



**A Myron L Company  
White Paper**

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**$FC^E$ ™ : Groundbreaking Measurement of  
Free Chlorine Disinfecting Power  
in a Handheld Instrument**

***Myron L Company's Free Chlorine Equivalent ( $FC^E$ ™):  
Innovative, ORP-Based, Better!***

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## INTRODUCTION AND OVERVIEW

The most popular germicide used in water treatment is chlorine, which kills bacteria by way of its power as an oxidizing agent. Chlorine is used not only as a primary disinfectant at the beginning of the treatment process, but also at the end to establish a residual level of disinfection during distribution as a guard against future contamination.

The most popular field test instruments and test systems for judging the level of residual chlorine, also called Free Available Chlorine (FAC), are based on colorimetric methods whereby dyeing agents are added to the sample being tested. These additives react to FAC causing a color change in the test sample. While they may detect the presence of FAC, they do not directly measure the electrochemical characteristic of FAC responsible for its disinfecting power: Oxidation-Reduction Potential (ORP). They give an incomplete and sometimes misleading picture of sanitizing strength. These methods have gained industry-wide acceptance. Unfortunately, so have the weaknesses and inaccuracies inherent to them.

The Myron L Company Free Chlorine Equivalent (FC<sup>E</sup>) feature avoids these pitfalls by directly measuring ORP, the germ-killing property of chlorine and other oxidizing germicides. It displays both the ORP reading (in millivolts DC) for the sample being tested as well as an equivalent free chlorine concentration in familiar ppm (parts per million). It accounts for the very significant effect of changing pH on chlorine sanitizing power; can be used for other types of oxidizing germicides and; will track the effect of additives, such as cyanuric acid, that degrade chlorine effectivity without changing the actual concentration of free available chlorine present.

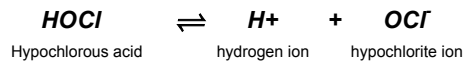
Myron L Company FC<sup>E</sup>: it is a Better way!

## CHLORINATION BASICS

NaOCl, common household bleach (5.3% NaOCl by weight) is the most popular chlorinating agent in use today. When added to water it hydrolyzes as:



Additionally, some of the HOCl dissociates into H<sup>+</sup> and OCl<sup>-</sup>:



Both HOCl and OCl<sup>-</sup> are oxidants and effective germicides, particularly against bacteria and viruses, with some effectivity against protozoa and endospores. HOCl is the stronger and more effective of the two species.

### Chlorine Demand

When chlorine is added to water, not all of it is available to act against future contaminants. Some is deactivated by sunlight. Some is consumed by reactions with other chemicals in the water or by out-gassing as Cl<sub>2</sub>. More commonly, it is used up directly by disinfection of the pathogens already present in the water or by combining with ammonia (NH<sub>3</sub>) and ammonium (NH<sub>4</sub><sup>+</sup>) (byproducts of living bacteria) to form various chloramine compounds.

Chlorine Demand is the amount of chlorine in solution that is used up or inactivated after a period of time and therefore not available as a germicide.

### Free Available Chlorine

Free Available Chlorine (FAC) is any residual chlorine that is available, after the chlorine demand is met, to react with new sources of bacteria or other contaminants. According to White's Handbook of Chlorination and Alternative Disinfectants, 5th edition, this is the sum of the all of the chemical species that contain a chlorine atom in the 0 or +1 oxidation state and are not combined with ammonia or other organic nitrogen. Some species of FAC that might be present are:

- *Molecular chlorine: Cl<sub>2</sub>*
- *Hypochlorous acid: HOCl*
- *Hypochlorite: OCl<sup>-</sup>*
- *Trichloride: Cl<sub>3</sub><sup>-</sup> a complex formed by molecular chlorine and the chloride ions (Cl<sup>-</sup>)*

In most applications the two most common species of free chlorine will be HOCl and OCl<sup>-</sup>. Much of the Cl<sub>2</sub> will hydrolyze into HOCl that, depending on pH, will stay in the form of HOCl or partially dissociate into OCl<sup>-</sup>. Cl<sub>3</sub><sup>-</sup> is very unstable and only trace amounts will be present. In fact, in most of the literature describing chlorination and the monitoring of chlorine residuals, free chlorine is considered to be the sum of HOCl and OCl<sup>-</sup>.

Chlorine dioxide, ClO<sub>2</sub>, is another chlorine derivative used in some public water supplies as a disinfectant. It is 10 times more soluble in water than chlorine and doesn't hydrolyze into HOCl or dissociate into OCl<sup>-</sup>. In the absence of oxidizable substances and in the presence of hydroxyl ions, ClO<sub>2</sub> will dissolve in water then decompose slowly forming chlorite ions (ClO<sub>2</sub><sup>-</sup>) and chlorate ions (ClO<sub>3</sub><sup>-</sup>), both of which are oxidants fitting White's definition of free chlorine.

All other things being stable (temperature, pH, etc.), ORP values are related to FAC concentration levels. As the concentration of FAC in solution rises or falls, regardless of the species (HOCl, OCl<sup>-</sup>, ClO<sub>2</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup> or Cl<sub>3</sub><sup>-</sup>), the ORP value does, as well.

**Combined and Total Chlorine**

The term Combined Chlorine usually refers to residual chlorine that has combined with NH<sub>3</sub> or NH<sub>4</sub><sup>+</sup> to form monochloramine (NH<sub>2</sub>Cl), dichloramine (NHCl<sub>2</sub>) or trichloramine (NCl<sub>3</sub>). Combined chlorine is noteworthy here because chloramines are oxidizers and are used as germicides, though their reduction potential and therefore, disinfecting power is lower than other species of chlorine, such as HOCl, OCl<sup>-</sup> or ClO<sub>2</sub>.

Total chlorine is the sum of FAC and Combined Chlorine. An advantage of ORP-based systems is that the aggregate ORP value of the water being tested includes the ORP levels contributed by all oxidizers, including chloramines. Therefore, ORP-based measurements automatically take into account Total Chlorine and can readily be used to judge total sanitizing strength.

**Chlorine as an Oxidizing Germicide**

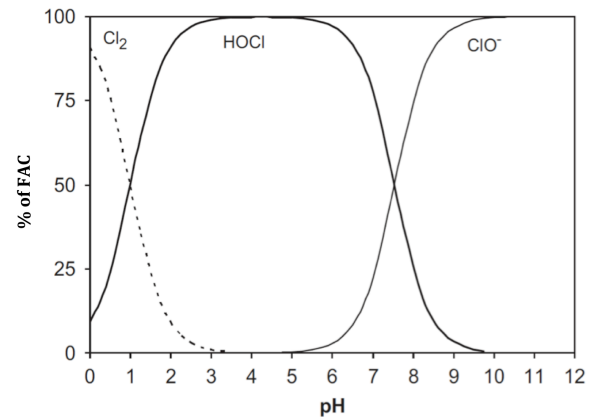
Both HOCl and OCl<sup>-</sup> are oxidants and as such their effectivity as germicides can be determined using

ORP measurements. The cytoplasm and proteins in the cell walls of many harmful microbes are negatively charged (they have extra electrons). Any oxidant that comes into contact with the organism will gain electrons at the expense of the proteins, denaturing those proteins and killing the organism.

When enough chlorine is added to water to reach an ORP value of 650mV to 700mV, bacteria such as *E. coli* and *Salmonella* can be killed after only 30 seconds of exposure. Many yeast species and fungi can be killed with exposure of only a few minutes. Even ORP values of 350mV to 500mV indicate effective levels of chlorination with satisfactory microbe kill levels, although exposure times are required to be in the minutes rather than seconds.

**The Importance of pH**

pH significantly changes relative effectiveness of chlorine as a disinfectant. Different species of chlorine ions are more prevalent at different pH levels. Under typical water treatment conditions in the pH range 6-9, HOCl and OCl<sup>-</sup> are the main chlorine species. Depending on pH level, the ratio of these two free chlorine species changes.



**Figure 1 – Distribution of Free Chlorine Species in Aqueous Solutions<sup>1</sup>**

Figure 1 shows that chlorine hydrolysis into HOCl is almost complete at pH ≤ 4. Dissociation of HOCl into OCl<sup>-</sup> begins around 5.5 pH and increases dramatically thereafter<sup>2</sup>. This is important because HOCl and OCl<sup>-</sup> do not have the same effectivity as disinfectants. HOCl can be 80-100% more effective as a disinfectant than OCl<sup>-</sup>. Optimum disinfection occurs at pH 5 to 6.5 where HOCl is the prevailing species of free chlorine present. As pH rises above

that level, the ratio shifts towards being primarily OCl<sup>-</sup>. At pH 7.5 the ratio is about even. When the pH value rises to 8 or higher, OCl<sup>-</sup> is the dominant species. Therefore, assuming the concentration of Cl<sub>2</sub> species is constant, the higher the pH of the solution rises above 5.5, the lower the oxidation capability and disinfecting power of the FAC.

The bottom line is knowing the concentration of FAC ions in a solution without taking pH into account can give an incomplete and sometimes incorrect picture of disinfecting power.

## WHY A CHANGE IS NEEDED

### The Problem with Colorimetric Testing

First and foremost, colorimetric tests only report how much chlorine is present, and as we saw in the previous section, knowing "how much" is not at all the same as knowing "how effective".

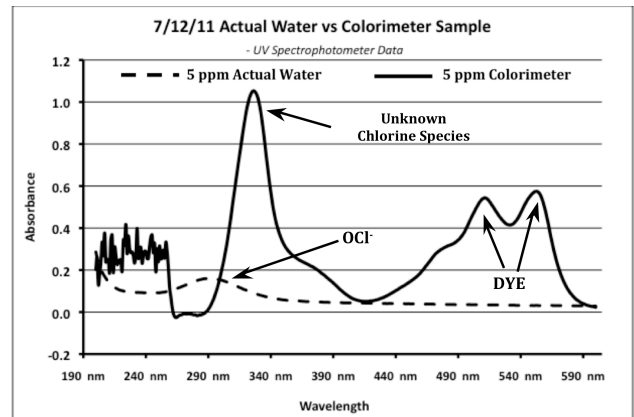
Colorimeters and DPD kits add a reagent or several reagents to the water being tested that causes a color change representing the amount of FAC in water. In fact, they fundamentally change the chemistry of the water just to get an easy measurement.

The most obvious change is related to pH. The typical reagent/dye used in the process forces the pH of the sample to a specific level, usually 6.5 pH and thus radically alters the HOCl to OCl<sup>-</sup> ratio. If the original sample was at a pH of 7.4 to 7.6 (suggested levels for pools and spas) about 50% of the FAC present would be in the form of HOCl. At a pH of 6.5 this ratio rises to nearly 90%. While the actual concentration of FAC may be correct, a fact entirely overlooked is that the FAC in the source water includes about 40% of the much weaker sanitizing OCl<sup>-</sup>.

If that were the only change being made to the chemistry of the sample, it would be severe enough.

Figure 2 shows the result of a comparison test made using a UV spectrophotometer on two samples of water. Both were taken from a master water sample containing 5 ppm Cl<sub>2</sub> prepared using a closed system that ensured no other oxidants or interferants were present. One was processed using a colorimeter

reagent according to its operator's manual instructions. The other was left untreated.



**Figure 2 – Chemical Alteration of Chlorinated Water by Colorimeter Additives**

UV spectrophotometric analysis shows how dramatically the chemistry of the sample was changed by the addition of the colorimeter's coloring reagent.

- The shift in the center of the spike indicates that the species of chlorine present has been altered. What was OCl<sup>-</sup> is now some other chemical species.
- The amplitude of the spike demonstrates how severely the amount of chlorine has been amplified.
- The absorption spectra where OCl<sup>-</sup> used to be is significantly depressed.

Because the area of UV absorption spectra where any OCl<sup>-</sup> would appear is so depressed, it is clear that a radical alteration is taking place above and beyond simply changing the pH. The "ppm" value reported for the chlorine content of the water seems to be converted to a single species whose concentration is significantly higher than the original OCl<sup>-</sup> content.

Even assuming a linear relationship between this altered chemistry and the original FAC content of the water that might be factored into the final colorimetric measurement, by completely divorcing the measurement from the pH of the source water, any direct correlation to the reduction potential of the FAC present and, therefore, real disinfecting power, is lost.

## **ORP = DISINFECTING POWER**

### **What is ORP?**

ORP is the acronym for Oxidation Reduction (REDOX) Potential. It is a differential measurement of the mV potentials built up between two electrodes exposed to solutions containing oxidants and/or reductants. ORP describes the net magnitude and direction of the flow of electrons between pairs of chemical species, called REDOX pairs. In REDOX reactions, one chemical of the pair loses electrons while the other chemical gains electrons. The chemicals that acquire electrons are called the oxidants (HOCl, OCl<sup>-</sup>, ClO<sub>2</sub>, bromine, hydrogen peroxide, etc.). The chemicals that give up electrons are called the reductants (Li, Mg<sup>2+</sup>, Fe<sup>2+</sup>, Cr, etc.). Oxidants acquire electrons through the process of reduction, i.e., they are reduced. Reductants lose their electrons through the process of oxidation, i.e., they become oxidized.

### **How is ORP Measured?**

ORP sensors are basically two electrochemical half-cells: A measurement electrode in contact with the solution being measured and a reference electrode in contact with an isolated reservoir of highly concentrated salt solution. When the solution being measured has a high concentration of oxidizers, it accepts more electrons than it loses and the measurement electrode develops a higher electrical potential than the stable potential of the reference electrode. A voltmeter in line with the two electrodes will display this difference in electrical potential (reported in mV). Once the entire system reaches equilibrium, the resulting net potential difference represents the Oxidation Reduction Potential (ORP). A positive reading indicates an oxidizing solution, and a negative reading indicates a reducing solution. More positive or negative values mean the oxidants or reductants present are stronger, they are present in higher concentrations or both.

### **What Does ORP Measure?**

Measuring ORP is the most direct way to determine the efficacy of oxidizing disinfectants in aqueous solutions. It measures the actual chemical mechanism by which oxidizers, like chlorine, kill bacteria and viruses. The higher the ORP value, the stronger the aggregate residual oxidizing power of

the solution, the more aggressively the oxidants in it will take electrons from the cells of microbes and, therefore, the more efficiently and effectively any source of new microbial contamination will be neutralized.

Also, because ORP measures the total reduction potential of a solution, ORP measures the total efficacy of all oxidizing sanitizers in solution: hypochlorous acid, hypochlorite, monochloramine, dichloramine, hypobromous acid, ozone, peracetic acid, bromochlorodimethylhydantoin, etc.

### **Can ORP Replace Free Chlorine Measurements?**

Yes.

When correlated with known disinfection control methods, measurements and bacterial plate counts, this type of measurement gives an accurate picture of the residual chlorine sanitizing activity reported as an empirical number that is not subject to visual interpretations. Solutions with certain ORP levels kill microbes at a certain rate. Period!

ORP was first studied at Harvard University in the 1930s as a method for measuring and monitoring microbial disinfection. It has been advocated as the best way to judge residual disinfecting power of chlorinated water by water quality experts since the 1960s. ORP has long been used in bathing waters as the only means for automatic chemical dosing. The World Health Organization (WHO) suggests an initial ORP value of between 680-720 mV for safe bathing water<sup>3</sup> and ~800 mV for safe drinking water<sup>4</sup>.

For the purpose of pretreatment screening to detect chlorine levels prior to contact with chlorine-sensitive RO membranes, some manufacturers of RO membranes and other water quality treatment equipment will also specify an ORP tolerance value for prescreening and influent control.

There are, however, applications where reporting residual disinfecting power in terms of FAC concentrations is preferred and sometimes required. While ORP measurements do not directly measure the concentration of FAC, they can be correlated to free chlorine levels in ppm. Variables such as pH and temperature must be accounted for or controlled. Interfering chemicals that might be present, such as

other oxidants or reductants, must also be accounted for, or better yet, removed.

Once all these factors are known or controlled, ORP values can be linked to concentrations either by way of laboratory experimentation or via mathematical formulas like the Nernst Equation, an equation that describes the relationship between the electrode potential of a specific chemical in a solution and its concentration. In either case this is an often complex and laborious process ... until now.

## **FC<sup>E</sup> = HANDHELD ORP ACCURACY**

### **ORP Relevance in a Handheld Instrument**

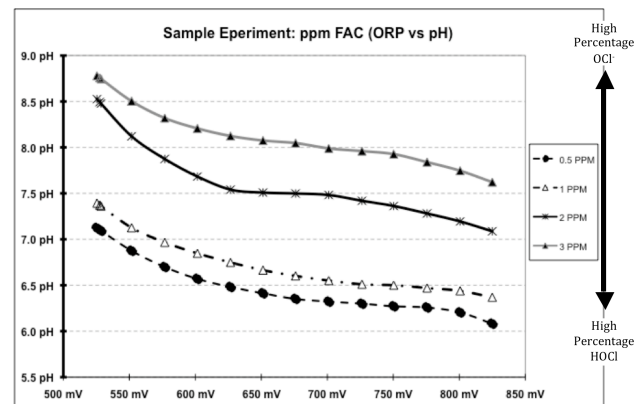
The Myron L Company has developed an innovative method for using ORP-based measurement to directly monitor the disinfecting power of free chlorine and report the result in both familiar ppm units as well as straight ORP mV values.

Myron L Company's FC<sup>E</sup> function utilizes the accurate and reliable electronic design of Myron L Company's instruments combined with simple one-button operation to make ORP-based chlorine measurement available in an easy-to-use, handheld field instrument. Other handheld instruments may measure ORP, but only a Myron L Company instrument equipped with FC<sup>E</sup> quickly correlates ORP and pH with FAC concentration. The FC<sup>E</sup> function also includes a predictive algorithm that extrapolates a final, stable ORP value of a solution without waiting out the long response time of the typical ORP sensor.

When the FC<sup>E</sup> function is active, the instrument display alternates between the Predictive ORP reading (mV) and the Free Chlorine Equivalent (FC<sup>E</sup>) concentration (ppm). Together these features combine to make ORP-based free chlorine measurement relevant in a handheld field instrument.

## **FC<sup>E</sup> – How and Why it Works**

The Myron L Company FC<sup>E</sup> feature cross-references ORP values with pH levels to automatically arrive at a concentration value for FAC that reflects the effect of pH on the ratio of HOCl to OCl<sup>-</sup>. This correlation is derived from a series of experiments in which exact amounts of chlorine (in the form of laboratory grade bleach: 5% NaOCl; 95% H<sub>2</sub>O) were added to deionized water in a closed system, thus controlling and excluding possible interferants. By using both a pH measurement and an ORP measurement, FC<sup>E</sup> can determine the relative contributions of HOCl and OCl<sup>-</sup> to the final ORP value and factors them into a final concentration calculation.



**Figure 3 – Sample Experimental Data Relating FAC ppm to ORP and pH**

Similar experiments were performed using water to which precise amounts of calcium chloride (CaCl<sub>2</sub>) and sodium bicarbonate (NaHCO<sub>3</sub>) were added to slightly buffer the water. This allows the FC<sup>E</sup> feature to correlate low ORP values to the typically low FAC concentrations of tap water after it has been in the municipal water system for several days.

## **FC<sup>E</sup> – pH Included, Not Ignored**

Unlike other FAC test methods that ignore the effect of pH on sanitizing power by artificially forcing the pH of their test sample to a single value, Myron L Company's FC<sup>E</sup> includes pH in its concentration calculation. This capability gives Myron L Company's FC<sup>E</sup> the ability to compensate for the effect of the changing ratio of chlorine species as pH changes, resulting in a FAC concentration value germane to the actual sanitizing power of the source water. OCl<sup>-</sup> is measured as OCl<sup>-</sup>, and HOCl is

measured as HOCl. Those users who are primarily concerned with or who prefer free chlorine concentration levels have a reliable measurement that gives consistent and comparable results, reading to reading, without having to rigorously control or artificially manipulate the sample's pH.

In addition, because the FC<sup>E</sup> function displays both the FAC concentration and a predicted, stable ORP value, the user can, by comparing these two values from successive measurements, track how ORP (and disinfecting power) falls as pH rises and how ORP rises as pH is lowered when concentration is constant.

**FC<sup>E</sup> – Chemistry Measured, Not Altered**

Both DPD kits and colorimeters may tell the user the FAC concentration of the sample in the test tube, but since the chemistry of that sample is quite different from the source water being analyzed, the results are imprecisely related to actual disinfection power. DPD kits and colorimeters only imply true disinfecting power; they do not measure it, and that is, after all, the whole point of the exercise.

The Myron L Company FC<sup>E</sup> method avoids these pitfalls and inaccuracies. FC<sup>E</sup> measures the real, unaltered chemistry of source water, including moment-to-moment changes in that chemistry.

The following controlled study shows exactly how differently the two methods respond, particularly at the high end where the effects of changes in pH are the greatest. In this study measurements were made with a digital colorimeter and a Myron L Company Ultrameter II 6P equipped with FC<sup>E</sup>. The solutions tested were made with various known concentrations of NaOCl in deionized water. The water was heated to above 80°C to remove any CO<sub>2</sub> and, therefore, avoid interference from REDOX reactions between HOCl, OCl<sup>-</sup> and carbonates (HCO<sub>3</sub>).

**Table 1 – Comparison of FC<sup>E</sup> to Digital Colorimeter**

Target FAC	pH	Approx* % OCl <sup>-</sup>	FC <sup>E</sup> Value	Colorimeter value
0.5 ppm ±.01 ppm	6.44 pH	7%	0.49 ppm	0.13 ppm
1.0 ppm ±.01 ppm	6.48 pH	7%	0.85 ppm	0.24 ppm
2.0 ppm ±.06 ppm	7.65 pH	65%	2.01 ppm	0.72 ppm
3.0 ppm ±.08 ppm	7.88 pH	73%	2.68 ppm	1.13 ppm
4.00 ppm ±.08 ppm	8.28 pH	85%	3.89 ppm	1.50 ppm
5.00 ppm ±.08 ppm	8.70 pH	94%	4.96 ppm	1.90 ppm

\*Estimates of %OCl<sup>-</sup> based on ratios depicted in Figure 1 above

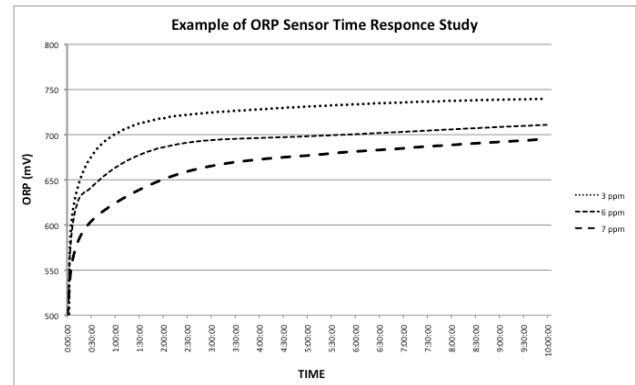
In this study as the pH rises and the ratio of OCl<sup>-</sup> to HOCl rises dramatically, the FC<sup>E</sup> is able to accurately track the changing concentration of FAC. The colorimeter's results do not.

**FC<sup>E</sup> – Handheld ORP Accuracy Without the ORP Delay**

One of the challenges in implementing an ORP-based free chlorine measurement in a handheld field instrument is the sometimes lengthy response time of ORP sensors. It is not uncommon for an ORP sensor to take 12 to 15 minutes to arrive at a valid stable reading. In extreme cases, such as an older sensor in poor condition and measuring a complex solution with a very low ionic strength, the ORP measurement can take up to an hour to fully stabilize. Obviously, for a handheld instrument these are unacceptably long times.

The Myron L Company FC<sup>E</sup> function includes a pioneering feature that dramatically reduces the wait for stable ORP readings. This unique feature determines an extrapolated, final, stabilized ORP reading within 1 to 2 minutes rather than the typical 15 minutes or hours for other ORP systems.

The Predictive ORP feature's calculations are based on a model of sensor behavior developed through a series of experiments that measured the response time of a representative sample of ORP sensors over a range of controlled chlorine concentrations. The results of this set of experiments revealed that the shape of the curve is very similar for various ORP levels differing only in the initial starting point and the final stabilized reading.



**Figure 4 – Example of ORP Sensor Response Study**



Using a proprietary curve-matching algorithm, the Predictive ORP feature determines what point along the typical sensor response curve a measurement occurred and extrapolates an appropriate final reading. This extrapolated value is used to calculate the FC<sup>E</sup> ppm value without having to wait for the sensor to stabilize and is also reported directly to the instrument's display.

**FC<sup>E</sup> – FLEXIBILITY FOR THE REAL WORLD**

Another advantage of an ORP-based measurement such as the Myron L Company FC<sup>E</sup> feature is that, within the limits of its range, it can be used to measure the disinfection effectivity of ANY oxidizing germicide. Myron L Company FC<sup>E</sup> measurement can be used with non-bleach oxidants, such as chloramines or even non-chlorine oxidants, such as peracetic acid, bromine or iodine.

The Predictive ORP value displayed when the FC<sup>E</sup> function is active is directly relevant for monitoring and controlling the sanitizing effectivity of oxidizing sanitizers besides HOCl and OCl<sup>-</sup>.

While the concentration values reported by the FC<sup>E</sup> function will not be absolutely correct for non-FAC oxidants, since they are based on a HOCl / OCl<sup>-</sup> model, FC<sup>E</sup> can still be an effective tool for monitoring relative changes in concentration levels. For absolute accuracy a correlative study should be performed to relate concentration levels of the oxidant in question to the ORP values displayed by the Predictive ORP feature and ppm values output by the FC<sup>E</sup>.

**FC<sup>E</sup> = Effective Chloramine Control**

A perfect example of the Myron L Company FC<sup>E</sup> 's flexibility is the use of chloramines as a germicide.

Chloramines are formed when chlorine (Cl<sub>2</sub>) and ammonia (NH<sub>3</sub>) come into contact, forming three different inorganic chemicals: monochloramine (NH<sub>2</sub>Cl), dichloramine (NHCl<sub>2</sub>) and trichloramine (NCl<sub>3</sub>). In some applications chloramines are considered an unavoidable side effect of the chlorination process; however, because they are also oxidants, there are other applications where they are used as the primary disinfectant in water treatment.

Chloramines are effective at killing bacteria and other microorganisms, but because their relative ORP levels are lower compared to HOCl or OCl<sup>-</sup> at the same concentrations, the disinfection process is slower.

*Table 2 – Electrode Potentials of Chloramines vs. HOCl<sup>5</sup>*

OXIDANT	E' VOLTS
HOCl Acid	1.48
Monochloramine	1.40
Dichloramine	1.34

On the plus side, chloramines last longer than HOCl and OCl<sup>-</sup> (as long as 23 days in some cases), impart a less strong flavor or smell and their sanitizing strength is not appreciably affected by changing pH.

Most importantly, chloramine-based water treatment methods produce much fewer hazardous byproducts. The US EPA limits the total concentration of the four chief hazardous byproducts of chlorination (chloroform, bromoform, bromodichloromethane, and dibromochloromethane), referred to as total trihalomethanes (TTHM), to 80 parts per billion in treated water. To avoid exceeding these standards, many municipal water districts prefer using chloramine rather than chlorine.

The following table shows typical ORP values for various concentrations of monochloramine (NH<sub>2</sub>Cl).

*Table 3 – ORP Values for NH<sub>2</sub>Cl in Pure Water<sup>6</sup>*

NH <sub>2</sub> Cl CONCENTRATION	TYPICAL ORP*
Typical Tap Water at Faucet	350 mV to 375mV
0.4 ppm	410 mV
0.6 ppm	440 mV
1.0 ppm	450 mV
1.5 ppm	460 mV
2.5 ppm	480 mV
3.0 ppm	490 mV
4.0 ppm	500 mV

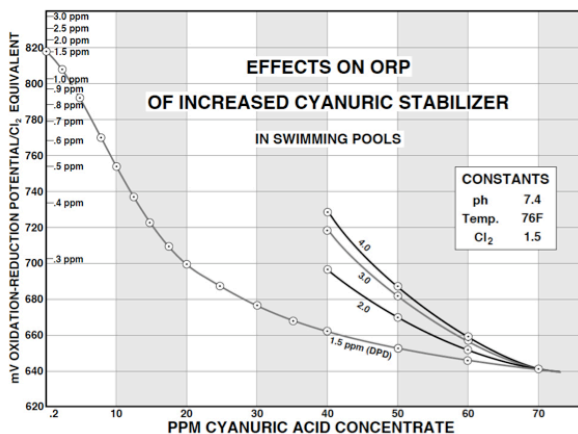
When ORP levels of NH<sub>2</sub>Cl approach and exceed 500 mV, effective sanitization occurs with exposure times of 20 to 30 minutes. This is more than adequate for municipal water treatment.

Since Myron L Company FC<sup>E</sup> function bases its measurement on ORP, it presents an empirical, easy to interpret measurement, both in terms of the Predictive ORP display and the FAC equivalent concentration, allowing the user to monitor falling chloramine concentration as disinfection proceeds.

## **FC<sup>E</sup> and Cyanuric Acid (CYA) - Don't Guess. Know!**

Outdoor pool maintenance is a prime application where ORP-based chlorine measurement should be preferred. The use of chlorine to sanitize pools runs afoul of the fact that much of the chlorine added to an outdoor pool is deactivated by exposure to UV radiation in sunlight.

Cyanuric Acid (CYA) is often added to the pool water to "protect" FAC. In a typical pool at 7.6 pH about 50% of the FAC is OCl<sup>-</sup>, which reacts to UV radiation that passes through the Earth's ozone layer (290nm). CYA combines with FAC to form *N-chlorinated-cyanurates*, which only react to UV radiation (215nm to 235nm) removed by the Earth's ozone layer. Since *N-chlorinated-cyanurates* are also oxidizers, they also act as germicides. Unfortunately, they have much lower reduction potentials and, therefore, a much lower strength as a germicide.



**Figure 5 – Effect of Cyanuric Acid on Chlorine ORP Values<sup>7</sup>**

Pool maintenance websites that advocate the use of cyanuric acid (not all of them do) often recommend levels of 40 to 80 ppm. Figure 5 shows how severely ORP and disinfecting power are affected by CYA.

The addition of only 20 ppm CYA decreases the pool water's ORP 120 mV, reducing the effectivity of FAC from 1.5 ppm to an effectivity that is equivalent to only 0.3 ppm. Adding 40 ppm, or worse, 80 ppm, reduces sanitizing strength even more severely. This is definitely a case where more is not better.

A 1972<sup>8</sup> study on water chlorination showed that water treated with enough chlorine to kill 100% of the E. coli present in 3 minutes or less required almost 6 times as much chlorine be added for the same effect when 50 ppm of CYA was added.

Cyanuric acid beneficially affects pool chlorination by greatly reducing that portion of chlorine demand related to loss due to UV. Unfortunately, if you are using a colorimeter or DPD kit, it will tell you that your FAC concentration is unchanged and significantly misrepresent sanitizing strength.

The Myron L Company FC<sup>E</sup> function's ability to react to changes in ORP makes it an ideal tool for keeping track of how CYA affects residual sanitizing power when added to a chlorinated pool. The Predicative ORP display provides a direct and effective way to monitor changes in ORP values as CYA concentration increases. Because the FC<sup>E</sup> ppm display reacts to changes in ORP and pH, it will reflect changes in the sanitizing strength as an "equivalent" or "effective" FAC concentration.

## **SUMMARY**

Judging the true effectivity of chlorine as an oxidizing germicide requires more than just knowing how much chlorine is present. Changing pH or the addition of additives like cyanuric acid can radically alter the effectivity of the chlorine present. To accurately measure the effects of these issues requires a test method based on the precise measurement of ORP (the chemical characteristic directly responsible for killing microbes like bacteria and viruses) and cross-referenced to pH.

The Myron L Company FC<sup>E</sup> is the first measurement function that allows handheld, field instruments to integrate ORP and pH measurements into a system for monitoring the residual disinfecting power of free available chlorine in aqueous solutions.

- *It provides an empirical measurement that does not require interpretation.*
- *It is not affected by water color or turbidity.*
- *It measures the true chemistry of the water, unaltered.*
- *It accounts for changes in pH.*
- *It reports the effects of CYA on disinfecting power.*
- *It can be used to monitor non-chlorine oxidants.*

It is a Better Way!

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## ENDNOTES

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- <sup>1</sup> *Adopted from: Reactions of chlorine with inorganic and organic compounds during water treatment—Kinetics and mechanisms; A critical review: Marie Debordea, Urs von Gunten, WATER RESEARCH Vol. 42 (2008); Pgs 13 – 51*
- <sup>2</sup> *Other more obscure chlorine species that could affect the ORP reading, such as Cl<sup>3-</sup>, chlorine hemioxide (Cl<sub>2</sub>O) or H<sub>2</sub>OCl<sup>+</sup> can also form at pH < 4, however under typical water treatment conditions their concentrations are very low*
- <sup>3</sup> *Guidelines for Safe Recreational Water Environments, Vol. 2, Swimming Pools and Similar Environments, World Health Organization, (2006), Pg 96*
- <sup>4</sup> *Water Treatment and Pathogen Control – Process Efficiency in Achieving Safe Drinking Water, Mark W. LeChevallier and Kwok-Keung Au, World Health Organization, (2004), Pg 49*
- <sup>5</sup> *Adopted from: Production of Chloramines and Chloramine Monitoring in Water Supply Systems; By Robert D. McVay PE; FLORIDA WATER RESOURCES JOURNAL; (April 2009)*
- <sup>6</sup> *ibid*
- <sup>7</sup> *Adopted from: Cyanurics, Benefactor or Bomb ~ Copyright, Kent Williams, (December 12, 1997), Newcastle, California*
- <sup>8</sup> *REDOX Potential Measurements for Determining the Disinfecting Power of Chlorinated Water; Journal of Hygiene, K. Victorin, K-G Hellström and R. Rylander; Vol 70 (1972); Pgs 313 – 323*

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