FEATURE

Less Waste, Easier Maintenance

Here's why you need to look closely at amperometric chlorine sensors

Michael Silveri

While colorimetric analyzers have been the method of choice for drinking water and wastewater utilities for many years, operators are looking for ways to lower operating costs and maintenance.

Reagent cost alone is roughly $700 USD per year per instrument. On top of that are the associated maintenance and labor costs. Amperometric sensors are a growing trend in the water sector. Many jurisdictions are mandating water reductions and there are technology developments in amperometric sensors that can help you address these pressing issues. Manufacturers of amperometric sensors have made steady improvements in the technology over the years.

Amperometric Sensor Innovation

One of these new technologies has its origins in a development project for the Office of Naval Research (ONR) from the U.S. Department of Defense. The project is to develop a sensor for measuring chlorine in seawater. The goal was a low maintenance, long calibration interval (3,000 hours or 125 days without calibration) sensor to be used on the U.S. Navy's Next Generation Reverse Osmosis unit. Flow independence also was a requirement. These difficult requirements forced a new approach (no membrane) to the design of amperometric chlorine sensors because the biofouling environment required continuous electrode cleaning. The successful outcome of this project led to the sensor's commercial use in ballast water treatment systems to prevent the transfer of invasive species, such as zebra mussels. This new technology also was ideally suited (due to its cleaning module) to the drinking water and wastewater applications. This sensor was designed for flow-independent operation, and is known for its direct pipe insertion type — something amperometric sensors were previously not capable of.

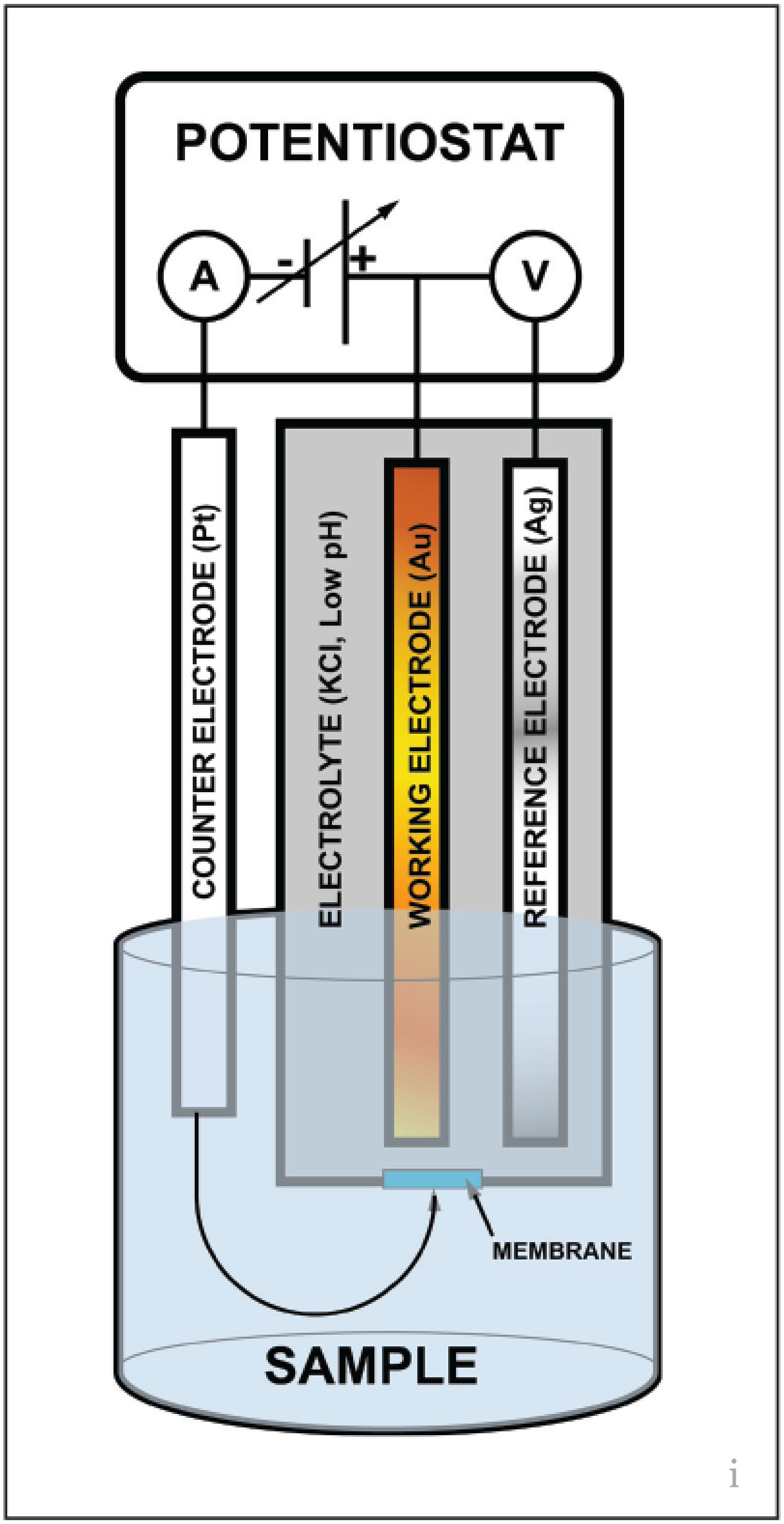
Saving Water: A Major Issue

For many years municipalities viewed water waste as the only way to get accurate data from older technology sensors and online n N, NDiethyl-p-Phenylenediamine (DPD) analyzers. These systems typically require a water waste stream of at least 261,000 L/yr (69,000 gal/yr) per sensor. It is a surprise to many operators that older amperometric sensors use as much or more water than colorimetric reagent systems.

As water becomes a more threatened commodity, waste cannot be taken for granted. Conservation of water is a high priority in most jurisdictions. In drinking water applications, mandates exist for water savings. Water consumption by water treatment sensors is often overlooked. One drinking water utility estimated water usage of 14.7 million L/yr (3.8 million gal/yr) for eight of its facilities when using conventional amperometric sensors — just to measure chlorine.

New amperometric sensors halve or even eliminate this problem by allowing for innovative installation types. Unless the sensor is Certified to NSF61, the water that touches the sensor cannot be put back into a potable water tank.

To address water scarcity, an important application is use of a sensor in remote well sites. Systems requiring regular maintenance are not an option for this application. Many of the sites that are being brought online are in remote locations.



Reclaimed Water Is Challenging

Reclaimed water facilities are notoriously difficult applications for any sensors. Frequent fouling results in "sensory deprivation" as the sensor is fouled, preventing adequate signal. In reclaimed water scenarios, amperometric sensor membrane fouling is much more prevalent. This leads to higher maintenance costs than in drinking water applications. Maintenance teams must proactively manage cleaning of lines and sensors, resulting in more calibrations needed. A self-cleaning sensor can use internal systems to remain clean, seldom requiring any manual cleaning.

Understanding Certifications

NSF61. If a sensor touches drinking water, it must be NSF61 certified. This standard — NSF/ANSI/CAN 61-2021: Drinking Water System Components – Health Effects — sets minimum health effects requirements for the chemical contaminants and impurities imparted from products, components, and materials to drinking water systems. Unless the sensor and all flow components are NSF61 certified, water from the waste stream must not be reused, only dumped to waste.

***Compliance monitoring for drinking water and EPA 304.0*.** Most people don’t realize that this standard applies to both inline use of amperometric or colorimetric DPD units. Quoting from EPA 334.0: "This method allows the use of any type of on-line chlorine analyzer (e.g., amperometric, DPD, etc.) for compliance monitoring when used in conjunction with a grab sample reference method that is approved for drinking water compliance monitoring."

The U.S. Environmental Protection Agency (EPA) does not provide chlorine analyzer manufacturers a certificate or formal stamp of compliance. Instead, it provides a guideline of the procedures for obtaining grab samples and determination of frequency of calibration checks and methods.

Available Options→

There are several different styles of amperometric sensors. All amperometric chlorine sensors are electrochemical devices that rely on the reaction below to measure chlorine.

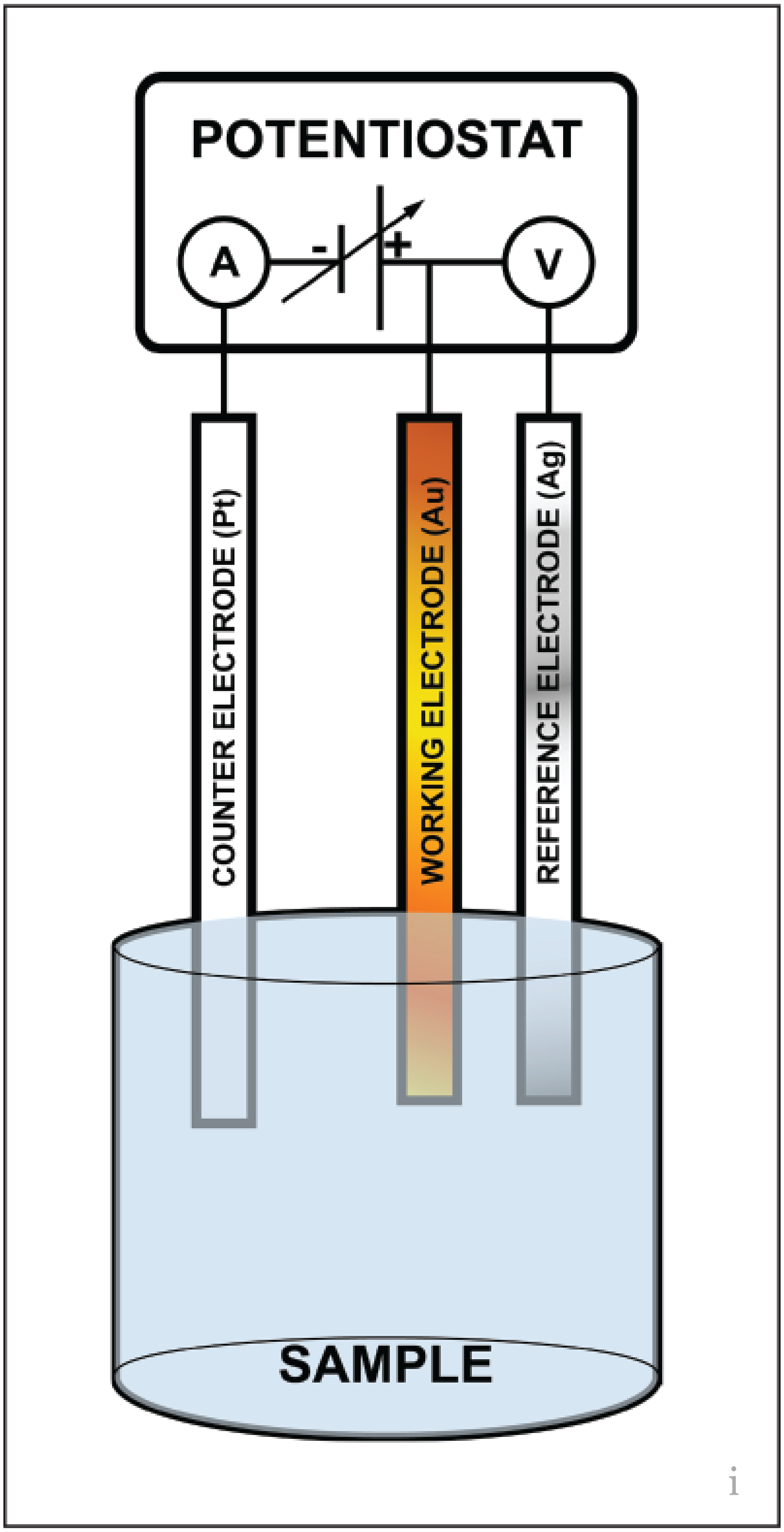
$$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O$$

Chlorine is reduced at the working electrode (cathode) and the loss of electrode is measured and generally proportional to the chlorine concentration. This is the reverse of what happens in a chlorine generator.

Galvanic Systems Versus Impressed Current

Perhaps the oldest amperometric sensors use bare electrodes; a copper anode and a platinum cathode with a grit cleaning system to keep the anode clean. The copper anode must be replaced annually because is wears out during use. The dissimilar electrodes are essentially a battery generating a voltage between the two electrodes. These systems often use vinegar or a pH 4 buffer to convert the combined chlorine residual to chlorine before the instrument measures it. These systems are generally reliable. They also require some maintenance, use a relatively high volume of sampling water, and require reagents.

Other amperometric sensors use impressed current and a three-electrode design. There are some two-electrode designs that combine the reference electrode and the counter electrode. The third electrode (reference electrode) produces a very stable chemical potential (virtual ground). A potentiostat circuit maintains a fixed (impressed) voltage between reference and working electrodes and is very stable, even as the solution conductivity changes (IR Drop). Accurate measurements are possible with this circuit. The applied voltage is optimized to ensure that the reaction above predominates so the sensor does not measure dissolved oxygen, for example.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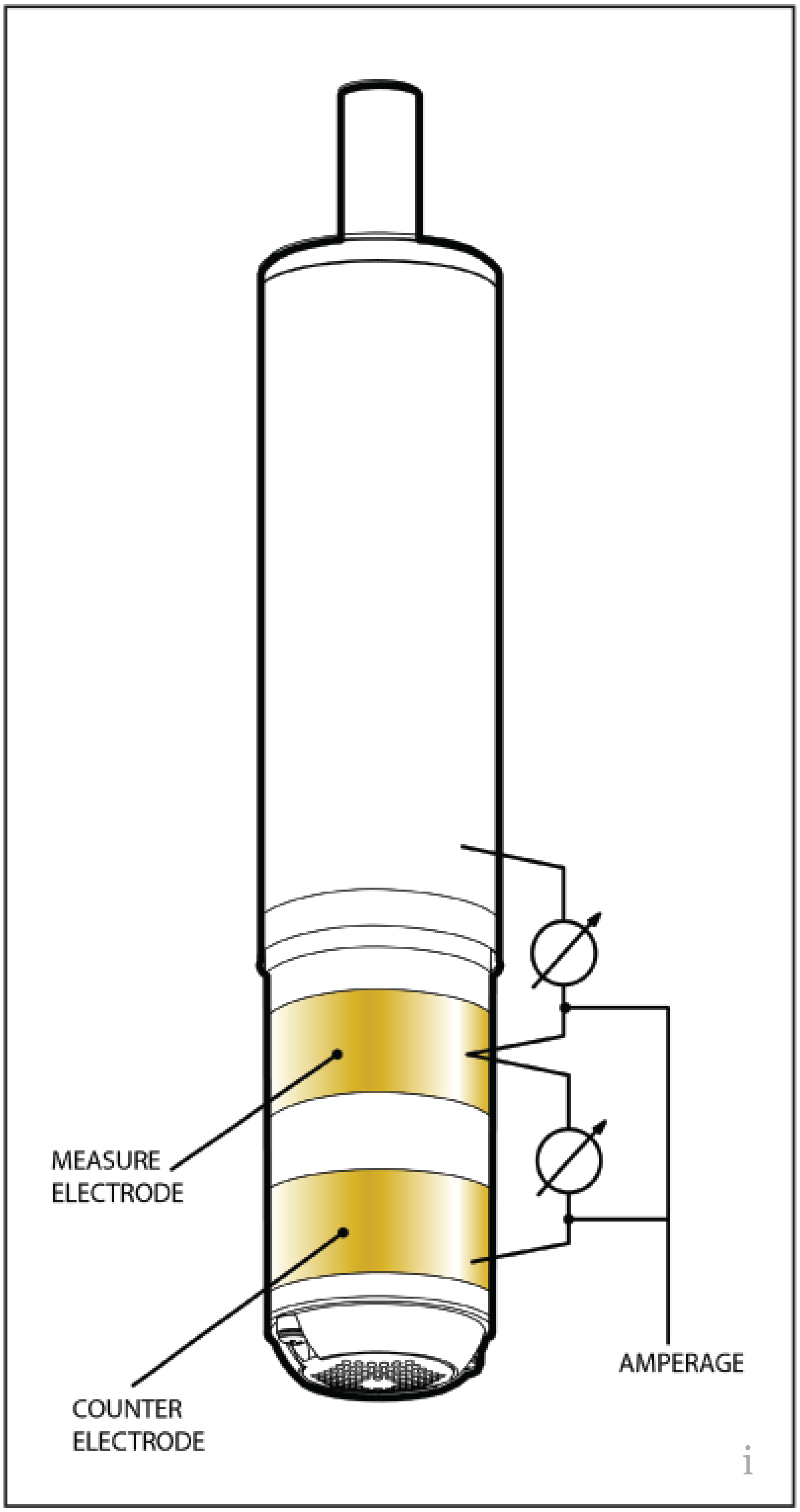


Two Dominant Styles of Sensors

There are two basic types of amperometric chlorine sensors popular today. Those with bare electrodes and those with a membrane and electrolyte chamber. Bare electrode sensors have been available since the 1950s but suffered from such problems as fouling and zero drift. Membrane style sensors were introduced in 1978 and greatly reduced fouling. Over the ensuing years, steady improvements have been made in both styles.

Membrane Style Sensors

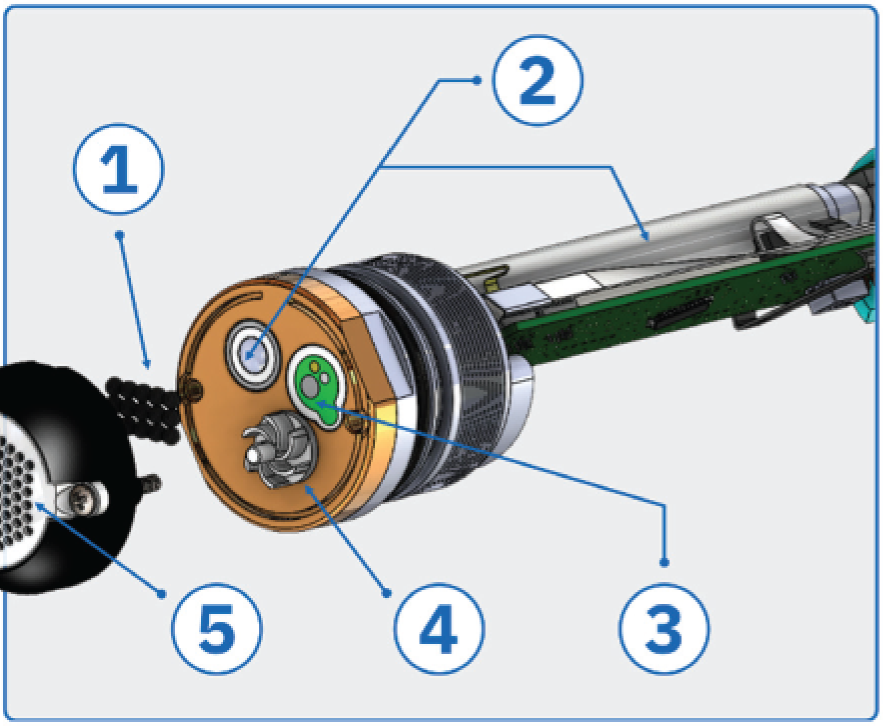
Membrane sensors use a porous membrane covering the working and counter electrodes. (See Figure 1, p. 50.) An electrolyte fills the chamber behind the membrane. This results in a slower sensor response since the reaction depends on the membrane’s diffusion rate. This solved a major fouling problem with the bare electrode sensors and eliminated the reagent feed.

Bare Electrodes

As seen in Figure 2 (above) bare electrode sensors are similar in design. The bare electrode sensors expose their measuring electrodes directly to the water sample, potentially fouling them and resulting in "sensory deprivation" because the signal is masked by salts, grease, or other contaminants. If you are familiar with electrolytic chlorine generation, you probably know that the cathode is subject to plating of calcium carbonate during operation. This must be cleaned off periodically. Chlorine sensors are no different. Electrode surfaces attract metals present in the water causing sensor drift over time.

Essential Consideration No. 1. Maintenance, Cleaning, and Calibration Steps and Timing

How the sensor or electrodes are cleaned is an essential consideration.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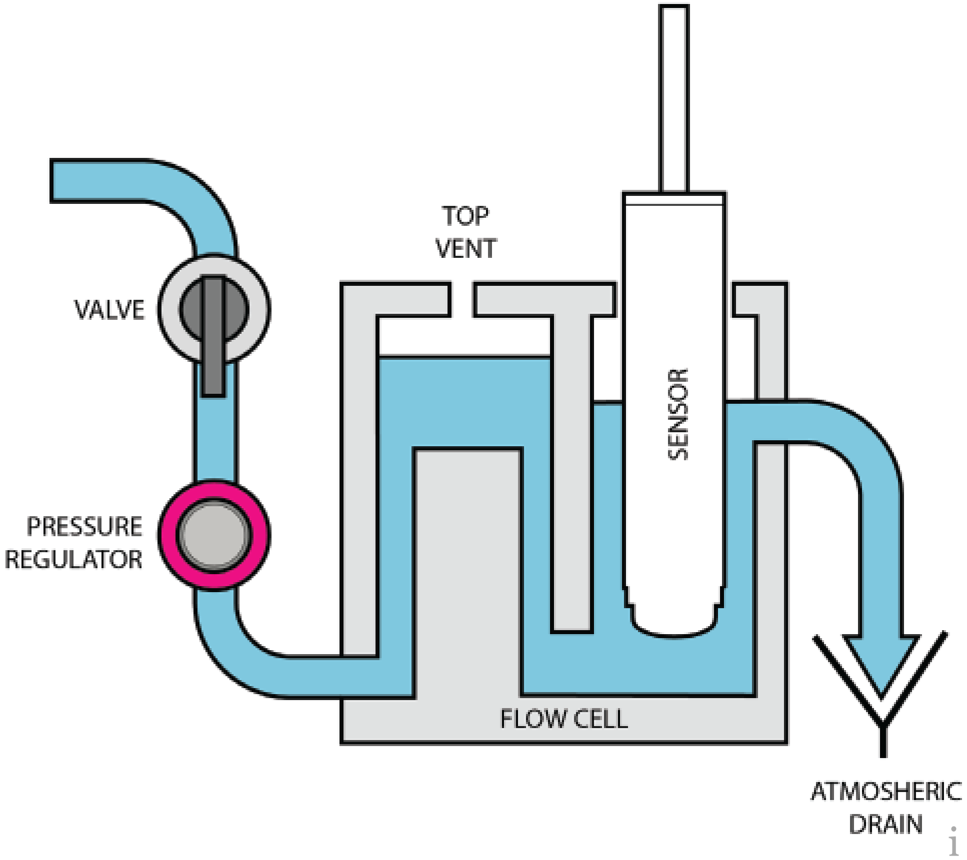
TOP VENT
VALVE
SENSOR
PRESSURE REGULATOR
FLOW CELL
ATMOSHERIC DRAIN

One advantage of bare electrode sensors is that the electrodes can be cleaned. While a membrane sensor protects its electrodes behind the membrane, the membrane cannot be cleaned automatically.

Bare electrode manufactures deal with electrode cleaning using several schemes. One is electrochemical cleaning. (See Figure 3, p. 51.) This system periodically cleans the working electrode by changing or reversing the voltage. The period is selectable by the user based on the individual requirements of the application or installation. It does not require any moving parts for the cleaning operation and results in minimal downtime. This produces hydrogen and oxygen at the electrodes. This method is effective for biofouling and calcium carbonate removal.

Mechanical cleaning used in the galvanic amperometric sensors is very effective and assisted by the reagent feed of vinegar or pH 4 reagent.

The direct pipe insertion style uses both methods to keep the electrodes clean continuously. The system shown in Figure 4 (above) uses cleaning beads to polish electrodes to remove biofilm, salts, and metals from the electrodes surfaces and the pH sensor. The impeller creates a constant flow across the electrodes to minimize the effect of flow changes in a pipe or tank. This flow motivates the captive beads to clean all interior surfaces.

When a new 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, but complete stability of the new electrolyte and new membrane within the 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.

All amperometric sensors are affected by flow and pH. There are several ways that sensor manufacturers deal with these factors.

Essential Consideration No. 2. Understanding Flow Changes

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. These changes, in turn, will affect the reading. Different manufacturers have various ways of addressing this issue. There are three approaches to dealing with flow changes and pressure spikes in amperometric sensor systems:

Flow regulation**.** Some manufacturers use pressure regulators or dole valves to maintain a constant flow. 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.

Overflow weir system**.** A properly designed vented flow cell (see Figure 5, p. 55) prevents the sensor from being exposed to over-pressurization or excessive flowrates. This system usually eliminates the need for a pressure regulator. If pressure or flow gets too high accidently, water simply spills out of the vent and does not pass by the sensor. This style also requires half of the typical waste stream required by other sensors.

Self-generated flow**.** Direct pipe insertion style sensors use an integral pump to provides constant flow across the electrodes (as shown in Figure 4). This constant flow allows the sensor, if properly aligned, to operate flow independently from zero flow to a velocity of 4 m/s. This feature overcomes the flow and pressure limitations of all other amperometric sensors. It enables the sensor to be installed directly in a pipe, immersed in a tank (zero flow), and/or any flow condition. This design eliminates the need for any waste stream. Unlike membrane sensors, it also does not have a memory when exposed to zero chlorine for extended periods.

Essential Consideration No. 3. pH Changes Affect Accuracy

All amperometric sensors are affected by pH changes in the process. pH measurement will usually improve the chlorine measurement accuracy. pH measurement does introduce another calibration and maintenance requirements which is a critical issue to understand in the selection process. There are three approaches that manufacturers take to pH compensation in amperometric sensors.

***pH stabilized gels in membrane sensors*.** If the pH of your process does not exceed 8.0, a simple option is the use a membrane sensor with a pH stabilized gel. Using a buffered electrolyte widens the pH range of operation. This can eliminate the need for an additional pH sensor. The buffered electrolyte reduces the pH inside of the sensor helping to convert the hypochlorite ion (OCl^-), which is undetectable by the electrodes, into hypochlorous acid ($HOCl$). This technique significantly improves the response to free chlorine at higher pH levels.

***Add on pH sensor*.** Most sensor manufacturers offer a pH sensor option to be included in their amperometric package. This provides automatic pH compensation. It must be calibrated separately.

***Integrated pH*.** The direct insertion type of sensor (see Figure 6, above) uses an integrated pH sensor. These specially developed pH sensors have a long life and will not be damaged when left dry for weeks or even months in ballast pipes. These sensors also are cleaned by the sensor’s self-cleaning system.

Weigh Your Options

Amperometric sensors are gaining popularity among water and wastewater operators and municipalities. Newer options result in dramatic savings in water, maintenance hours, and reagent costs. As more wells are brought online, remote monitoring is now an option for even smaller sites. These new tools offer water resource recovery facilities a new option for more reliable operation with lower capital and operating expenses. These technologies deserve careful consideration as tools to deploy to the front line of our water systems. As with all new technologies, system planners and operators should undertake a careful review to ensure that any technology is a match to your process.

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