

Monitoring Chlorine in Turbid Cooling Tower Water with the Hach AT1000 Titrator and CL17 Analyzer

Introduction

Microbiological control of cooling tower water is commonly accomplished through the addition of oxidizing microbiocides, particularly chlorine. Effective dosing of chlorine requires accurate residual monitoring. Chlorine residuals must also be monitored during discharge to ensure compliance with local regulations. With adequate sample filtration, the Hach® CL17 Chlorine Analyzer may be used for colorimetric monitoring of most cooling tower matrices. However, for matrices containing high levels of color, total suspended solids (TSS), and/or turbidity, chlorine should be monitored with an alternate analytical technique. The Hach AT1000 Titrator (amperometric titration), or CL10sc Analyzer (direct amperometry) are recommended for measuring chlorine residuals in turbid or colored samples.



Hach CL17 and AT1000

Background

Cooling tower systems provide an excellent environment for microbiological growth. If left uncontrolled, this biofouling impairs the proper functioning of the cooling tower. Application of microbiocides such as chlorine inhibits microbiological growth. The Hach CL17 Chlorine Analyzer provides continual monitoring of chlorine residuals ensuring that chlorine dosing is sufficient to provide antimicrobial protection, and that chlorine has been effectively removed from discharge waters.

The CL17 uses the N,N-diethyl-p-phenylenediamine (DPD) chemistry to measure free and total chlorine. At the pH buffered by the CL17 reagents, chlorine oxidizes DPD to produce a magenta colored dye (see Figure 1). The intensity of the magenta color is directly proportional to the concentration of chlorine in the sample. The color is measured photometrically at 520 nm. When used in turbid matrices, the standard CL17 strainer (40 mesh) should be cleaned periodically. Additional inline sample filtration is also recommended, provided that sufficient flow is maintained.

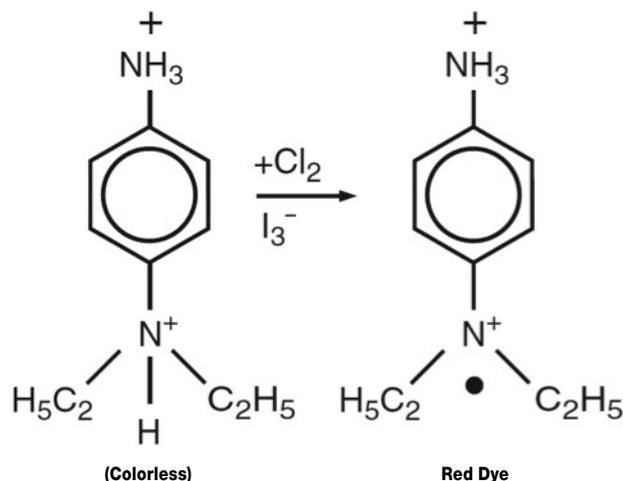


Figure 1: Oxidation of *N,N*-diethyl-*p*-phenylenediamine

In addition to microbiological contamination, cooling tower water frequently contains high levels of suspended solids. Precipitated scale, salts, corrosion products, macroorganisms, and airborne particulates can all accumulate in cooling water, leading to high levels of TSS, turbidity, and possibly color. These conditions can interfere with photometric measurements. Solids and color can obscure, absorb, and scatter the passage of light through the photometer's measurement cell. This obstruction can be interpreted by the detector as the analyte of interest, in this case chlorine.

Samples containing high levels of suspended solids must be filtered prior to photometric measurement. A 40 mesh strainer and filter installed at the inlet of the CL17 will remove larger solids and minimize the effect of turbid matrices. Any filter should be replaced or cleaned periodically to ensure adequate sample flow to the analyzer. Small particulates will not be removed by an inline filter, and can still greatly affect the accuracy of the photometric measurement.

The Hach AT1000 titrator is not affected by turbidity or color. Chlorine is measured through an amperometric titration. Amperometric titration avoids several of the analytical concerns associated with continuous direct amperometry: pH control, sample flow, temperature. Amperometric titration is not a continuous measurement, however, and must be performed in a batch fashion.

Chlorine is titrated with phenylarsine oxide (PAO) (see Figure 2). As PAO is oxidized by chlorine in the sample, the resulting current change is measured until all the chlorine is consumed and the breakpoint is reached.

Since they do not participate in the redox reaction, matrix components such as turbidity and color do not influence the chlorine measurement. When used in intermittent fashion, the AT1000 tubing should always be purged and the measurement cell treated for chlorine-demand prior to analysis. The tubing purge function is described in the user manual.

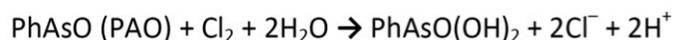


Figure 2: Phenylarsine oxide reaction

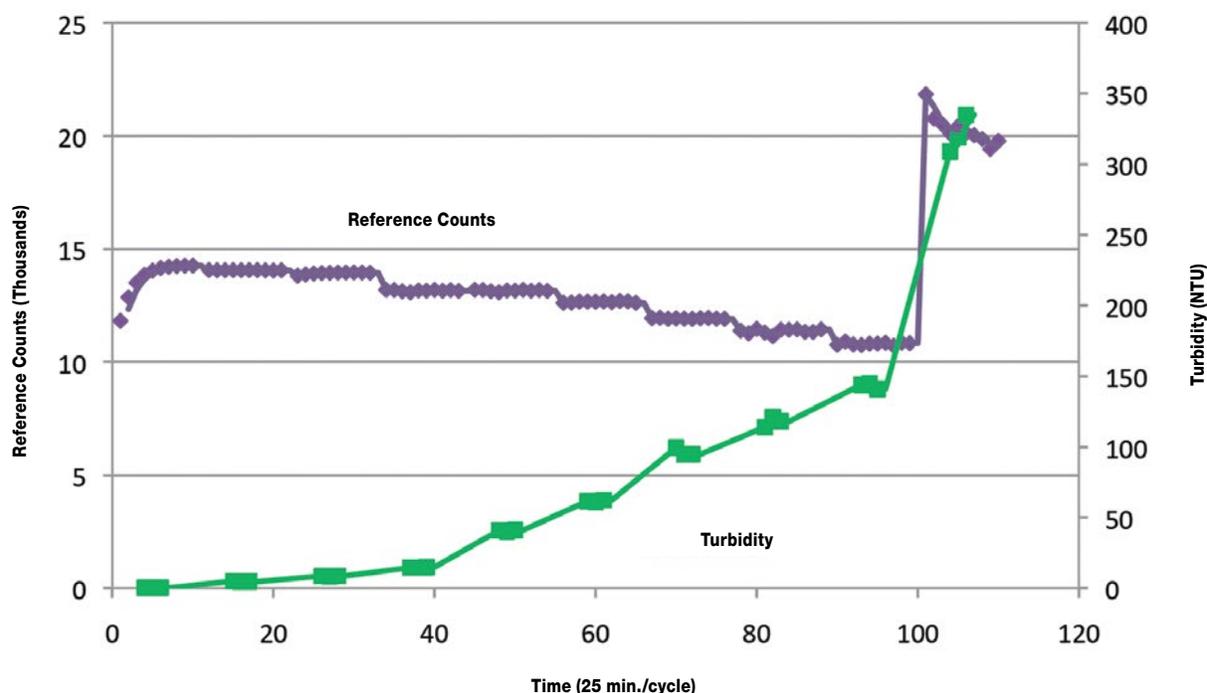


Figure 3: Reference Counts vs. Turbidity

Data and Results

The effects of turbidity on the CL17 and AT1000 were explored in order to determine the best chlorine monitoring scheme for turbid cooling tower matrices. Deionized water containing various concentrations of kaolinite was fed to a CL17. Ten consecutive CL17 measurements were taken at each kaolinite concentration. Triplicate grab samples were taken at each kaolinite concentration for measurement with an AT1000 and a Hach TL23 turbidimeter. All turbidity data are specific to the kaolinite used in this study.

The CL17 reagents were replaced with dyed water producing a visual chlorine result equivalent to ~ 0.45 mg/L Cl_2 . Dye was used so that the test would not be influenced by chlorine-demand from the kaolinite. In this way, the CL17 results reflect the effect of turbidity only. Free chlorine was spiked into the AT1000 reaction cell immediately prior to analysis, minimizing the potential for chlorine consumption from kaolinite chlorine-demand. The spike volume was chosen to match the dye concentration for comparison purposes.

The CL17 adjusts for certain amounts of color or turbidity by zeroing on the sample prior to the addition of the DPD reagents. These zero measurements are recorded as "reference counts," and are analogous to light transmittance. When the sample matrix is free of color and turbidity the reference counts are $\sim 14,000$. As the sample turbidity increases, the reference counts (transmittance) decrease.

Figure 3 plots reference counts against increasing turbidity. The reference counts decrease with increasing turbidity until the turbidity was increased to ~ 300 NTU. At this point the reference counts jumped to $\sim 20,000$. The CL17 is designed to increase the LED lamp intensity to account for its degradation over time based on light throughput. The jump in reference counts at ~ 300 NTU indicates that the CL17 interpreted the high turbidity as lamp degradation and increased the LED intensity in response.

APPLICATION NOTE: CHLORINE IN COOLING TOWER WATER

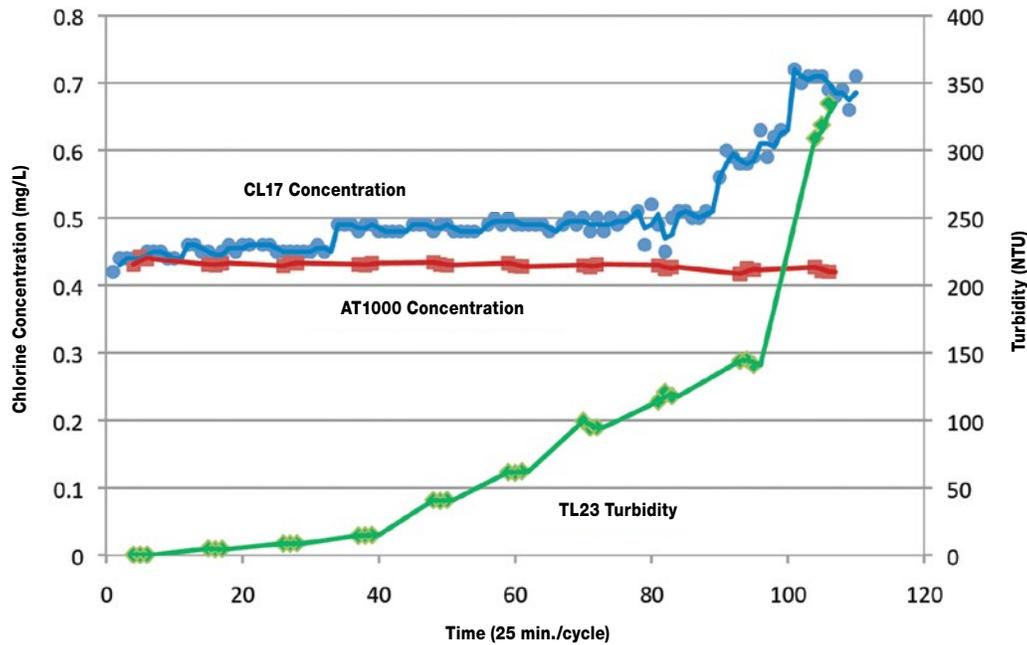


Figure 4: Chlorine Concentration vs. Turbidity

In Figure 4, CL17 dye data are plotted against AT1000 chlorine data for increasing levels of turbidity. Several conclusions are evident from this chart. First, CL17 values are stable for increasing turbidities, up to turbidities of ~100 NTU. At this point CL17 values become somewhat imprecise. Second, CL17 values increase with increasing turbidity. This effect is minor at lower turbidities (<5% high); more pronounced as turbidity reaches ~15 NTU (~10% high), and extreme when above ~100 NTU (>35% high). Finally, the AT1000 chlorine values are consistent regardless of turbidity. There is a slight decrease with increasing turbidity which is associated with chlorine demand of the high concentrations of kaolin.

Conclusion

It is clear that the photometric CL17 chlorine measurement may be negatively affected by high levels of turbidity. While low levels of turbidity may only moderately bias CL17 measurements, higher levels of turbidity which may be present in certain cooling tower operations will cause a significant high bias in CL17 chlorine monitoring trends.

In circumstances where high turbidity is known to exist, it is recommended that chlorine be measured with a non-photometric technique. The AT1000 amperometric chlorine titration is a suitable technique, and is recommended for chlorine monitoring in these applications. A combination of photometric and amperometric analyses may be used, where online photometric monitoring is performed with the CL17 analyser and periodic grab sample verifications are performed with the AT1000 titrator. This combination of techniques will provide both continuous monitoring and verification of accuracy.

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