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water environment and technology

Measuring Total Residual Oxidants

Ion selective electrode technology can help meet stringent wastewater management standards

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Measuring total residual oxidants (TROs) in effluent water is an important regulatory requirement for many industries, including power, manufacturing, food, and marine enterprises operating cooling water and wastewater management systems. Many of these systems require the use of chlorine- and bromine-based biocides to control biological growth in pipes, tanks, and other water management infrastructure. However, without careful monitoring and effective treatment to reduce TRO concentrations, using oxygen-scavenger biocides can cause serious harm to aquatic wildlife if released into the environment.

In the U.S., all biocides in effluent discharge, including bromine, chlorine, and chloramines, are measured as TROs and regulated by National Pollutant Discharge Elimination System (NPDES) permits. Companies that fail to adhere to stringent NPDES permit requirements — often enforcing TRO levels of less than or equal to 100 parts per billion (ppb) — can face large fines and risk costly reputational damage.

Robust process control is, therefore, essential to ensure biocide dosing levels provide effective and cost-efficient prevention of biological growth while making certain that TRO levels in discharged water are safely reduced to support full compliance with environmental regulations. With standards for wastewater management tightening, industries require reliable and cost-effective solutions for TRO monitoring that deliver against regulatory requirements across the full breadth of wastewater management applications.

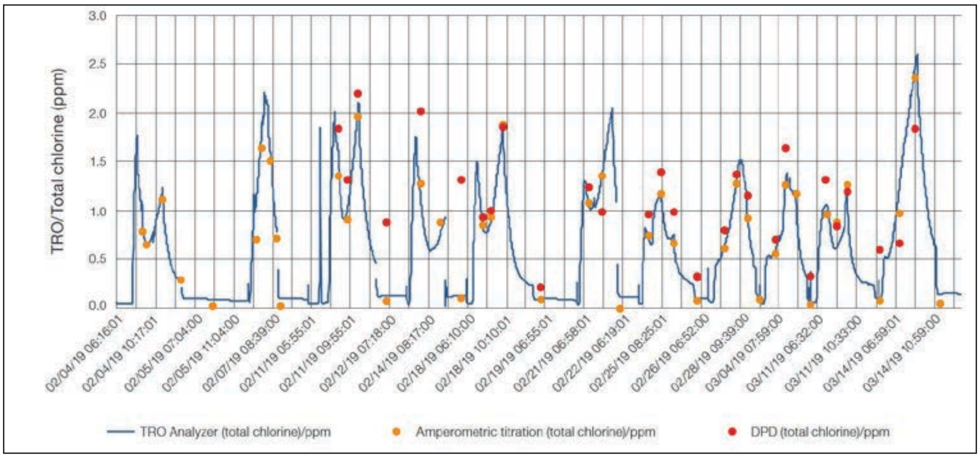
TRO Monitoring Challenges

The most widely used techniques for measuring TRO levels in wastewater are colorimetric and amperometric methods. Colorimetric techniques involve measuring the color change associated with the reaction between oxidants and reagents, such as N,N-diethyl-1,4-phenylenediamine sulfate (DPD), to analyze residual chlorine and other chlorine-based oxidants. Amperometric methods such as chlorine sensors, on the other hand, determine TRO levels by measuring differences in the electrical current associated with chemical reactions at specific oxidant concentrations.

Despite the availability of multiple TRO measurement technologies, implementing online monitoring solutions that can tolerate various water matrices and potential interferences is widely regarded as challenging, as each technique suffers from specific limitations.

DPD colorimetric measurements, for example, can be hindered by dissolved and suspended materials present in wastewater. The presence of these contaminants can jeopardize the accuracy of measurements. By contrast, colorimetric methods

Figure 1. Comparison of Total Chlorine Levels



This chart shows total chlorine (ppm) levels in power facility cooling water over a 6-week period as obtained using an ISE-based TRO analyzer (blue), amperometric titration (yellow), and a DPD colorimetric method (red).

are less sensitive than other techniques and typically are associated with large errors at parts per billion (ppb) TRO levels. These errors can be exacerbated by degradation and discoloration of the DPD reagent over time, further compromising measurement accuracy and confidence in results. These performance challenges plus the requirement for batch sampling rather than continuous monitoring are major drawbacks of DPD colorimetric methods.

Amperometric sensor technologies can support continuous monitoring. However, pH and flow variations can affect the accuracy of measurements. Also, amperometric sensors can be challenging to maintain, as they incorporate membrane electrodes that can become clogged by particulate matter and microbial films that necessitate intensive cleaning, recalibration, or replacement to overcome sensor drift effects.

Moreover, as wastewater monitoring stations often are located in hard-to-access locations, these regular maintenance steps can be time- and resource-intensive.

Oxidation–reduction potential (ORP) sensors can be used as an alternative measurement method to indicate disinfection levels. However, these sensors often are associated with slow response rates and do not provide direct TRO readings.

With environmental regulations becoming more stringent, accurate, sensitive, and operationally reliable technologies for efficient TRO monitoring are urgently required.

Ion Selective Electrode Technology

Ongoing advances in electrochemistry and improvements in instrument design are helping wastewater operators to monitor the landscape and meet their relevant regulatory requirements with the next generation of TRO analyzers.

One family of technologies gaining traction due to its ability to deliver highly accurate, precise, and sensitive measurements across a variety of wastewater matrices are ion selective electrode (ISE) systems.

Modern ISE systems are not compromised by suspended solids or water coloration, and they offer rapid, high-accuracy TRO measurements with errors of less than 10 ppb. ISE-based TRO analyzers also offer much greater sensitivities to chlorine- and bromine-based oxidants, with some systems enabling detection limits as low as 1 ppb. This compares to typical detection limits of around 30 ppb for DPD colorimetric methods. By offering much greater measurement accuracy at low-level TRO concentrations, ISE technologies are helping to improve confidence in results and provide much greater control over wastewater treatment processes.

Case Study: Measuring Total Chlorine

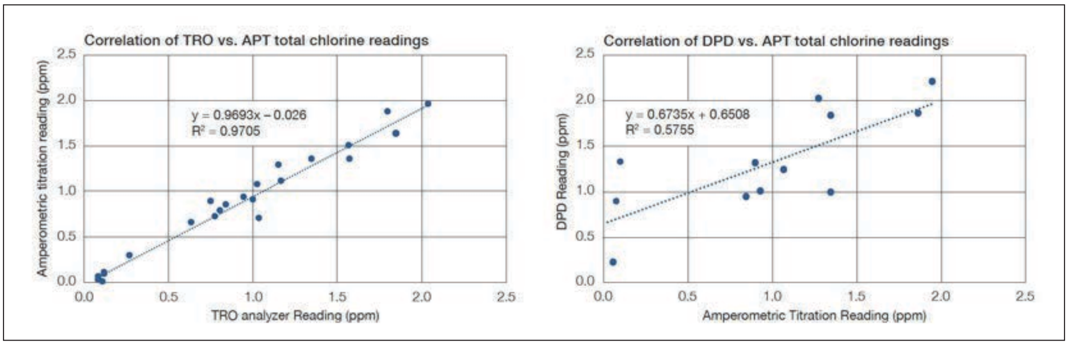
ISE-based TRO analyzers have proven to deliver robust and reliable measurement data for a range of industrial wastewater management applications, including power facility water cooling systems. A recent study at a power facility in the Southeastern U.S. compared various methods for monitoring total chlorine levels in discharged cooling water treated with sodium hypochlorite.

Figure 1 (above) highlights the total chlorine levels measured over a 6-week period, determined using an ISE-based online TRO analyzer, as well as off-line amperometric titration and DPD colorimetric methods. The total chlorine measurements represent all chlorine-based oxidants and include chloramines, trihalomethanes, and haloacetic acids generated from potential reactions between sodium hypochlorite and organic matter and trace ammonia in the water.

The ISE-based TRO analyzer provided was programmed to record data every minute and ran continuously for 6 weeks without onsite maintenance or calibration. The amperometric titration and DPD colorimetric measurements were made by collecting grab samples hourly during the facility's chlorination and dechlorination cycle.

With total chlorine levels fluctuating between zero and 2.5 parts per million (ppm) due to the chlorination and dichlorination cycle, the accurate low-level measurement of total chlorine was essential. The data highlight the strong agreement between the ISE and amperometric titration measurements, reflecting the high accuracy of the ISE technique. Conversely, the data collected by the

Figure 2. Correlation Between Total Chlorine Measurements



This chart shows the correlation between amperometric free chlorine measurements and readings obtained by (left) ISE or (right) ORP methods.

DPD colorimetric method are in poor agreement with both the ISE and amperometric titration method, with measurement errors of up to 1.2 ppm. In large part, this error is likely explained by changes in the turbidity of the water and the presence of color-absorbing natural organic matter, which can have a significant effect on colorimetric DPD measurements. In contrast, ISE measurement methods are unaffected by turbidity and water coloration effects.

The ISE-based method also offered enhanced performance over ORP sensors. Figure 2 (above) highlights the strong correlation between total chlorine measurements obtained by ISE and amperometric methods. However, readings taken using an ORP sensor correlate poorly with the amperometric measurements.

These results highlight that by providing a more accurate and reliable measurement of TRO levels than both DPD colorimetric and ORP methods, TRO analyzers based on ISE technology can support more precise control of biocide dosing and wastewater management.

Maintenance Needs

While TRO measurement accuracy is a key concern within wastewater management applications, cost-efficiency is another important factor for operators. Fortunately, improvements in the reliability and ease of maintaining the latest ISE systems are greatly reducing the operational costs associated with regulatory compliant wastewater management. The use of automated solutions that deliver on-demand TRO measurement is minimizing reagent consumption and lessening the burden of operator intervention by providing the option to initiate analysis only when biocide is being dosed into the sample, or when sample flow is present.

Some ISE-based TRO analyzers will enter standby mode if no sample flow is present, thereby stopping any further reagent delivery and reducing overall reagent consumption costs. ISE-based TRO analyzers also can provide additional measurement options, including continuous analysis and regularly scheduled readings, depending on the individual requirements of the water management system.

Other advances in system design are helping to eliminate or simplify maintenance requirements and reduce operational costs. The self-cleaning cell designs found in some ISE-based analyzers are minimizing instrument downtime by preventing biological and chemical fouling, helping monitoring workflows stay up and running for longer. Additionally, the extended sensor lifetime of modern ISE analyzers supports considerably longer intervals between system recalibrations. Furthermore, the fact that ISE analyzers do not use membranes that can become blocked and are unaffected by water turbidity and color means that measurement drift and interference is much less of an issue for these types of systems. Some of the latest ISE-based TRO analyzers show no more than a 5% change in measurement accuracy over 6 months, a significant improvement over the weekly or daily maintenance requirements associated with other technologies for on-line TRO analysis.

As international standards for wastewater management become more robust, industries operating across the full spectrum of effluent water monitoring and process control applications need accurate, reliable, and cost-effective TRO measurement technologies to maintain full regulatory compliance. Recent improvements in the design of modern TRO analyzers based on ISE technology are increasing the accuracy and sensitivity of measurements, while reducing the maintenance requirements and operational costs associated with wastewater management.

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