ORP Sensor Response in Chlorinated Water

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Proper maintenance of pools and spas requires frequent testing of the pH and sanitizer level in the water. This is traditionally done with colorimetric test kits. Today however, more and more pools and spas use chemical automation which relies on the use of electronic sensors, usually pH and ORP (Oxidation–Reduction Potential) electrodes.

Numerous studies have shown that ORP is an excellent monitor of the chemical activity of the sanitizer and, consequently, of biological conditions in the water. However, little information has been presented on the operational properties of the sensor itself. The present study was therefore designed to evaluate the response of ORP sensors in chlorinated water, in terms of reproducibility and reliability and in response to various operational parameters.

In order to establish a basis for comparison with conventional testing methods, a preliminary study was conducted to determine the accuracy and reliability of amperometric titration, colorimetric analysis and DPD test kits.

The reproducibility of ORP sensor readings was determined by immersing 10 new sensors in the same chlorinated water solution. They showed standard deviations of 5, 4 and 1.9 millivolts respectively after 5 minutes, 20 minutes and 16 hours of immersion. Total Dissolved Solids concentrations of up to 3,500 ppm (mg/l) of sodium chloride (NaCl) showed no effects on ORP response.

Pre–conditioned ORP sensors immersed in free chlorine concentrations of 0.2 and 3.0 ppm were found to require a minimum of 10 to 12 minutes to reach a stable reading.

ORP sensor response as a function of pH was studied for chlorine concentrations between 0.2 ppm (mg/l) and 10 ppm (mg/l) and pH values between 6.5 and 8.5. The results were compared with earlier published data and with theoretical analysis of oxidation–reduction reactions.

Finally, a longevity study was undertaken to evaluate the long–term stability of ten randomly selected sensors. Initial results show no deterioration of the sensors in over a year.

Oxidation–Reduction Reactions

The successful application of chemical automation to swimming pools and spas over the recent years is due in a large part to the availability and reliability of the Oxidation–Reduction Potential sensor, usually called ORP probe or Redox electrode (Figure 1).

An oxidation–reduction reaction is a paired reaction between two different types of chemicals that involves an exchange of electrons. Chemicals that acquire electrons are called oxidizers while the chemicals that lose electrons are called reducers.

The two most common sanitizers used in water treatment – hypochlorous acid (HOCl) and hypobromous acid (HOBr) – are both oxidizers as well as sanitizers. Other oxidizers used in water treatment are ozone (O_3), hydrogen peroxide (H_2O_2), potassium monopersulfate ($KHSO_5$) and potassium permanganate ($KMnO_3$). These are strong oxidizers that are used for shock treatment and for the destruction of organic contaminants.

Reducers include inorganic and organic contaminants, such as chloramines, oils, urea, perspiration, germs, bacteria, algae, leaves, etc.

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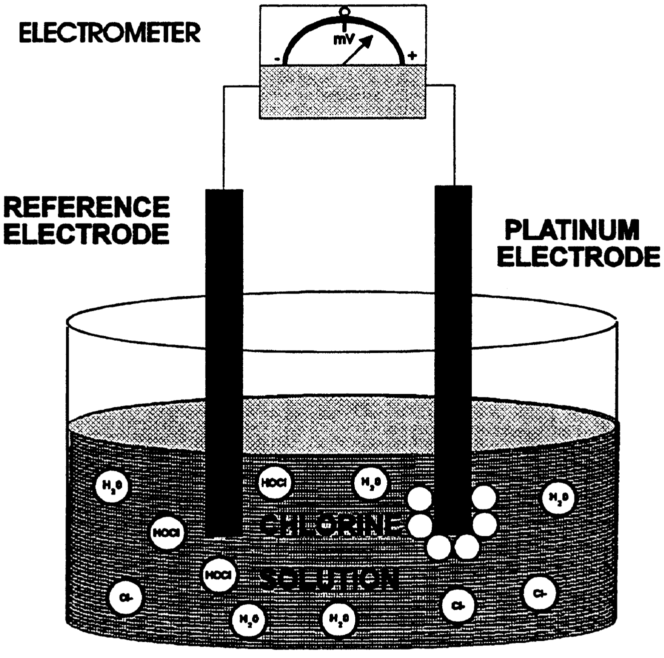

Figure 1 – Schematic of ORP Cell

Because the oxidation–reduction reaction involves an exchange of electrons, it can be used to generate measurable electrical currents, using an arrangement similar to the one shown in Figure 1.

The electrical circuit shown in Figure 1 is made up of two electrodes that are inserted in an aqueous solution containing an oxidizer, in this case chlorine. One of the electrodes is an inert electrode made of a noble metal, such as platinum or gold, that does not react chemically but can transmit electrons. The other electrode is a reference cell that contributes a constant voltage to the measurement.

The theoretical reference electrode is the so-called hydrogen electrode which is stable and is arbitrarily assigned the voltage of 0. In practice, a more practical electrode is generally used which is a calomel or silver/silver chloride reference producing a stable potential of –200 mV.

The oxidation–reduction reaction shown in Figure 1 can be represented by the equation:

$$\mathrm{HOCl} + \mathrm{H}^+ + 2e^- \rightleftharpoons \mathrm{Cl}^- + \mathrm{H_2O} \qquad (1)$$

Equation (1) shows that the oxidizer – in this case the active form of free chlorine, hypochlorous acid (HOCl) – captures two electrons and is reduced to chlorine ions (Cl^-). It should be realized that this is a much simplified representation of the actual reactions of free chlorine, which, in reality, can take many varied forms.

Advantages of ORP

Conventional test kits measure only sanitizer concentration and depend on human eye interpretation of color variations. They also can give misleading results under certain conditions, such as excessive sanitizer concentrations that bleach out the colors.

ORP measurements present the advantage of measuring not only the concentration of the sanitizer but also its activity in the water. In particular, it shows the effects of key operating parameters, such as pH and cyanuric acid stabilizer, both of which affect the effectiveness of the sanitizer, i.e., its ability to destroy germs and bacteria.

Another key advantage of ORP is that it is an electrical measurement that produces an electrical signal that can be easily interfaced with monitoring and control equipment.

The ORP Sensor

Laboratory electrodes used for precise measurements use two electrodes, one for measuring and one as a reference. Modern electrodes used for chemical automation however are of the combination type which include both the measuring and the reference electrodes in a single concentric configuration, as shown in Figure 2.

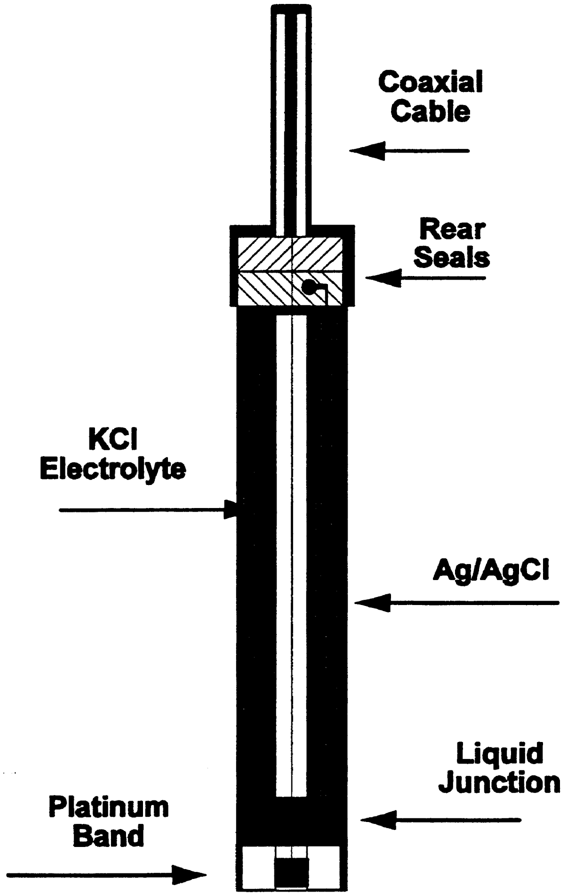

Figure 2 – The ORP Sensor

Although there have been numerous studies showing that ORP values are very useful in predicting the biochemical properties of the water and therefore its sanitary condition, very little data is available concerning the actual measurement of ORP, that is the reliability and accuracy of the sensor itself. The purpose of the present study was therefore to study the response of commercially available ORP sensors in chlorinated water and the effect of several key operating factors, such as immersion time, pH and conductivity.

The ORP sensor is a complex measuring instrument that requires sophisticated and precise manufacturing techniques.

Besides the chemistry of the water which affects the theoretical response of the ORP sensor, its actual output can be influenced by small changes in fabrication technology. These include trace impurities in the platinum band material, variations in the interconnection between the platinum band and the glass junction, variations in the porosity of the junction and the shape and volume of the electrolyte.

The determination of the reproducibility of sensor readings is of particular importance to the pool or spa operator because there is no convenient buffer solution that can be used for calibration of the ORP sensor in the millivolt range used for water treatment applications. ORP sensors are therefore used as received from the manufacturer and depend on quality control during the manufacturing process.

Experimental

The present study was conducted under carefully controlled laboratory conditions in the Water Chemistry Laboratory of Santa Barbara Control Systems in Santa Barbara, CA. Additionally, water samples from local pools and spas were used for comparison with laboratory test data.

Water – Unless otherwise indicated, chlorine–demand free water used was commercially available Sparkletts distilled water with conductivity of about 2 micromhos/cm.

Unless otherwise indicated, the water used in all the tests had a pH of 7.5, an alkalinity level of 100 ppm and a TDS between 200 to 500 ppm..

Chlorine Solutions – Commercially available, swimming pool grade 12.5% sodium hypochlorite solutions were used to prepare all samples of chlorinated water. Stock solutions of about 12.5 ppm (12.5 mg/l) were prepared by successive dilutions of up to 10,000 times in distilled water. The final concentrations were determined by amperometric and colorimetric testing as well as with test strips.

ORP Sensors – The ORP sensors used in the study were commercial–grade, dual–junction combination electrodes fabricated for the CHEMTROL$_{TM}$ division of Santa Barbara Control Systems. The surface area of the platinum band is approximately 0.5 cm^2 and the volume of the electrolyte is 50 cc.

Amperometric Titration – Amperometric titration gives a direct quantitative measurement of free and combined chlorine concentrations in water by measuring the amount of phenylarsine oxide C_6H_5AsO required to reduce them. However, since it is more complicated and time consuming than colorimetric methods, it is used primarily as a baseline method to establish the validity of the other methods.

In this study, amperometric testing was performed with a Fisher Scientific Model 397 Cl Titrimeter using dual plate platinum electrodes. As shown in Figure 3, a 200–ml chlorine solution was progressively reduced with phenylarsine oxide while measuring the current passing through the electrodes with a microammeter. The endpoint of the oxidation–reduction reaction is easily determined from the breakpoint in the current curve.

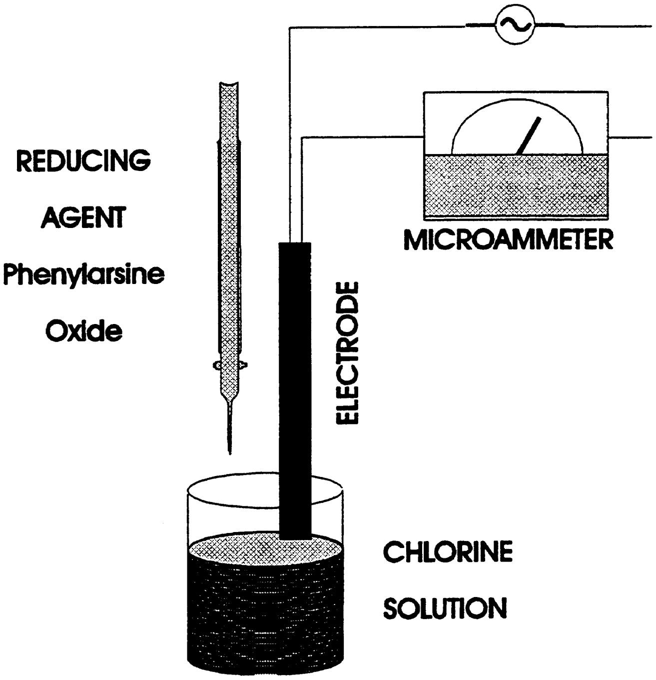

Figure 3 – Amperometric Titration of Chlorine

For the measurement of free chlorine (Hypochlorous Acid (HOCl) and Hypochlorite ions (OCl^-)), the reaction with phenylarsine oxide is the following:

$$C_6H_5AsO + HOCl + H_2O \rightarrow C_6H_5AsO(OH)_2 + HCl \quad (2)$$

For the measurement of combined chlorine, since it does not react directly with phenylarsine oxide, it is first converted by adding potassium iodide to the solution which releases iodine in proportion to the combined chlorine. The iodine in turn is titrated with

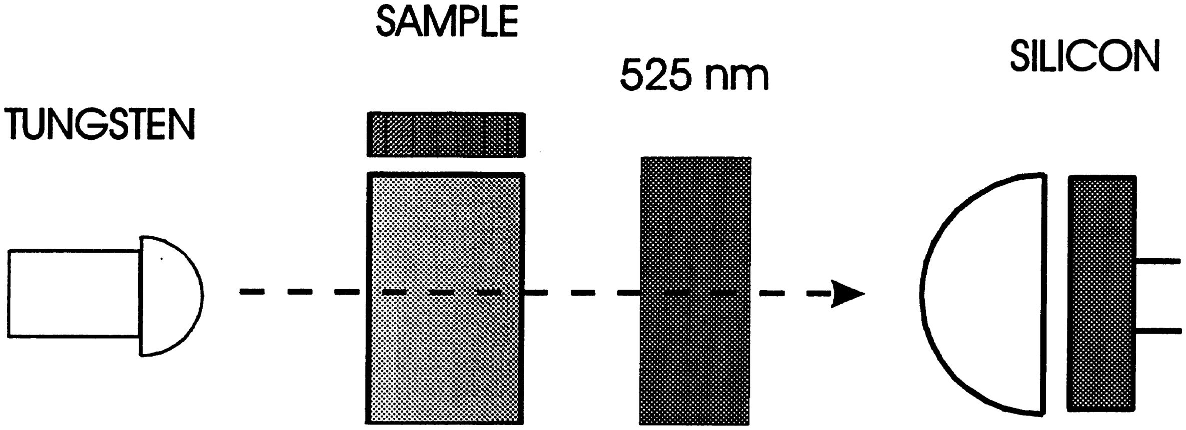

Figure 4 – Colorimetric Analysis of Free Chlorine

phenylarsine oxide, according to the reaction:

$$C_6H_5AsO + I_2 + 2H_2O \rightarrow C_6H_5AsO(OH)_2 + 2HI \qquad (3)$$

Colorimetric Analysis – Colorimetric analysis of free chlorine was performed with a HACH Company Colorimeter Model DR700, as shown in Figure 4. It uses the same colorimetric reagent, DPD (diethyl–p–phenylene–diamine), as is used with conventional DPD test kits. In the EPA–approved method, a magenta filter with a wavelength of 525 nanometers and a silicon photodiode photometer are used to measure the amount of light absorbed by the chlorine solution, indicating the results in mg/l.

DPD Test Kits – Testing of free chlorine was also performed with two types of DPD test kits commonly used in the pool and spa industry.

The AQUALITY DuoTest DPD test kit uses a color scale with five calibrated reference plates between 0 and 3.0 ppm.

The TAYLOR Professional DPD test kit uses a scale with nine calibrated liquid reference samples between 0 and 3.0 ppm with a parallel path for compensation of light absorption by the solution sample.

In order to evaluate the accuracy of these test kits, chlorine solutions with free chlorine concentrations of about 0.25, 0.5, 1.0 and 2.0 ppm respectively were prepared and analyzed with the colorimeter to determine their exact concentration. Each solution sample was then submitted for analysis to 10 participants, both male and female, none of them color blind, using the two DPD test kits. After testing, the solutions were again tested with the colorimeter to make sure that there had been no drift in chlorine concentration.

Conductivity and TDS Measurements – The conductivity measurements were made with a VWR Digital Conductimeter using a platinum electrode with a cell constant k = 1. The conductivity readings in microsiemens/cm were converted to ppm of Total Dissolved Solids with a multiplication factor of 0.66, which is representative of most saline solutions.

Results and Discussion

Free Chlorine Testing

Amperometric vs. Colorimetric Testing – Testing of chlorinated water solutions ranging from 0.3 to 2.2 ppm of free chlorine showed a very good correlation between the values obtained by amperometric titration and by DPD colorimetric analysis using the HACH colorimeter. The test data shown in Figure 5 indicates that the results obtained by colorimetric analysis are slightly lower than those obtained by amperometric titration. However the differences are less than 8%.

While realizing that amperometric titration gives

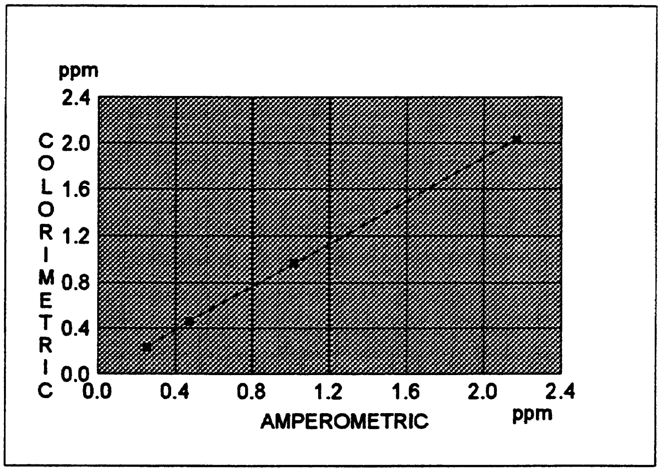

Figure 5 – Comparison of Amperometric Titration and Colorimetric Analysis of Free Chlorine

a more direct measurement of free chlorine concentration, it must be recognized that it is also more tedious and time consuming to perform. The above results proved that colorimetric analysis is just as reliable and it was therefore used exclusively for the calibration of chlorine solutions in the rest of the study.

DPD Test Kits – DPD test kits are used extensively in the pool and spa industry because of their low cost and ease of use. However, there is a question regarding the accuracy of the readings and their reproducibility because, unlike a colorimeter, they are dependent on human eye interpretation of color scales.

The results obtained with the two DPD test kits are summarized in graphic form in Figure 6, where the baseline represents the colorimeter readings. Each data point represents the average value of the 10 readings obtained for each sample solution. The lines are best fit straight lines for each test kit.

The data shows that there are significant differences in readings both for each of the test kits and between individual users.

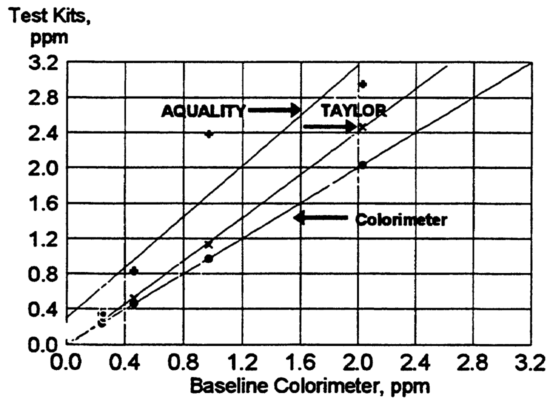

Figure 6 – Comparison of DPD Test Kits

Both test kits produced significantly higher readings than the baseline colorimeter. The TAYLOR Test Kit gave readings that were about 25% higher than the colorimeter while the AQUALITY readings were 50% higher.

The effect of the differences in color perception between individual users was analyzed by determining the standard deviation for each sample solution.

The standard deviation is given by the formula:

$$\sigma = \sqrt{\frac{\Sigma(X-M)^2}{N}} \qquad (4)$$

where σ represents the standard deviation, X the individual readings, M the mean value for the series of tests and N the number of readings for that series.

For both test kits, the standard deviations were about 25% of mean values. According to statistical analysis, this means that 65% of the readings produced by a random population should be within $\pm\sigma$, or ±25%, and 95% of the readings would be within $\pm 2\sigma$, or ±50%, of the mean value for that particular test kit.

These results therefore indicate that the readings obtained with DPD test kits are qualitative, or at best semi–quantitative. In other words, they can indicate the presence or absence of free chlorine, and the approximate concentration levels but not with the degree of accuracy that is generally expected and relied upon.

Although this may come as a surprise to many pool and spa operators, the consequences are not as dramatic as it may seem at first. In particular, it is essential to recognize that effective sanitation at a pH of 7.5 is obtained with Free Chlorine levels as low as 0.5 ppm. It is therefore mostly irrelevant to know whether the actual level is 1.0 ppm or 1.5 ppm. The higher levels of chlorine normally used in pools and spas are required by the health departments as a necessary safety cushion to overcome the lax supervision in pools and spas that are not chemically automated.

Another important conclusion of this study is directly related to the use of automatic controllers for chemical automation. The lack of accuracy of the DPD test kits is important to keep in mind when calibrating automatic controllers with standard DPD test kits, as is generally recommended by the manufacturer. Small variations in readings may often be due to the inherent errors of testing and not to actual changes in chemistry caused by the controller.

Also, these results confirm that it cannot be emphasized too strongly that responsibility for calibration of the automatic controller should be assigned to only one operator. This reduces errors caused by differences in color perception for different users and prevents excessive recalibration of the controller.

ORP Sensor Readings

Reproducibility of ORP Sensor Readings – ORP sensors used for chemical automation of pools and spas cannot be calibrated since there is no convenient reference solution available in the millivolt range used for water treatment. Since the output of the sensor can be influenced by the physical or chemical parameters of the sensor, it was important to determine the consistency of ORP readings obtained with different sensors.

For this test, 10 new ORP sensors were chosen at random and immersed in the same chlorinated water solutions. ORP readings were made at several interval, i.e. 5 minutes, 20 minutes and 16 hours. The

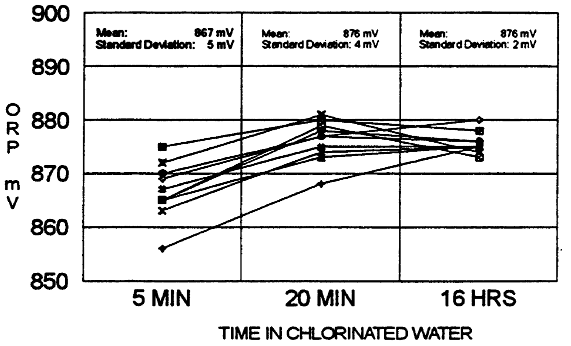

Figure 7 – Reproducibility of ORP Sensors

results are shown in Figure 7.

The first measurements after only 5 minutes of immersion show an average ORP value of 867 mV with a standard deviation of 5 mV. The average value then rises to 876 mV after 20 minutes and it remains constant even after 16 hours of immersion. The standard deviation however continues to decrease from 4 mV after 20 minutes to just 2 mV after 16 hours.

These results show that, after 20 minutes of immersion, 95% of a batch of new ORP sensors read within ±2σ, i.e. within ±4 mV of the average value. Since typical ORP control levels for pools and spas are within 650 to 750 mV, the desired level of accuracy should be easily accomplished with normally functioning sensors.

Response Time of ORP Sensors – A more detailed study was conducted to determine the actual initial response of ORP sensors in the first few minutes of immersion in chlorine solutions at concentration levels of 0.3 and 2 ppm. As shown in Figure 8, the response curve is similar for both concentrations. There is a slow increase in ORP readings for about 10 minutes, after which the readings level off and remain constant.

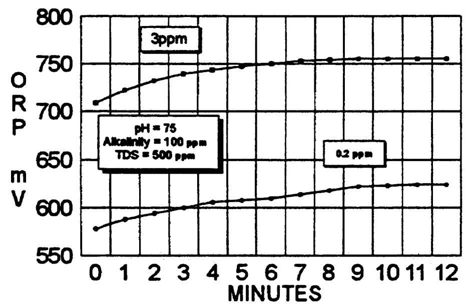

Figure 8 – Time response of ORP Sensor

These results confirm that meaningful ORP readings can be obtained only after a minimum immersion time of about 10 minutes and not, as is advocated by a few manufacturers, by dipping the sensor in water for only a few minutes.

Total Dissolved Solids (TDS) and ORP – Because dissolved solids are capable of impeding the motion of ionic species in water and therefore reducing their mobility, it has been suggested that they may also have an effect on the ORP readings of free chlorine.

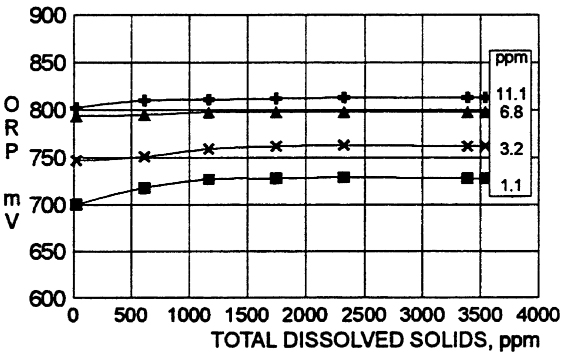

Figure 9 – Effect of TDS on ORP

Proper maintenance of pools and spas requires that the TDS level be maintained at around 1,000 ppm and definitely below 2,000 ppm. Above this level, the sanitizer loses its effectiveness and there is increasing corrosion of metal parts. The water should then be dumped and replaced with fresh water.

A series of tests was performed in this study with several samples of chlorinated water to which were added increasing amounts of Sodium Chloride, NaCl, thereby raising the TDS concentration from near zero to above 3,000 ppm.

The curves shown in Figure 9 for free chlorine concentrations varying from 1.1 to 11.1 ppm actually show that there is no reduction in ORP values at higher TDS levels. If there is a reduction in ORP levels in pool or spa waters under high TDS level conditions, this must be a result of specific chemical reactions between chemically active dissolved solids and free chlorine. Since Sodium Chloride is chemically inactive with regard to free chlorine, it does not appear to affect the ORP readings even at high concentration levels.

In fact, it should be noted that lower ORP readings are observed at very low TDS concentration levels. These may be attributed to decreased mobility of electrons and ions in water of low conductivity.

Variation of ORP with pH – Back in the early 70s, the UNILOC Company of Irvine, CA released a set of curves showing the variation of ORP of free chlorine with pH. Unfortunately, the methodology of the study was not specified. In particular, there is no information on the properties of the water used for testing and on the methods used for the determination of free chlorine concentrations.

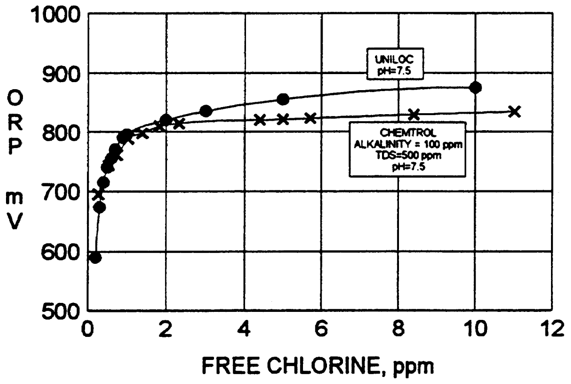

Figure 10 – Comparison of UNILOC and CHEMTROL$_{TM}$ ORP Data at pH 7.5

One of the major objectives of the present study was therefore to reevaluate the variation of ORP for free chlorine under controlled laboratory conditions. This was done for pH values ranging from 6.5 to 8.5 and for free chlorine concentrations ranging from 0.2 to 10 ppm, as determined by colorimetric analysis.

For comparison with the earlier study, Figure 10 shows both the UNILOC data and the new CHEMTROL$_{TM}$ data for pH 7.5. The two sets of data show good agreement at low ppm values, i.e., up to 2 ppm. However, the UNILOC readings are significantly higher at higher ppm values. In the absence of information on the test conditions at UNILOC, it is difficult to explain this discrepancy.

While the range of agreement covers most of the normal range for water treatment, there is also significant interest in the higher concentration range, primarily for shock treatment or superchlorination. Additional studies are therefore planned in this area.

The variations of ORP vs. pH and ppm of free chlorine are shown in the traditional two–dimensional diagram in Figure 11 and in the full three–dimensional representation in Figure 12.

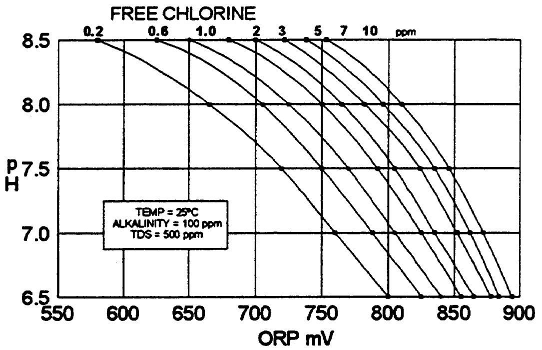

Figure 11 – ORP vs pH and ppm of free chlorine (two–dimensional diagram)

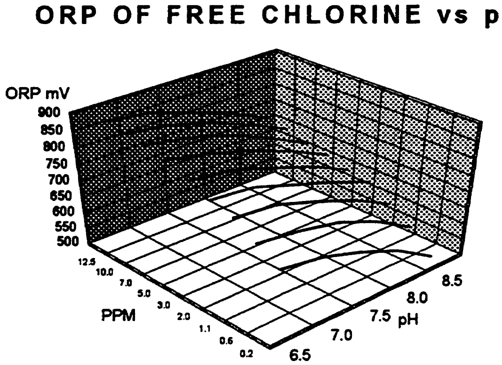

Figure 12 – ORP vs pH and ppm of free chlorine (three–dimensional diagram)

Theoretical Calculations

A simple example of an oxidation–reduction reaction is that of a strip of Zinc being placed in a Silver Nitrate solution. Because of the difference in electronegativity or oxidation potential of Silver and Zinc, Silver deposits on the zinc metal forming silver plating.

Electronically, the reaction occurs through an exchange of electrons between silver and zinc.

Zinc metal, which is originally neutral, gives up two electrons as it is oxidized to form Zinc Nitrate in solution. This is called an oxidation reaction which is shown as:

$$Zn \rightleftharpoons Zn^{2+} + 2\,e^- \tag{5}$$

Silver, on the other hand, is converted from its ionic state in solution Ag^+ to the neutral metallic state by acquisition of an electron.

$$Ag^+ + e^- \rightleftharpoons Ag \tag{6}$$

The complete reaction is given as:

$$2AgNO_3 + Zn \rightleftharpoons Zn(NO_3)_2 + 2Ag \tag{7}$$

Zinc is the reducing agent which is oxidized into the Silver Nitrate solution by giving up electrons while Silver is the oxidizer which gets reduced by gaining electrons to form silver metal.

Chlorine undergoes similar oxidation reactions but unfortunately chlorine chemistry is more complicated because chlorine can enter into many different reactions, such as:

$$HOCl + H^+ + 2e^- \rightleftharpoons Cl^- + H_2O \tag{8}$$

and:

$$HOCl + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^- \tag{9}$$

The voltage developed at a platinum electrode is expressed by the Nernst equation, as:

$$E_{mV} = \frac{RT}{nF} \log_{10} \frac{\text{Oxidizer}}{\text{Reducer}} \tag{10}$$

where RT/F is equal to 59.2 at 25°C and n is the number of electrons, which is 2 for the above chlorine reactions.

Theoretical calculations of ORP are quite complex, especially for chemicals like chlorine that have a complicated chemistry.

Theoretical calculations can therefore be used only for modeling and not for actual derivations of ORP values. From the Nernst equation above and assuming that there are two electrons involved in the oxidation–reduction equation for HOCl, one can derive a theoretical expression for the ORP of Free Chlorine:

$$E_{mV} = E_o + 30 \log_{10} \frac{[HOCl]\,[H^+]}{[Cl^-]} \tag{11}$$

which can be rewritten as:

$$E_{mV} = E_o + 30\log_{10} [HOCl] + 30\log_{10} [H^+] - 30\log_{10} [Cl^-] \tag{12}$$

or in terms of pH:

$$E_{mV} = E_o + 30\log_{10} [HOCl] - 30\,pH - 30 \log_{10} [Cl^-] \tag{13}$$

This equation shows general agreement with the trend of experimental measurements of ORP for free chlorine.

The last term shows the effects of the chloride ions which remain fairly constant in chlorinated water and therefore do not greatly affect ORP measurements.

The second term shows that ORP readings at constant pH vary by approximately 30 mV for each decade variation of HOCl. This is much less than actual measurements which show a variation of about 100 mV per decade of HOCl at a pH of 7.5. This indicates that there are more complicated reactions of oxidation of HOCl with different stoichiometries resulting in less than one electron per reaction.

The next term confirms the decrease in ORP for increasing pH values.

The actual effect of pH is actually stronger than indicated above because it also affects the ratio of HOCl and OCl^- through the ionization equilibrium:

$$[HOCl] \rightleftharpoons [OCl^-] + [H^+] \tag{14}$$

The reaction has the equilibrium constant K_{HOCl} at 25°C:

$$K_{HOCl} = \frac{[OCl^-]\,[H^+]}{[HOCl]} = 5.6 \times 10^{-8} = 10^{-7.5} \tag{15}$$

showing the 50% distribution of the two species at a pH of 7.5.

$HOCl^-$ undergoes its own oxidation reaction:

$$OCl^- + 2H^+ + 2e^- \rightleftharpoons Cl^- + H_2O \tag{16}$$

The expression for Total Free Chlorine is therefore:

$$[PPM] = [HOCl] + [OCl^-] \qquad (17)$$

leading to:

$$\log [HOCl] = \log [PPM] - \log \left[1 + \frac{K_I}{10^{-pH}}\right] \qquad (18)$$

and finally in terms of Total Free Chlorine:

$$E_{mV} = E_o + 30 \log_{10} [PPM] - 30\,pH - 30 \log \left[1 + \frac{10^{-7.5}}{10^{-pH}}\right] - 30 \log_{10} [Cl^-] \qquad (19)$$

The last term in the equation represents the chloride ion concentration and remains fairly constant. The rest of the equation shows the general variation of ORP with the log of free chlorine concentration and with pH. It is in general agreement with the experimental data, as shown in Figure 11.

Long–Term Stability

A long–term stability study has been undertaken to evaluate the longevity of ORP sensors. Ten (10) randomly selected probes were placed in a container of chlorinated water and tested every month over a period of a year. From January 1996 to February 1997, all ten sensors have shown remarkable stability with no failure of any of the sensors. The study is still ongoing to determine an experimental mean time before failure.

Conclusions

The reliability of ORP sensor measurements of free chlorine has been established and found to compare favorably with that of DPD test kits used for pools and spas.

Response curves of ORP sensors have shown that a minimum of about 10 minutes of immersion in free chlorine solutions is required to obtain meaningful readings.

The variations of ORP with pH has been found to be in general agreement with previous experimental data and with theoretical calculations of oxidation–reduction reactions.

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