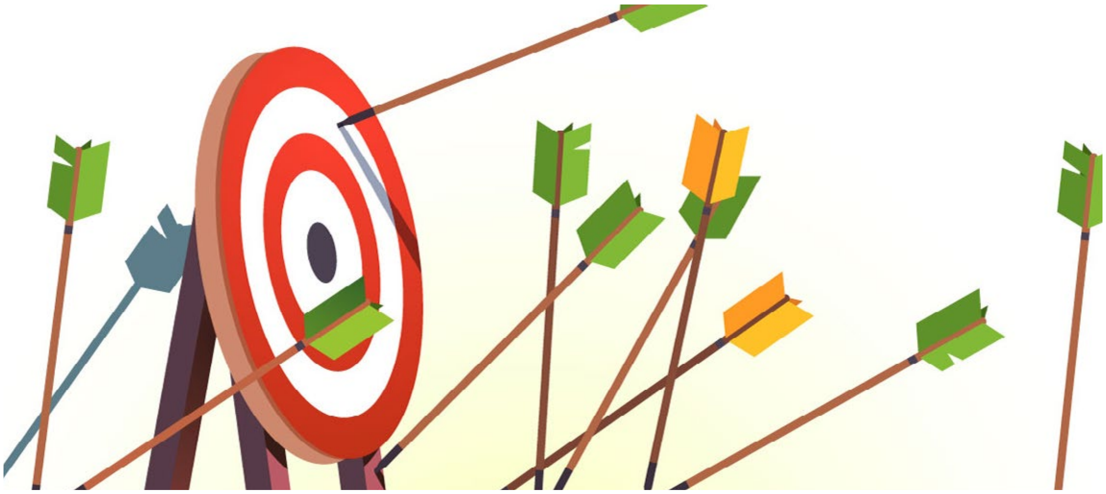
HACH®

Be Right™

Is ORP Really Your Best Option For Dechlorination Measurement?

With multiple variables of pH, temperature, oxidants, and reductants all contributing to a specific oxidation reduction potential (ORP) value, trying to identify low levels of total chlorine presence in water can become a bit of a guessing game. Here are some considerations for achieving more reliable accuracy when quantifying dechlorination results for applications ranging from RO membrane protection to wastewater discharge compliance.



Chlorine's Complicated Relationship With ORP

Unlike direct chlorine-measurement methods — such as colorimetric DPD — ORP readings have an inferred relationship with the volume of chlorine in a flow of water, one that can be complicated by other variables in the water. ORP readings are more easily used in the case of chlorine addition to address the question of "Do we have enough oxidizer (i.e., chlorine) to neutralize the bacteria in this water?" But in the inverse case of trying to use ORP to identify minimal chlorine residuals at a parts-per-billion (ppb) level, it is much harder to determine "Have we eliminated all the chlorine possible to protect our RO membranes or meet our wastewater discharge requirements?" That is where RO applications that depend on a chlorination/dechlorination process to reduce opportunities for biofilm growth without compromising RO membrane life can benefit from the improved ultra-low- range (ULR) accuracy of new colorimetric DPD instrumentation (Figure 1).

When making chlorination/dechlorination decisions, it is important to understand ORP measurement technology — the difference in electrical potential (expressed in millivolts) between a measurement electrode exposed to the solution being evaluated and a reference electrode exposed to a concentrated salt solution. In a solution with a controlled temperature and pH, and with chlorine as its primary oxidant, the positive electric potential measured by the ORP probe in that solution can be correlated to the concentration of chlorine. Unfortunately, that inferred relationship could be complicated by a variety of extraneous factors that can impact the ultimate ORP reading, create a risk of polyamide membrane damage, or cause an exceedance of chlorine limits in wastewater discharge:

- **Water Conditions.** Because ORP is an electrochemical measurement used to infer the chlorine level, it can be affected by a number of variables that can impact that inferred relationship. For example, as the pH reading increases, the ORP reading will fall. Because ORP readings are also affected by water temperature, which in many applications is difficult to maintain at a constant temperature, those ORP readings can become questionable. ORP reading will fall. Because ORP readings are also affected by water temperature, which in many applications is difficult to maintain at a constant temperature, those ORP readings can become questionable.

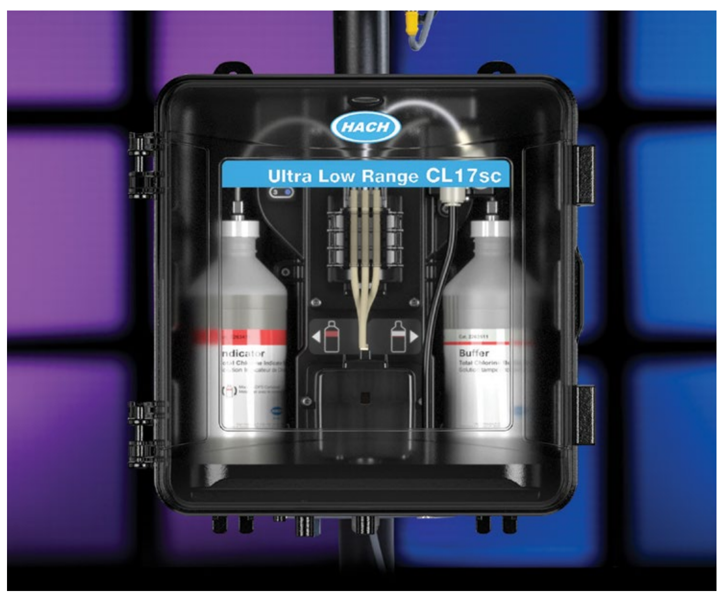


Photo courtesy of Hach.

Figure 1. With highly accurate readings as low as 0.008 mg/L, this ULR online chlorine analyzer can automate the process of monitoring chlorine levels in a continuous flow of water by sampling it every 2.5 minutes. A cumulative chlorine counter with user- selectable alarm limits also helps users know the long- term impact of an RO membrane's exposure to residual chlorine or of GAC bed aging.

- **Other Oxidants/Reductants.** Since ORP is measuring the difference in electrical potential of the sample and a standard reference, any oxidants (not just chlorine) and any reductants (or reducing agents) can impact the numerical ORP reading to reflect a different value than just the chlorine concentration in the sample.
- **Reference Standard.** Unlike a dedicated chlorine analyzer, ORP instrumentation cannot be calibrated to a specific value. It can only be verified to read closely enough to a reference standard ORP value. If the reading is far off that standard, the sensor will need to be replaced or a new baseline and slope will need to be established based on an in-depth understanding of the water makeup.
- **ORP Non-Linear Response.** ORP sensors respond very quickly to an increase of oxidants in the water, allowing for a fast reaction to those situations, such as an addition of sodium bisulfite (SBS). However, their response to overfeed of the reducing agent and restoring of chlorine absence is usually very slow.
- **Exceptional Situations.** In the event of a gross overfeed of SBS, the ORP sensor readings can cross the hydration curve and continue to show higher and higher ORP readings even as more SBS is added. Also, transition metals such as iron or manganese can act as catalysts for free chlorine, compounding the damaging effects of present chlorine on RO membranes. This is why it is crucial to know the actual chlorine concentration, not just a surrogate reading for it.

By contrast, a direct chlorine analysis provided by colorimetric DPD technology makes it possible to detect and measure total chlorine accurately, regardless of other circumstances or changes in the feed water.

How ORP Misinterpretations Can Hurt

Any Misperception that online or grab sample ORP measurements only respond to free chlorine can be a cause for misguided dechlorination decisions. Because ORP is not designed to measure chlorine levels directly — but rather the balance between the presence of any oxidants (taking on electrons) and/or reductants (giving up electrons) — other factors can come into play. Variability in water temperature, pH, or the presence of other oxidants/reductants can generate misleading ORP readings that do not reflect true chlorine concentrations, thereby making the appropriate dechlorination actions much harder to determine and control.

A misleading low ORP reading can miss chlorine concentrations that will damage and shorten the life of RO membranes. And if it is incorrectly assumed that chlorine is the primary cause of a high ORP number, overdosing a scavenger such as SBS can reduce dissolved oxygen too much, creating an anaerobic environment. That, combined with the resulting higher levels of sulfite supporting anaerobic bacterial growth, can exacerbate anaerobic biofouling on RO membrane surfaces.

A Better Way To Optimize Dechlorination Activities

When chlorine concentrations need to be known to avoid negative impacts on product quality, process efficiency, human consumption, or the environment, the ability to quantify a precise numerical reading of total chlorine residual becomes more valuable.

Until recently, the best limit of detection for a true reading of total chlorine (free chlorine plus combined chlorine) was 0.03 mg/L with an accuracy of + 0.04 mg/L in the range of 0 to 10 mg/L of Cl2. New ULR chlorine analyzers are able to detect total chlorine accurately at levels as low as 0.008 mg/L, with a precision of 0.003 mg/L. That offers a new level of control for decision-makers concerned about minimizing the impacts of chlorine on their processes.

For applications where overall costs are a greater concern, a small CAPEX investment in a more accurate means of measuring total chlorine can generate repeating long-term OPEX savings through reduced clean-in-place maintenance, reduced membrane damage, and reduced chemical costs of dechlorination.

This head-to-head comparison of the characteristics between ORP and colorimetric technologies (Figure 2) offers a good frame of reference based on the particulars of the application at hand.

Analytical Technology	Measure Principle	Main Benefits	Major Deficiencies
Oxidation-Reduction Potential (ORP)	Electrochemistry (Potentiometry)–change in mV output proportional to change in oxidation potential	Fast response to appearance of oxidants in water, reagentless	Indirect, non-specific, matrix influence (sample pH, flow/pressure, etc.) non-linear response
Colorimetric	Colorimetry–change in color intensity proportional to chlorine concentration	Direct and accurate measurement, independent of sample conditions, stable calibration	Non-continuous response (batch analysis), reagents

Chart courtesy of Hach.

Figure 2. Compared to the variability of ORP readings under different water conditions, direct numerical measurement of free, combined, and total chlorine by online ULR colorimetric chlorine analyzers can provide accurate readings regardless of pH, temperature, flow, or pressure variables.

HACH®

World Headquarters: Loveland, Colorado USA | hach.com

United States 800-227-4224 fax: 970-669-2932 email: orders@hach.com
Outside United States 970-669-3050 fax: 970-461-3939 email: int@hach.com

Layout ©Hach Company, 2022. Article ©Water Online (www.wateronline.com). All rights reserved.
In the interest of improving and updating its equipment, Hach Company reserves the right to alter specifications to equipment at any time.