water Poise and Calibration

Every individual water source has a different dissolved chemical composition which can affect the background ORP value. The 877 chlorine calibration is designed to determine this characteristic “poise” (ORP balance & stability) of the water and record this poise as a shift in the ORP value. The “poise” of a water sample varies with each water source, and will affect the zero point of the ORP relative to chlorine concentration, but not the span. This poise is usually best determined after the system has been in operation for at least 24 hours and while normal operating conditions are observed. Therefore, only a single-point “poise” calibration is performed.

### Advantages of pH/ORP Method

1. No reagents or buffers added
2. No moving parts
3. pH and temperature compensated

4. Easy to set up and calibrate
5. Dedicated relay control for chlorine and pH

## Disadvantages of pH/ORP Method

1. Does not measure free chlorine directly
2. Any oxidant present in the water sample will be read as an increase in free chlorine

## Galvanic vs. pH/ORP?

Free available chlorine can be determined using galvanic measurement or the pH/ORP method; both of which have their advantages. IC Controls offers the model 877 pH/ORP method and two galvanic analyzers, models 875 and 876. The following is an explanation of the measurement method for each application.

## Model 877 pH/ORP Chlorine Analyzer

Included with the 877 analyzer are two temperature compensated pH and ORP electrodes. The microprocessor analyzer has a pre-programmed comparison of ORP (oxidation-reduction potential) versus HOCl concentration. The ORP of the process is continuously monitored and related to the corresponding free available chlorine measurement. At the same time, the pH of the solution is monitored and the HOCl concentration is calculated relative to this pH. The 877 allows the user to access the HOCl concentration, the ORP in millivolts, and the pH of the process solution at any time to monitor all factors and ensure optimum disinfection.

For example, systems such as cooling towers require significant sterilization to minimize biological growth and scaling to help maintain high efficiency. These systems require fairly consistent chemical composition. This becomes important when using an indirect monitoring method such as ORP to measure the free available chlorine levels.

Due to the dependence of the ORP measurement, the 877 will achieve the most accurate results in systems that maintain a relatively consistent chemical composition. The ORP of a solution is not specific to any compound in the solution, but rather the ORP accounts for all chemicals and chemical reactions in solution. Variations in chemical composition can cause an increase or decrease in the ORP of the solution thus causing inaccuracies in the free available chlorine. Therefore, when using the 877, calibrating for the baseline or poise is important for accurate chlorine monitoring.

With ORP being an indirect calculated value, it is essential that the baseline ORP is measured so that the ORP reading taken by the analyzer relates most accurately to the free available chlorine level. However, once the poise is calculated through calibration, accurate chlorine readings are realized by the pH/ORP free available chlorine method.

## Model 875/876 Chlorine Analyzer

Processes such as industrial and municipal wastewater treatment can vary significantly in ORP measurement due to different substances being introduced at any given time. While disinfection in processes such as these is important, complete sterilization is not necessarily required, and therefore the dependence on pH is significantly reduced. The 875 and 876 chlorine analyzers monitor the free available chlorine directly, without the use of ORP.

The sensor used with the 875 and 876 is a galvanic cell that is separated from the process by a chlorine permeable membrane. As the HOCl in the process diffuses through the membrane a galvanic reaction occurs which produces a current that is proportional to the free available chlorine concentration. An advantage of the galvanic cell is that an absolute zero measurement can be obtained; i.e. no chlorine present equals no chlorine produced. Many manufacturers use amperometric technology as opposed to galvanic. Amperometric cells rely on an induced voltage to produce a current. As this residual current is always present, an absolute measurement cannot be obtained, and the HOCl concentration measured may be artificially high. Another disadvantage of the amperometric method that does not affect galvanic measurement pertains to iron coating. Polarization attracts iron ions that may be in the process water which can cause coating of the membrane; iron deposits on the membrane can skew the chlorine readings.

Another common analysis method used in measuring free available chlorine is the colorimetric DPD measurement. With this is an effective measurement method, it introduces a number of potential problems solved by the direct measurement method of galvanic technology:

- No reagents required: Colorimetric measurement is a reagent based typically requiring a separate waste outlet. Added reagents require time for reaction, therefore, there is usually a lag time in response. Galvanic measurement does not require reagents, allowing for reduced stock and maintenance costs.

- No mechanical parts: Galvanic direct measurement does not require reagent addition or sample mixing, so there is no need for additional pumps, tubing etc. which also reduces the maintenance required.

- No response lag time: Reagents need to be pumped into the sample chamber and thus require time to react with the sample prior to a measurement being taken, therefore, measurement is not instantaneous as with the direct method.

## Sample systems

All of the IC Controls free chlorine analyzers are available as complete sample conditioning systems. The 875, 876 or 877 is mounted on a stainless steel panel with a flow cell containing the appropriate sensors. The sample conditioning system includes a pressure regulator valve, head tank, sample point and atmospheric drain. The only installation requirement of the user is to provide plumbing to inlet and outlet.

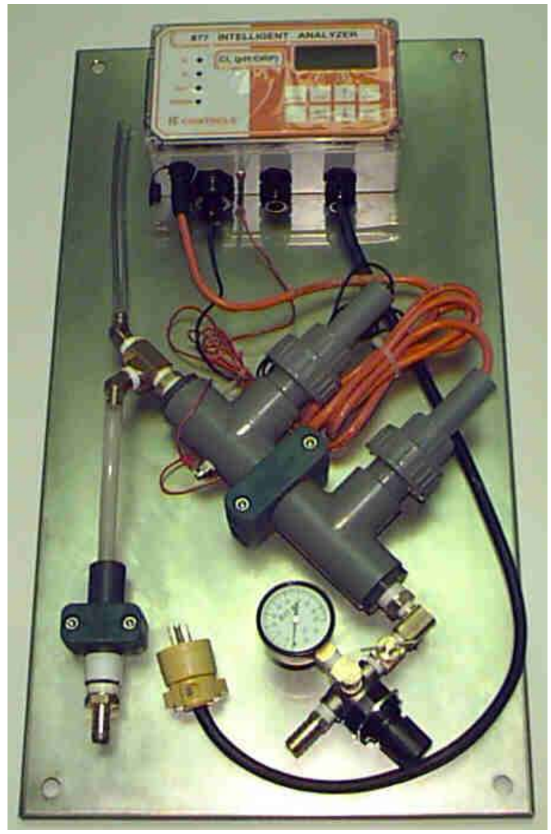


*Figure 6: Model 877 pH/ORP Chlorine System*

## Summary

There are a variety of methods available for monitoring free available chlorine; IC Controls provides two different measurement methods. Overall, it is important to note the differences in the two types of monitoring techniques and thus where to use each system for best chlorine control. The pH/ORP method is best used in systems such as cooling towers or potable water, where the baseline ORP is consistent and the pH is an important component of good control. Conversely, the galvanic sensor is best in situations where the water composition is not stable and/or continuously changing.