Power plant uses total residual oxidant analyzer to maintain cooling water discharge compliance

Introduction

Due to increased environmental regulations on total residual oxidant (TRO), a power plant in the Southeastern United States was searching for a better online process analyzer to monitor TRO in cooling water and wastewater discharge. This power plant uses sodium hypochlorite as biocide to control biological growth in cooling tower. With abundant natural organic matter and trace ammonia in the water, free chlorine generated from sodium hypochlorite converts to chloramines, trihalomethanes (THMs), and haloacetic acids (HAAs). TRO represents all oxidant species including free chlorine, chloramine, and hypochlorite (even bromine and chlorine dioxide for sites that uses these biocides). To ensure proper bio-control, the plant would like to measure its free chlorine and total chlorine concentration very precisely for biocide dosing control. Total chlorine concentration is equivalent to TRO concentration when only chlorine or chloramine is used as disinfecting oxidant.

If free and total chlorine (TRO) concentrations are higher than the discharge permit, then the plant is required to quench the TRO with oxygen scavenger, e.g. sodium bisulfite, at an appropriate corresponding concentration based on their TRO measurement. Overdosing of oxygen scavenger is a common practice to reduce TRO concentration. This ensures environmental compliance and avoids fines based on discharge regulations.

Background

Personnel at the power plant had tried various online analyzers and laboratory methods to measure TRO concentration in their cooling water. However, the local river water used for cooling water makeup has high concentrations of organic matter and turbidity, which interferes with colorimetric measurement of N, N-Diethyl-1.4-Phenylenediamine Sulfate (DPD) method. The cooling water makeup water compositions are listed in Table 1.

Table 1. Water quality of cooling water makeup from river water

Date	Alkalinity	TDS	TSS	Chloride	Ca	Mg	Si	Hardness	Al
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	as CaCO3 (mg/L)	(mg/L)
10/24	24	91	68	9.2	6.25	2.38	4.72	25.4	1.93
11/8	36	158	8	19	10.2	3.35	4.19	39.3	0.232
11/21	34	125	6	18	9.19	3.34	4.14	36.7	ND
12/14	30	173	ND	20	9.49	2.9	3.97	35.6	ND
1/12	33	199	ND	20	9.23	3.06	3.64	35.6	0.105

The turbidity in the cooling tower is high because it runs at around seven cycles of concentration. Additionally, the plant chlorinates twice a week, so the cooling water can experience zero- or low-ppb levels of chlorine for days.

The DPD method is not very accurate at measuring chlorine at such low levels. Amperometric sensors struggle to survive in such conditions because their membranes have a tendency to get clogged by high turbidity in the water and require frequent maintenance, recalibration or replacement.

After evaluating various online amperometric and DPD analyzers, the plant realized that none of these analyzers would suffice for the challenging water conditions. They concluded that the only method that can provide accurate readings for free chlorine and total chlorine (TRO) at this power plant is an offline amperometric titration method coupled with regular cleaning and maintenance., So they were actively searching for more advanced technology to monitor free chlorine and total chlorine (TRO) online and help the plant maintain environmental compliance, while reducing operation cost related to the use of hypochlorite and oxygen scavenger.

Solution

The Thermo Scientific™ Orion™ 7070iX TRO Analyzer was developed to measure TRO online with the use of ion selective electrode (ISE) technology coupled with maintenance-free automatic self-cleaning. Orion has over 50 years of manufacturing and supplying ISE based sensors that have been successfully deployed in the field. This analyzer has an on-demand measurement feature that reduces reagent consumption and minimizes manual intervention. The instrument will automatically initiate its analysis mode when sample flow is present. If no sample flow is present, the analyzer will not consume reagents and will shut down automatically. The analyzer can run analysis in continuous mode or interval mode, and it can be controlled remotely to reduce manual intervention.

The analyzer uses the EPA approved iodometric method for measuring total residual chlorine, in which iodide, together with an acid reagent, is added to the sample to react with and convert all chlorine, bromine, or chloramine species present to iodine. The combination of solid-state electrodes use ISE technology to directly sense the formed iodine. The analyzer is equipped with a self-cleaning cell design that improves response speed and prevents biological and chemical fouling.

Table 2. Comparison of ISE-based Orion 7070iX TRO Analyzer performance with DPD colorimeteric analyzer and amperometric sensor.

ISE technology features	Advantage of ISE vs. DPD colorimetric / amperometric	ISE technology benefits
ISE without interference from suspended solids and color water sample	Measurement not impacted by suspended solid levels or color; does not have a membrane that can become clogged	Long sensor life, minimal- to no-maintenance required
Total residual oxidant sensing	Greater sensitivity to chlorine, bromine, chloramine, etc.	More accurate measurement, especially at low ppb level
Stable calibration	Reduce field calibration needs	Reduced resource and maintenance cost
Self-cleaning cell design	Prevent chemical or biological fouling	Minimized down-time and cleaning efforts
Continuous measurement	Continuous measurement vs. DPD-batch measurement	On-demand real-time measurement
Fast Response	30s vs. 3 minutes	Fast Response for accurate oxidant control

Conventional online technology for biocide measurement and control (ORP sensor, DPD analyzer, and amperometric chlorine sensor) have limitations.

The performance of an online DPD colorimetric measurement is affected by various parameters, such as higher detection limit, larger error at low ppb level, interference from turbidity, color, Cu and Mn ions in different water matrixes, drift due to discoloring reagent and intermittent batch measurement.

An ORP sensor does not provide direct chlorine or TRO readings and has a very slow response, while amperometric chlorine sensor technology faces additional challenges, such as frequent fouling of membrane, interference due to flow and pH, and drifting calibration.

Leveraging Ion Selective Electrode technology, the newly developed Orion 7070iX TRO Analyzer solves many of these issues with significantly improved detection limit and accuracy using the US EPA-approved 97-70 electrode. Comparing with traditional methods, the ISE based TRO analyzer is continuous, free of interference from solids, Cu ion, sample turbidity and color, and able to perform in a wider dynamic range with better accuracy and lower limit of detection.

Table 2 highlights the advantages of our TRO analyzer performance over other methods.

Results and discussion

The Orion 7070iX TRO Analyzer was installed next to the cooling tower. Sample water was introduced into the TRO analyzer from the cooling tower basin. A grab sample was collected either from the cooling tower or from the fast loop of the TRO analyzerfor amperimetric titration. The instrument was programmed to record data each minute, while the DPD colorimetric method and amperometric titration were done on an hourly basis during the period of chlorination and dechlorination. The Orion 7070iX TRO Analyzer was calibrated at the Thermo Scientific factory before it was sent to the customer. The analyzer ran at the customer's site continuously for six weeks without any onsite calibration and maintenance. After six weeks, the analyzer tube and measurement cell are clean without fouling or deposit based on operator's observation, which was not the case for DPD analyzers and amperometric sensor that he evaluated earlier.

Figure 1 proved that the continuous reading from the Orion TRO analyzer matched the amperometric titration reading. The TRO analyzer was able to measure total oxidant (chlorine) from single digit ppb levels to over 2ppm in the customer's cooling water. The DPD colorimetric method reading was off from both amperometric and TRO analyzer readings on a number of occasions with errors up to 1.2 ppm due to color / turbidity interference (as shown in Table 1).

Figure 2a shows that the TRO analyzer readings match the amperometric titration reading with an R-squared value of 0.97, however the colorimetric method reading did not correlate well with the amperometric titration reading with a R-squared value of 0.5755 as shown in Figure 2b. The analysis shows that the Orion 7070iX TRO Analyzer is a superior method compared to the DPD method in determing TRO in cooling water of this power plant.

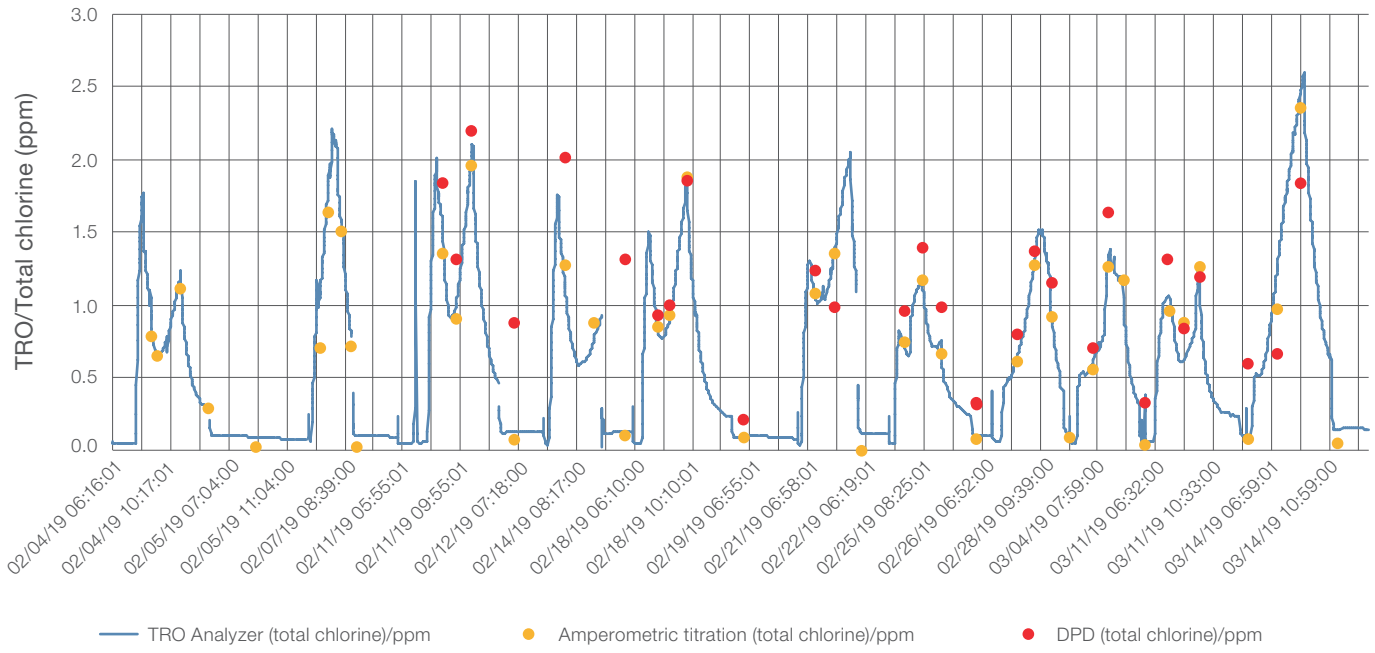

Figure 1. TRO measurement by the Orion TRO analyzer 7070iX, amperometric titration, and DPD colorimetric method in cooling water of a power plant over six weeks.

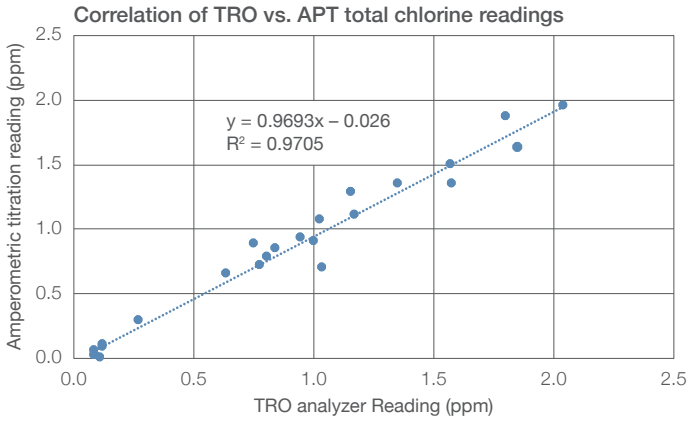

Figure 2a. Correlation analysis of Orion 7070iX TRO Analyzer readings vs. amperometric titration readings.

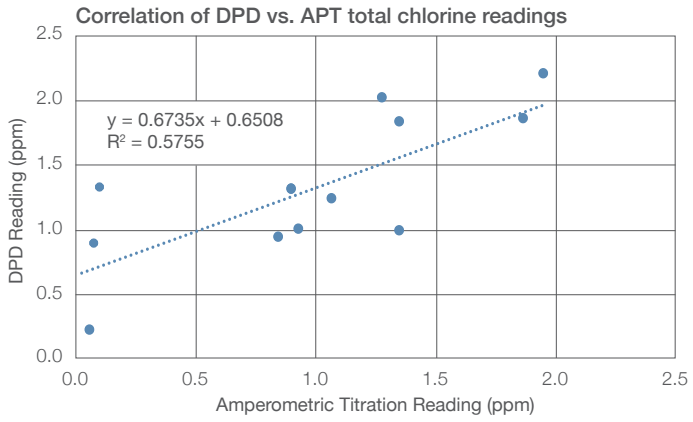

Figure 2b. Correlation analysis of DPD readings vs. amperometric titration readings.

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As shown in Figure 3, the difference in readings of DPD analyzer and lab amperometric titration is much larger than the difference in TRO analyzer and lab amperometric titration. The confirms that the TRO analyzer is more accurate than DPD analyzer in measuring total chlorine.

In addition, a strong correlation with R-squared value of 0.92 was found between free chlorine reading and TRO analyzer reading for chlorination control (Figure 4). The TRO analyzer reading can be converted to a free chlorine reading at this site using the equation below from regression analysis.

Free chlorine (ppm) = 0.7075*TRO – 0.1095.

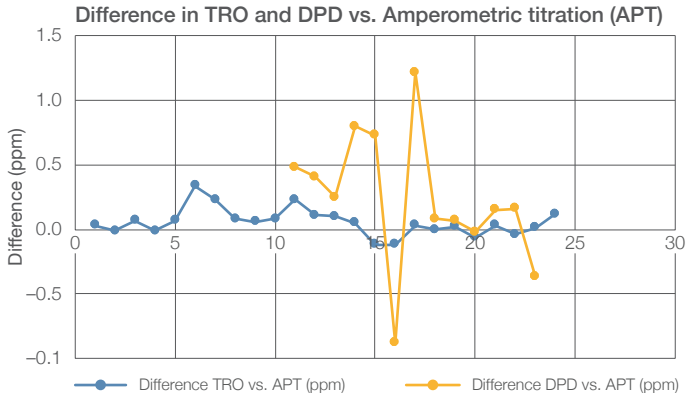

Figure 3. The difference in TRO readings between the Orion 7070iX TRO Analyzer and amperometric titration (in blue) vs. the difference in TRO readings between DPD method and amperometric titration (in orange).

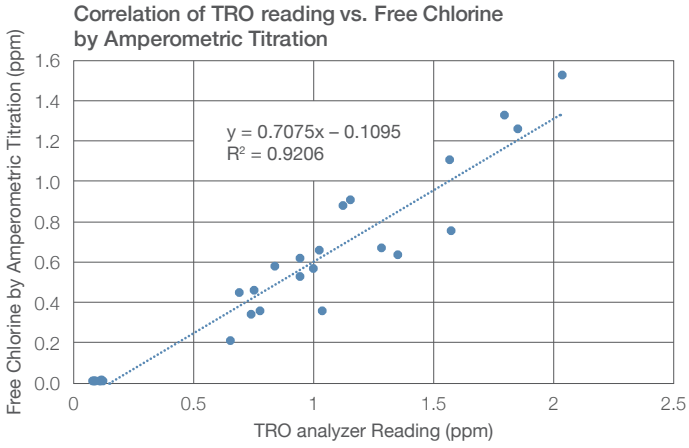

Figure 4. Excellent correlation of free chlorine reading by Amperometric titration and Orion 7070iX TRO Analyzer reading.

The plant chemist was able to use our TRO analyzer to guide the dosing of sodium hypochlorite for bio-control. In comparison, ORP had a poor correlation with free chlorine as shown in Figure 5 (R-squared value of 0.53 vs. 0.92 for TRO). This enabled the customer to have more accurate control of biocide dosing than traditional ORP-based control of biocide.

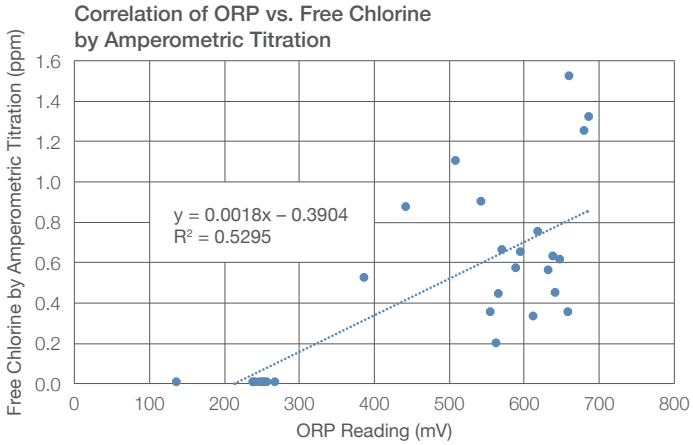

Figure 5. Poor correlation of free chlorine reading by Amperometric titration and ORP reading.

In summary, the Orion 7070iX TRO analyzer was able to provide continuous accurate reading in challenging cooling water to support operation decisions on chlorination for biocontrol and dechlorination before discharge, which result in proper water treatment with biocide dosing and dechlorination with oxygen scavenger. The data proved that water treatment decisions enabled by the Orion 7070iX TRO Analyzer ensures compliance with environmental regulation and mitigates risk of any regulatory non compliance. Additionally, the online TRO analyzer reduces the need and time for lab measurements of TRO, improves labor productivity and increases operation efficiency.

Find out more at **thermofisher.com/troanalyzer**

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