

Understanding On-line Amperometric Chlorine Measurements

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INTRODUCTION

Whether monitoring disinfectant levels in a potable water treatment plant, or tracking biocide residuals in a cooling water system, on-line chlorine analyzers are of great value to the water treatment operator. Traditionally, on-line chlorine monitors in the water plant have utilized colorimetric measurement. Chlorine analyzers utilizing amperometric sensors are certainly not new to the industry, but in recent years there have been technological and operational developments that have made them more attractive, and as a result, they have become much more prevalent in water treatment plants. Still there are sensor design differences that result in some probes working better than others.

This presentation will briefly review the evolution of on-line chlorine measurement, and discuss the key features of amperometric technology that are important to consider when selecting an analyzer to best meet the needs of the application. Case study data showing comparisons between on-line colorimetric devices (DPD) and amperometric sensors will also be included.

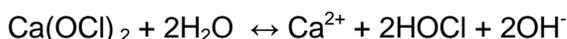
BACKGROUND CHEMISTRY

The chemistry involved with the chlorination of water can be somewhat complex. Proper measurement of chlorine concentrations in water is essential for accurately controlling chlorination processes (disinfection, biological control, etc.).

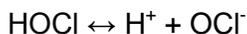
When the source of chlorination is gaseous chlorine, hydrolysis forms HOCl (hypochlorous acid).



Likewise, when sodium hypochlorite (bleach) or calcium hypochlorite are the sources of chlorination, hydrolysis will also form HOCl.



HOCl will dissociate as follows:



So HOCl and OCl⁻ (hypochlorite ion) are the oxidizing chemical species that are formed when chlorine is added to water (and if gaseous chlorine is fed, dissolved Cl₂ gas could be present too), and together they are referred to as Free Residual Chlorine (or Free Available Chlorine).

HOCl has a much more potent oxidizing impact, and therefore is much more biocidal (reportedly 80 to 100 times more effective), than OCl⁻.

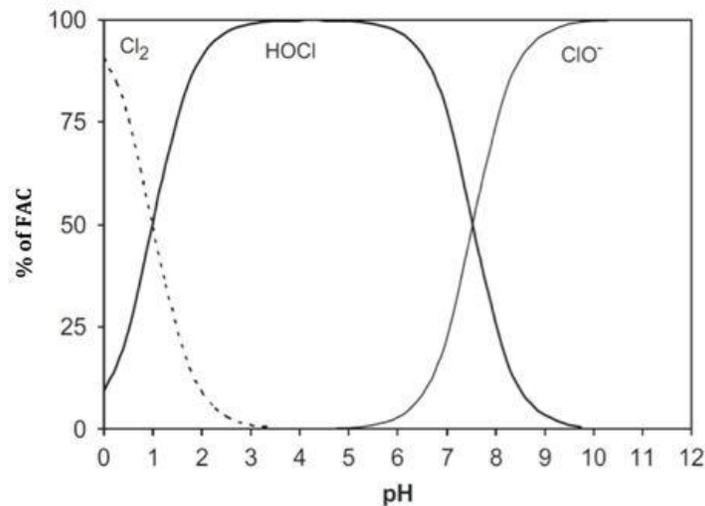


Figure 1. Free Chlorine Species in Water

The proportion of chlorine, HOCl, and OCl⁻ in solution depends primarily on pH (and somewhat on temperature). For example, in waters with pH below 6.5, mostly HOCl will be present; and in waters with pH above 8.5, mostly OCl⁻ will be present. However, in waters with pH between 6.5 and 8.5, varying amounts of both species (HOCl and OCl⁻) can be present.

Lastly, the chlorine residual which exists in water in combination with ammonia (natural or added), or organic nitrogen compounds, is referred to as Combined Chlorine. Total Residual Chlorine is the sum of the Free Chlorine and Combined Chlorine.

ON-LINE CHLORINE ANALYZERS

On-line chlorine analyzers are of great value to the water treatment operator. Selecting the best analyzer for a given application based on operation and performance, maintenance requirements, overall costs, etc., is a challenge.

The two most common approaches for measuring chlorine are:

1. Colorimetric (photometric)
2. Amperometric (electrochemical)

The colorimetric analyzers require chemical reagents to be added to the water. When the reagents are introduced, a color change occurs that is proportional to the concentration of chlorine present in the water. The resulting color is measured photometrically to determine the chlorine level.

The first “on-line” colorimetric chlorine analyzer was introduced in 1929. It utilized an orthotolidine reagent, and was not able to measure free chlorine. Today the colorimetric analyzers primarily utilize DPD (N,N-Diethyl-p-Phenylenediamine), which was first introduced in 1957. The DPD approach can be used to measure either free or total chlorine. Through the

years the DPD approach has become the most widely used method for measuring chlorine concentrations in water and wastewater.

On-line Amperometric analyzers for measuring free and total chlorine have been around, in various forms, for over 60 years. Amperometry is an electrochemical method that measures changes in electric current across two electrodes (anode and cathode) which result from a chemical (redox) reaction taking place at the electrodes. The resulting electrical current is proportional to the concentration of the analyte (e.g., HOCl). This is a very basic description of an amperometric sensor's operating principle, and it should be understood that several variations in design have developed over the past several decades.

AMPEROMETRIC CHLORINE ANALYZER EVOLUTION

Early on, the electrochemical approach to chlorine measurement earned a reputation for being less accurate than colorimetric. However, changes in technology over the years have improved the accuracy significantly, and there are now very reliable amperometric analyzers for chlorine monitoring that are easy to use, cost effective, and in most cases very suitable for regulatory reporting requirements. But some of the less advanced amperometric designs are still in wide use, and many users do not understand how to tell the difference. For this reason it is helpful to look at the evolution of the electrochemical approach, as it allows for better discrimination between the various products available on the market today, and helps explain the advantages of certain design features.

1950s

It was around this decade when the first on-line amperometric chlorine instrument appeared. The sensor (Figure 2) had an open-cell design, with bare electrodes consisting of two dissimilar metals (gold and copper), and redox reactions produced a galvanic current proportional to the concentration of chlorine in the water.

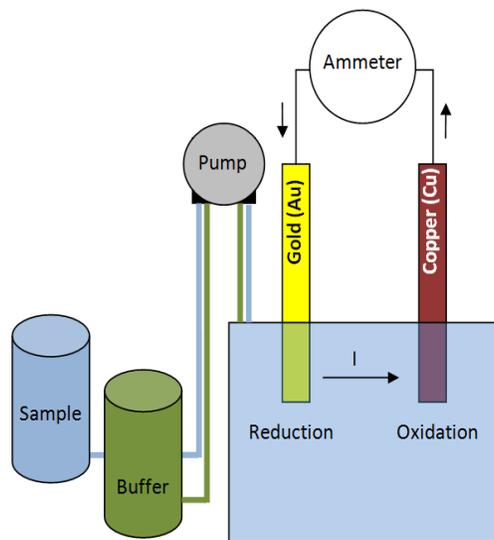


Figure 2

This sensor design provided a fast response time, but the technology suffered from several problems:

1. The cell only measured HOCl, and was not capable of detecting the OCl⁻, requiring the use of a pump to feed an acid buffer to lower the sample pH to <6.5
2. Surface reactions and fouling on both electrodes caused measurement instability, requiring the electrodes to be kept clean using a grit cleaning system with a mechanical stirrer
3. The copper electrode was consumed in the measurement process
4. The results were impacted by changes in temperature and conductivity
5. Frequent calibrations were required to maintain acceptable accuracy
6. Zero drift was an issue, requiring both zero adjustments to be performed frequently
7. The issues described above resulted in unstable readings and an instrument that required a high level of maintenance

1970s to 1980s

Membrane-Covered Sensors

During this period, membrane-covered sensors (Figure 3) became popular. The membrane-covered tip of the probe allowed for chlorine species to diffuse through to the electrodes, while it also acted as a protective barrier in an effort to minimize electrode fouling. This meant there was no longer a need for a grit cleaning system, which ultimately reduced the size and cost of the analyzer, and also helped to lessen and simplify maintenance. But measurement accuracy was still falling well short of many users' expectations, there was still the need for external buffers to lower pH, zero drift problems, and the anode was still consumed by the measurement process.

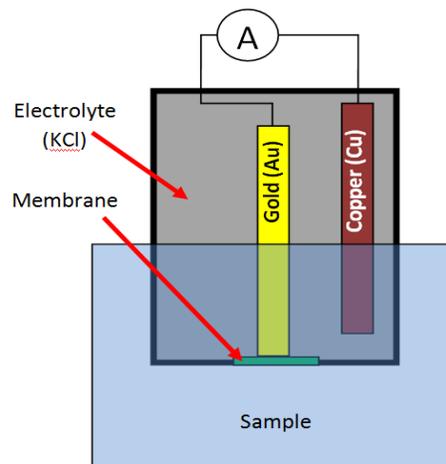


Figure 3

Single-Potential Amperometry

Experimentation with applying a voltage to the cathode to facilitate reduction of HOCl helped improve the sensor performance by boosting response to HOCl and helping to reduce “zero drift” issues, leading to improved accuracy. This technique was used with both bare (Figure 4) and membrane-covered (Figure 5) electrodes. A trade-off was in the response time, as the probe needed time to polarize before reading accurately.

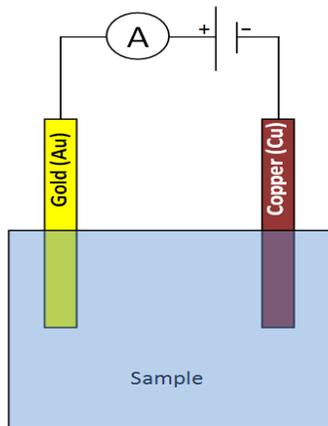


Figure 4

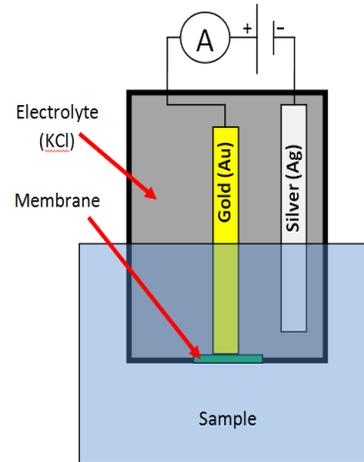


Figure 5

Acidified Electrolyte

In the late 1980s there were a few companies that started to experiment with acidified (buffered) electrolytes. The electrolyte (or fill solution) resided on the electrode side of the membrane; opposite from the sample flow. The buffered electrolyte reduced the pH inside of the sensor helping to convert OCl^- (which was undetectable by the electrodes) into $HOCl$. This significantly improved the response to free chlorine at higher pH levels (Figure 6). This innovation meant that for most applications there was no longer any need for pH compensation or pumps to deliver external pH buffers to the sample. This made a significant improvement in regards to accuracy and simplicity of design and operation.

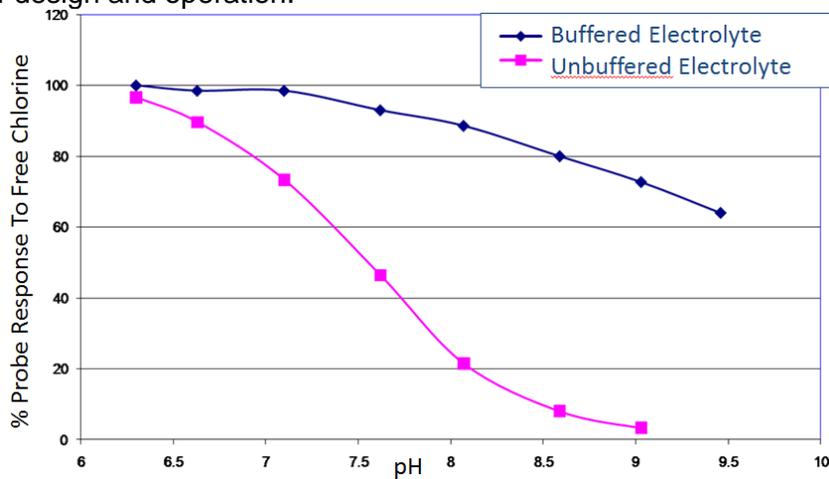


Figure 6

1990s to Present

Three-Electrode Design

The “latest generation” of amperometric chlorine probes include a three-electrode design controlled by a potentiostat (Figure 7). Along with the working electrode (i.e., cathode), there is a counter electrode and a reference electrode. The reference electrode provides a very stable reference potential against which the voltage at the cathode is applied. By keeping a more consistent applied potential at the Cathode, the response generated by the reduction of HOCl at the cathode is also made more stable (meaning less drift in accuracy). The reference electrode, typically made of silver, maintains better stability due to the current not needing to pass over it. Current instead flows between the working and counter electrodes. This keeps the electrochemical reaction much more stable, and eliminates zero drift, resulting in improved accuracy.

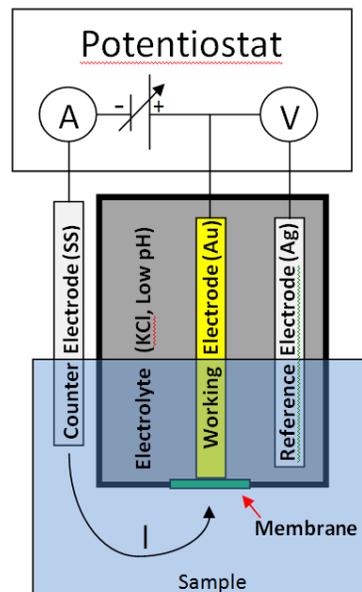


Figure 7

Probe Refurbishment

Some probes on the market can have their sacrificial anode, or reference electrode, replaced or refurbished. This even includes some three-electrode probes where the reference electrode can last 10 years, or longer. This can amount to hundreds of dollars in savings as some applications have chemistry which is quite aggressive at attacking the reference material, and therefore shortens the probe life. If the reference electrode cannot be refurbished, then the customer would be forced to spend more money to purchase a new probe.

Other Improvements

Some of the other more recent design improvements are considered “trade secrets,” and few details are given. Those trade secrets might include the benefits of using certain electrolyte formulations, reference electrode coating compounds, or specialty membrane materials. Obviously, having better knowledge in regards to materials of construction allows certain suppliers to outperform their competition in both reliability and accuracy, even though both products appear to share other performance-enhancing design concepts such as using a three-electrode probe with an acidic electrolyte. Without doing side-by-side performance testing, or

checking with references who have used a particular probe for at least 3 or more years, it is difficult to know which amperometric probes on the market excel the highest in regards to materials of construction, and which probes will provide the best overall performance.

SELECTING AN ANALYZER

As certain manufacturers have continued to make advancements in technology which have significantly improved the accuracy and reliability of amperometric analyzers, the popularity of these products continues to grow. But the uninformed buyer, who assumes all amperometric analyzers work the same, runs a higher risk of purchasing a product that will not provide them with the desired level of performance. Below is a list of questions that can be asked of the supplier to help identify whether an amperometric probe has the latest design features of interest:

1. Is the probe membrane-covered or bare-electrode? If it is bare-electrode, how are the electrodes kept clean?
2. What is the expected replacement frequency of the membranes? Note: Provide supplier with application details including the known contaminants in the sample to be measured.
3. Does the probe use an acidic electrolyte to help improve measurement accuracy? How often does the electrolyte need to be replaced?
4. How much does pH impact the reading? Is external pH buffering or pH compensation recommended? Note: Provide supplier the expected range of pH for your application.
5. Is there a voltage applied to the electrodes, or does the sensor operate on the galvanic principle?
6. Does the probe incorporate a two- or three-electrode design?

Along with the above questions, it can also be helpful to ask for three or more customer references that are using the probe in the same type of application. When speaking to those references, ask how well the probe maintains its accuracy, what sort of pH and temperature fluctuations the probe is exposed to, how often the membrane has to be replaced, and how the overall reliability has been.

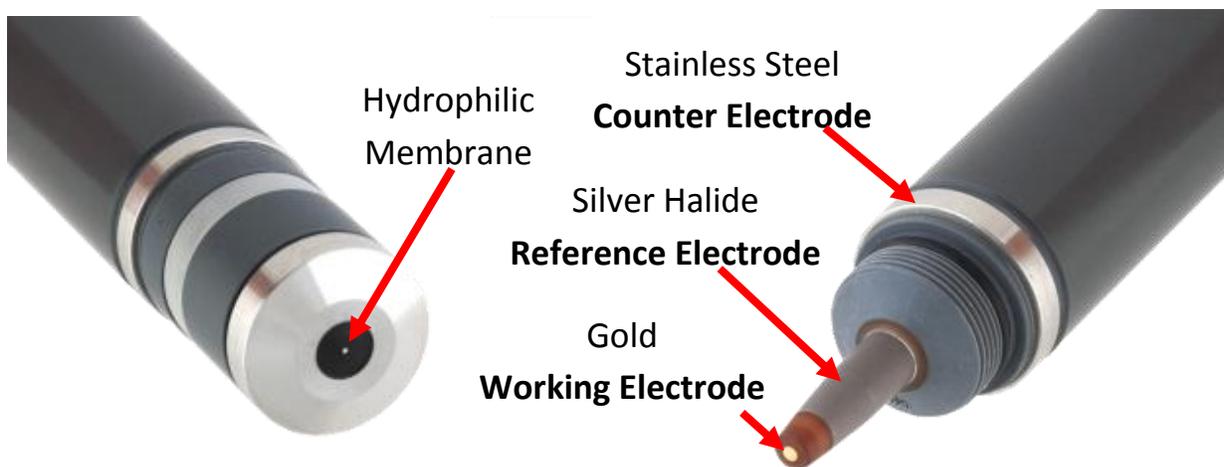


Figure 8

Figure 8 shows an example of a newer generation three-electrode amperometric probe. In the image on the left, the membrane tip can be seen (small dot in the black circular area). The picture on the right shows the probe with the membrane cap removed, revealing the counter, reference and working electrodes.

APPLICATIONS

Due to the design improvements, and a better understanding of the technology, amperometric sensors have become more widely used and accepted. The recognition that amperometric technology had improved led the U.S. Environmental Protection Agency (EPA) to make changes to federal regulations that dictate how disinfection residuals could be measured and reported. In 2009 the EPA published, "Method 334.0: Determination of Residual Chlorine in Drinking Water Using an On-line Chlorine Analyzer." This method allowed for the use of on-line amperometric chlorine analyzers in drinking water treatment processes for compliance monitoring, provided that specified measures were followed to verify that the instrument maintained calibration and reporting accuracy. This opened the door for a wider use of amperometric chlorine measurement in the drinking water industry.

This change was largely due to the fact that water treatment plants had been using and were showing that the latest generation of amperometric probes can be just as reliable and accurate as on-line DPD measurement. As a result, a large number of drinking water treatment plants in the U.S., as well as many wastewater plants, have replaced their on-line DPD analyzers with amperometric analyzers.

The use of amperometric sensors is certainly not limited to just the municipal drinking water and wastewater industries. These probes are also commonly utilized in industrial water treatment applications, food processing, cooling water systems, and even (although less commonly) on the wet end of paper machines.

CASE HISTORY

"DPD vs. Amperometric"

Bear Creek WTP, Bogart, GA

The plant management team decided to explore the idea of replacing an aging on-line DPD free chlorine analyzer with one that uses amperometric technology. As a part of the investigation, Kenneth Moore, Plant Manager, wanted to conduct a side-by-side comparison between their existing DPD colorimetric unit (that had recently been serviced), and an amperometric chlorine analyzer from Chemtrac, Inc.

With EPA Method 334.0 compliance testing already in place, the plant personnel began to collect data for their instrumentation study as well. Over a two-week period, they observed and recorded the results from both on-line analyzers, while also performing routine free chlorine analyses with their benchtop spectrophotometer. This was to ensure that each on-line unit stayed within +/- 15% of target (as mandated by Method 334.0).

Figure 9 plots a direct comparison of the results from the on-line DPD analyzer results, to the results from the on-line analyzer with the amperometric probe. Although the graph shows that the two instruments trended well together, their results did not always stay within 15% of each other.

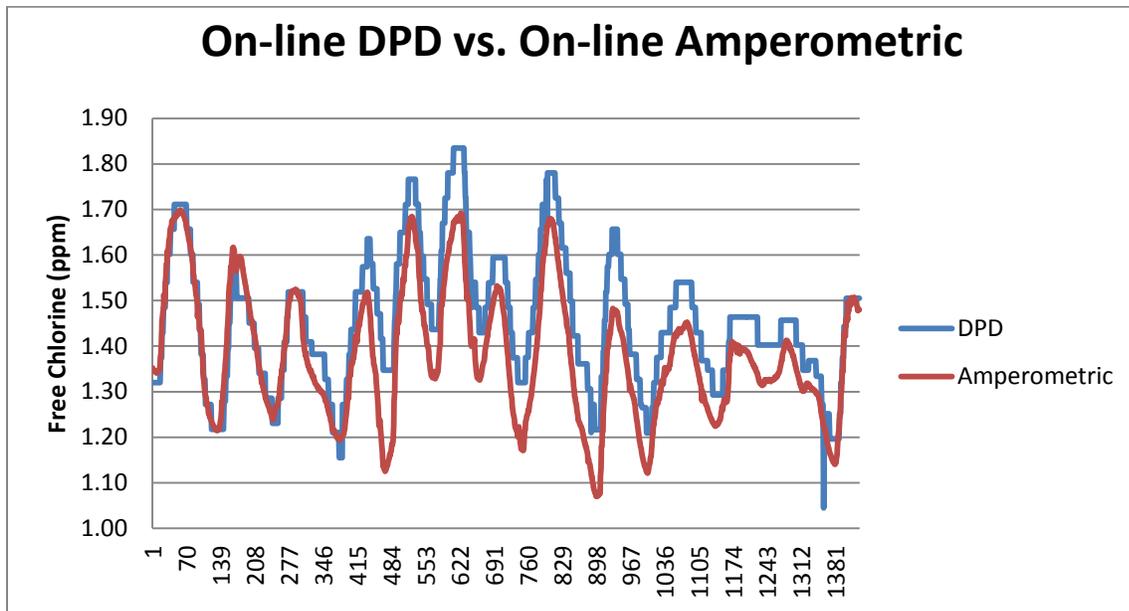


Figure 9. Comparison of On-line Technologies (DPD vs. Amperometric)

Figures 10 and 11 illustrate how the results from the benchtop DPD unit (which is considered to be the more accurate measurement) compared to the results from the on-line DPD unit, and on-line amperometric unit, respectively. Per Method 334.0, the on-line units need to remain within 15% of the benchtop in order to be used for compliance monitoring and reporting.

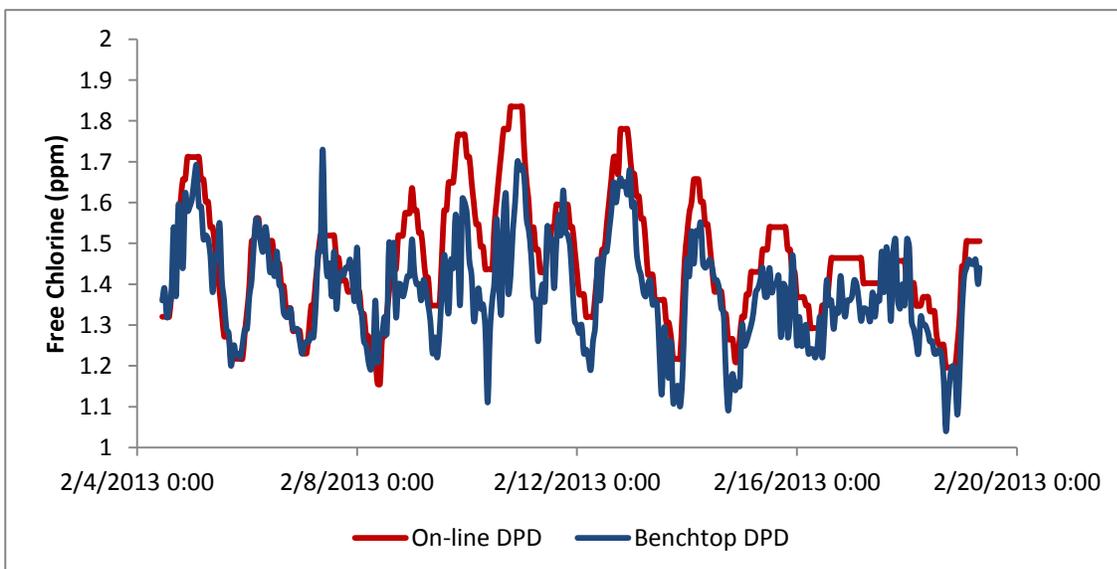


Figure 10. Comparison of On-line DPD to Benchtop DPD

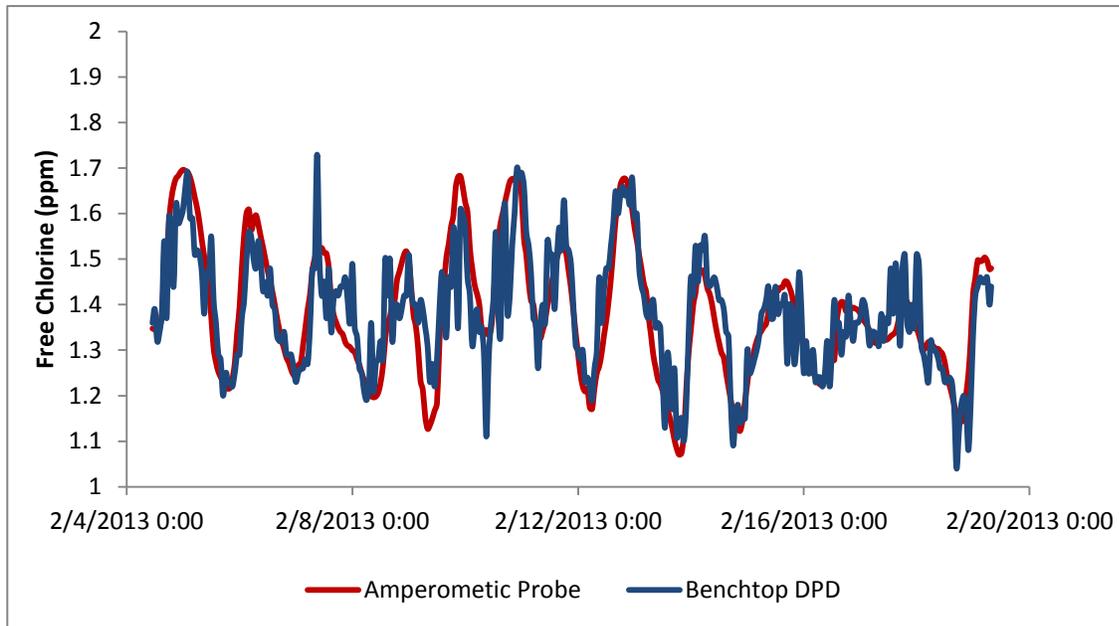


Figure 11. Comparison of Chemtrac On-line Amperometric to Benchtop DPD

A comparison of the two graphs shows that in this study, the Chemtrac on-line amperometric analyzer clearly followed the benchtop unit with a greater degree of precision and accuracy than the on-line DPD analyzer did.

IMPACT OF pH ON MEASUREMENT ACCURACY

As previously mentioned, amperometric technology used for measuring free chlorine is only capable of measuring HOCl (hypochlorous acid). When the pH is > 6.5, the HOCl concentration is known to decrease significantly with increases in pH (Figure 1). Due to this fact, changes in pH will have an obvious impact on the measurement accuracy of amperometric chlorine analyzers unless corrective measures are taken. Since most manufacturers do offer some type of standard or optional corrective measure for pH, the actual impact pH has on the measurement accuracy will vary by manufacturer, and will depend largely upon the corrective measure used. Some designs incorporate an external buffer (e.g., acetic acid) that is used to suppress the sample pH to achieve a near 100% concentration of HOCl. Other designs utilize a pH probe to compensate the amperometric signal in an effort to provide a more accurate chlorine reading. And a third option utilized by some analyzers with membrane-covered probes is the use of an acidic electrolyte, or what is also referred to as an “internal buffer.”

The use of an internal buffer helps convert OCI^- (hypochlorite ion) to HOCl as it passes through the membrane. This is very cost-effective, and a much simpler approach compared to feeding an external buffer. External buffering requires a pump to introduce an acid into the continuous flowing sample. The pump adds cost, complexity, and hardware that requires servicing. Buffering, whether internal or external, is generally viewed as a more reliable alternative to that of incorporating a pH measurement for automatic correction of the amperometric signal. When using a pH probe to facilitate automatic correction of the signal to obtain a more accurate chlorine reading, the most commonly overlooked aspect is the accuracy of the pH measurement. Since the correction factor becomes larger as pH increases, any inaccuracy

exhibited by the pH reading will be magnified and transposed onto the chlorine reading as the pH goes higher. For probes that do not utilize a buffered sample, the correction factor can be as high as 5X, which makes pH measurement error more problematic in obtaining accurate chlorine readings.

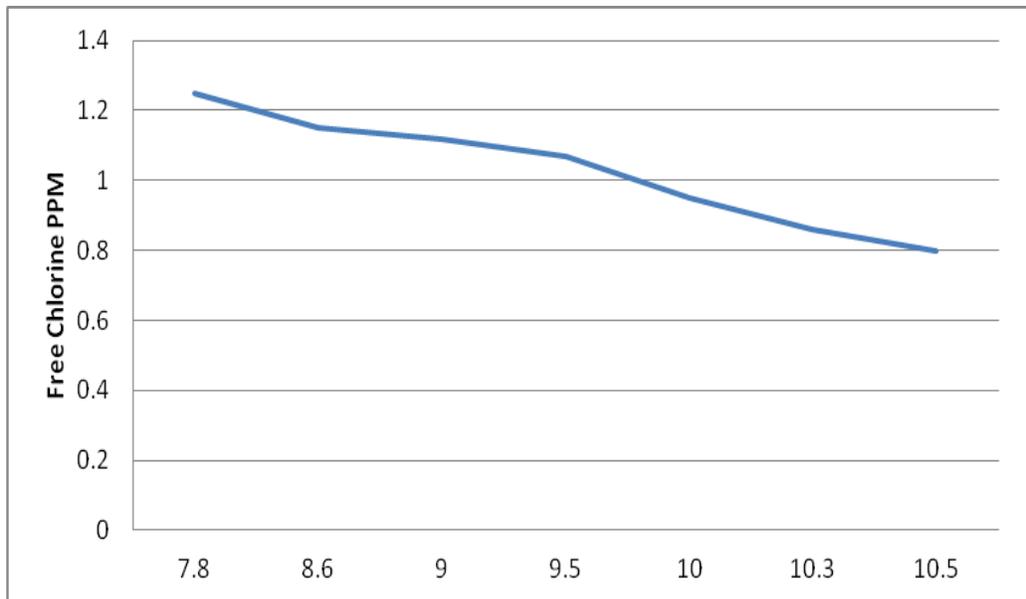


Figure 12. Amperometric Measured Chlorine at Elevated pH Levels (1.2 ppm Actual Chlorine Concentration As Determined By DPD)

With the internal buffering approach, at pH ranges of 7.5 and below, there is virtually no drift in chlorine detection accuracy when the pH of the sample happens to change. For applications with pH values between 7.5 and 10.5, there will be some loss in free chlorine detection as shown in Figure 12. Here we see the response from an internally buffered probe as the pH was incrementally increased, while maintaining a Free Chlorine concentration (as determined by DPD testing) of 1.2 ppm (+/- 0.1 ppm) during the test. The testing showed just over a 35% drop in measurement accuracy as pH was increased from 7.8 to 10.5, which is a far larger variation in pH than most applications will experience. For applications with pH >7.5 and <9.0, and fluctuations no larger than 1 pH unit, the loss in measurement accuracy will be closer to 10%.

If it is deemed necessary, the measurement accuracy of an internally buffered probe can be further improved with the incorporation of a pH measurement to provide an automatic pH correction of the amperometric signal. The pH correction applied to a probe that is measuring a buffered sample requires much smaller correction factors as compared to non-buffered samples, and thus any inaccuracy in the pH reading will have less impact on chlorine reading. Many amperometric chlorine analyzers on the market today have the capability of accepting a pH probe and come with automatic pH compensation features.

Given these performance characteristics, the accuracy of an internally buffered, membrane-covered, three-electrode amperometric probe is generally suitable for most applications.

STABILIZATION TIME, RESPONSE TIME, AND CALIBRATION BEST PRACTICES

When a newly made-up membrane-covered amperometric probe is first installed, or whenever the membrane is replaced, it is typically recommended to allow at least 6 hours for a probe to fully condition (i.e., polarize) prior to calibrating. Much of the initial polarization of the sensor occurs in the first 2 hours (Figure 13), but complete stability of a newly made up (new electrolyte, new membrane) sensor takes a few hours longer. For this reason, it is a common practice to let the sensor run overnight before calibration is performed. It is also recommended to perform at least two to three DPD chlorine analyses to look for measurement repeatability when calibrating the amperometric chlorine analyzer.

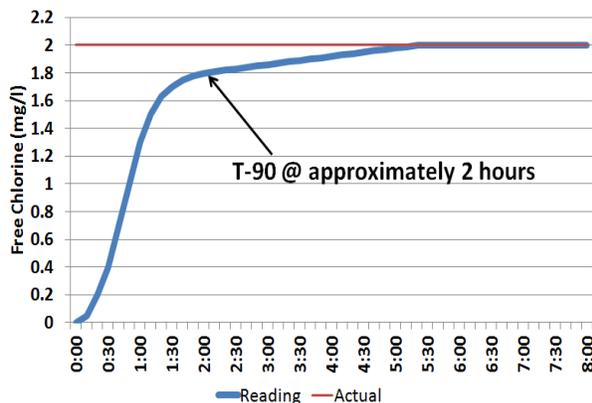


Figure 13

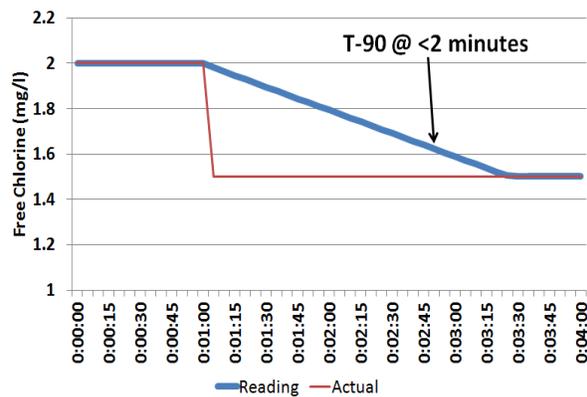


Figure 14

Once an amperometric probe has reached stabilized operation, the reading will begin to update in response to any changes in chlorine concentration within 30 seconds or less. The time to achieve 90% response (T90) to the process change will be 2 minutes (figure 14). In comparison, on-line DPD analyzers perform batch testing, and the reading is only updated every 2.5 minutes.

It is important to closely evaluate the amperometric chlorine analyzer performance in the initial days or weeks of operation. Performance of the instrument will depend on the probe design and the application where it is being used. Verification of the amperometric chlorine analyzer readings should be performed at least once a day until confidence in the probe's performance is established. If the amperometric chlorine analyzer maintains an acceptable level of accuracy (as compared to carefully performed DPD testing) over a 7 to 14 day time period (e.g., Figure 11), then it is deemed acceptable to perform verifications less frequently. But a recommended SOP is to verify the readings against DPD testing at least weekly.

After a probe is made down with new electrolyte (part of routine maintenance), or after prolonged exposure to a sample with no flow or a zero chlorine residual, the probe will require time to re-stabilize, which typically should take no longer than two hours (Note: stabilization time after replacing the membrane can take 6-12 hours). The length of time required to achieve stable readings depends on the condition of the membrane, how long the probe was not exposed to chlorine, and the measured level of chlorine. For samples with >2 ppm of chlorine, the re-stabilization time is likely to be less than one hour. For samples with <0.5 ppm, the stabilization time may extend closer to two hours. Probes that exhibit slower stabilization times may require a new membrane.

For applications where the chlorine concentration may drop to 0 ppm for periods longer than one hour, the re-stabilization time could prove to be problematic for achieving process control goals. Some customers address this issue by temporarily switching the sample flow (manually or automatically) to a tap water sample anytime that chlorine feed is stopped, or levels are expected to drop to 0 ppm (see “optional for shutdown” in Figure 15). This ensures that the amperometric probe will continue to be exposed to chlorinated water during a process shutdown. If using this optional configuration to keep the probe “ready” for accurate analysis, take note whether the municipal water supply is treated using chloramination, as this will not keep a free chlorine probe polarized.

SAMPLE PRESSURE AND FLOW

It is very important to provide the proper sample flow and pressure when installing and operating membrane-covered probes. Changes in flow and pressure can cause fluctuations in the level of chlorine passing through the membrane which will in turn have an impact on the reading. Different manufacturers have various ways of addressing this issue. Some recommend that pressure regulators or drole valves be installed, and others recommend constant head pressure devices (overflow weirs) be used. In some cases, these flow and pressure controls are built right into the flow cell.

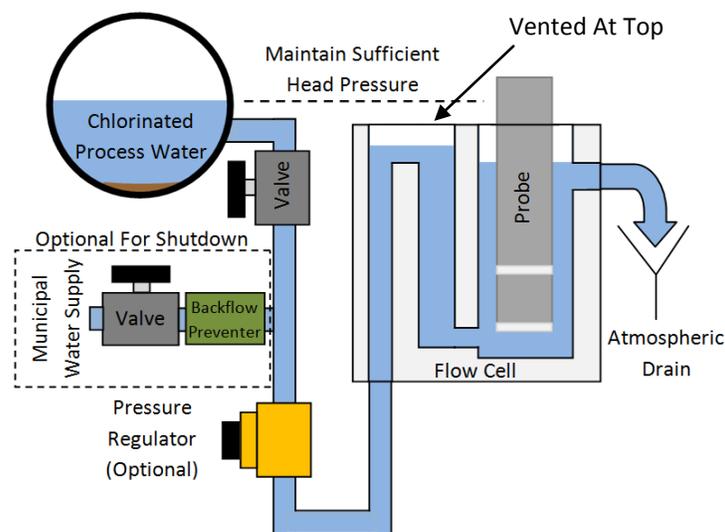


Figure 15

A properly designed vented flow cell, like the one shown in Figure 15, prevents the sensor from being exposed to over-pressurization or excessive flow rates, and usually eliminates the need for a pressure regulator. If too high of a pressure or flow is accidentally applied to the flow cell, water simply spills out of the vent and does not pass by the sensor.

For membrane-covered probes to perform accurately, sample flow across the surface of the membrane is required. If flow is stopped, the reading will drop towards 0 ppm even if there is chlorine in the sample. The requirement for stable flow and pressure is why these probes are never recommended to be installed directly into a pipe or submerged into a tank. For best performance, accuracy, and probe life, always use the flow cell provided by the manufacturer,

and closely follow their recommendations for sample flow and drain requirements. It is normally recommended to use a short line directly into an atmospheric drain in order to guard against pressure buildup and fluctuations that can otherwise adversely impact readings.

MAINTENANCE

Routine maintenance for membrane-covered probes includes electrolyte replacement every two to six months (varies depending on manufacturer). Membrane replacement intervals also vary largely between the different manufacturers. Some provide membranes that only last a few months, while others utilize membranes that can last one to two years (although the recommendation is usually to replace them on an annual basis). The units with higher quality and longer lasting membranes tend to have a higher replacement cost, but the payback comes in less frequent membrane replacements and more accurate readings.

While accuracy is a very important consideration with any technology, so is reliability and serviceability. It should be noted that on-line DPD analyzers operate with moving mechanical parts, and require lamps, optics, and pump tubing to all be in good condition in order to produce accurate and repeatable readings. Following the recommended service for on-line DPD analyzers is important and often omitted by the end user due to the complexity. If proper service is not performed by a qualified technician, the potential for error greatly increases as parts and tubing start to age. Amperometric probes, in comparison, have no moving parts, and are much easier to service.

Lastly, with no reagents to purchase and no specialized service required on a regular basis, amperometric analyzers have an obvious advantage over DPD analyzers in terms of operation and maintenance costs. The following table compares the approximate annual maintenance costs for a DPD unit and the Chemtrac amperometric analyzer. The difference between the two totals (approximately \$685), reflects the anticipated annual savings when choosing to take the amperometric approach.

	Price	Interval	Cost / yr.
DPD Colorimetric Analyzer			
• Reagent & Buffer	\$50	Every 4 weeks	\$650
• Maintenance	\$160	6 months	\$320
Annual Total for DPD			\$970
Amperometric Analyzer			
• Membrane Cap	\$185	Annual	\$185
• Electrolyte	\$140	Every 1.5 to 2 years	\$100
Annual Total for Probes			\$285
<i>Estimated Annual Savings using an Amperometric Chlorine Analyzer</i>			\$685

CONCLUSIONS

Colorimetric on-line chlorine analyzers have traditionally been the most common type used in the water treatment industry for monitoring and compliance reporting. However, colorimetric analyzers do require the addition of chemical reagents, and the maintenance costs associated with these analyzers have been leading the users to seek other options.

Amperometric on-line chlorine analyzers are becoming more widely accepted, and more popular for compliance reporting. These analyzers are simple to operate, are relatively interference free, and do not have any hazardous chemical considerations.

Since chlorine measurement probe designs still vary, it is recommended to research available options, and give strong consideration to chlorine analyzers utilizing the three-electrode membrane-covered probes with internal electrolyte buffering capabilities.

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