

Uncovering the Unexpected In Drinking Water Disinfection Applications Using Continuous Monitoring

What chlorine measurement method should I choose?

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Preface

The following report includes data and conclusions from tests performed with Hach's CL17. Hach® introduced the CL17sc as the successor to the CL17, and the information contained in the following report is relevant and applicable to both analyzers. The CL17sc uses the same proven chemistry and DPD method for measuring residual chlorine and complies with the same EPA and ISO methods (40 CFR 141.74, 40 CFR 136, 7393-2). Because of the shared chemistry and methodology, the conclusions drawn from the following report can be used to describe CL17sc behavior and benefits, as well as those of the CL17.

It should be noted that the study below was conducted prior to the introduction of US EPA Method 334.0, which added amperometric chlorine monitoring to the list of approved methods for regulatory reporting. Some statements regarding amperometric measurements may therefore be outdated. For the most current information on chlorine monitoring technologies and instrumentation, including a practical guide to choosing the right technology for online monitoring, visit our Chlorine Analyzers page on <http://www.hach.com>.

What's new with the CL17sc?

Using the foundation of the CL17, Hach improved usability and performance features to help make water professionals' jobs easier. These improvements include:

Maintenance made easy

The CL17sc reduces your routine maintenance touch time with programmable alerts, simplified tubing replacement, and step-by-step maintenance instructions.

Peace of mind through comprehensive diagnostics

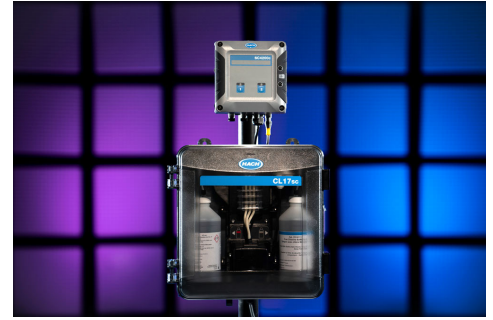
With upgraded features like a flow meter, colorimeter window, multi-color status light, and predictive diagnostic software, you know your instrument is operating as intended.

Expanded connectivity. Increased flexibility.

By pairing the CL17sc with Hach's SC controller platform, your options increase significantly: internal data logging; external analog and digital communication alternatives; and multi-parameter instrument flexibility.

Claros Enabled

This instrument connects to Claros, Hach's innovative Water Intelligence System. Claros allows you to seamlessly connect and manage instruments, data, and process – anywhere, anytime. The result is greater confidence in your data and improved efficiencies in your operations. To unlock the full potential of Claros, insist on Claros Enabled instruments.



Abstract

A new Total Chlorine Reagentless Amperometric analyzer equipped with flow sensor and optional pH probe was installed side-by-side with a DPD colorimetric process instrument in a finished drinking water disinfection application. The data received from the amperometric unit showed excellent trending of the colorimetric analyzer, however, with presence of multiple spikes not visible in the DPD-based instrument or laboratory test results.

In order to identify the root cause for the spikes, the continuous data logged by the amperometric instrument were thoroughly analyzed. This analysis revealed significant instability of the sample matrix, in terms of pH and chlorine concentration values, which was unexpected for the customer. The pH instability alone should not have caused the unstable chlorine readings due to the internal pH compensation available for the amperometric unit. This phenomenon pointed to potentially incomplete mixing and reaction between free chlorine and ammonia. The produced assumptions were proven when the amperometric analyzer was moved farther away of the original sampling point and the spikes disappeared. Thus the continuous chlorine analysis helped to pinpoint the unexpected problem with mixing disinfection chemicals in the drinking water application, prior to final product discharge.

The conducted study also allowed for summarizing major characteristics of the instrumentation and applications to help choose the most suitable online chlorine monitoring equipment per application.

Introduction

Regulatory Environment

Online chlorine monitoring is used extensively in water and wastewater treatment to ensure disinfection and regulatory compliance. The Surface Water Treatment Rule¹ suggests continuous monitoring of residual chlorine on distributed water for systems serving more than 3,300 people. Similar monitoring is required by the recently adopted Ground Water Rule².

What Technologies are Available & Which is Best?

The two most common methods for online chlorine analysis are colorimetric and amperometric detection. DPD colorimetric detection is a method based on N,N-Diethyl-p-Phenylenediamine (DPD) reaction with active halogens. This reaction is a standard analytical approach for analysis of residual chlorine and other chlorine oxidants and is based on the formation of colored products with DPD. The DPD method has been approved by US EPA for online analysis of chlorine residual and therefore is widely used as a reference method.

Amperometry is an electrochemical technique that measures the change in current resulting from chemical reactions as a function of the analyte concentration. A typical amperometric sensor consists of two dissimilar electrodes – an anode and a cathode (i.e. silver/platinum or copper/gold). The anode may be essentially split into two parts – a reference and an auxiliary (or counter) electrode making the measurement more stable. Such systems are called three-electrode sensors. Typically, the sensor electrodes are covered with a membrane and a small electrical voltage (potential) is applied across the electrodes, providing for better stability of the readings and selectivity of the analysis.

Currently, no “ideal” method exists for quantifying chlorine and inorganic chloramines in water. All common methods of chlorine analysis display some lack of specificity and are not adequately selective to be completely free of interferences. However, most of the limitations associated with the traditional DPD chemistry (e.g. calibration linearity, reagent stability, reaction product stability, etc.) have been sufficiently addressed. On the other hand, newer methods including the online amperometric chlorine determination should be characterized very thoroughly from the interference standpoint³. Once there is a complete understanding of those methods, especially in terms of the application specifics, they can be successfully used for online chlorine monitoring and may, sometimes, provide additional benefits to the customers.

Continuous Measurement versus Batch Analysis

One of the most well known and discussed benefits is the continuous nature of amperometric measurement vs. continual (batch) method employed by the DPD-colorimetric instrumentation. This benefit is, however, difficult to completely understand based on manufacturer specifications. The response time is normally specified and it is usually expressed in number of seconds required by the analyzer to detect a certain level of chlorine concentration when it has changed. In our case of comparison between two technologies, it is either 100% for a batch method or 90% (T90) for continuous analysis, assuming the concentration has reached its final level at the time when the analysis is performed.

In order to explain this concept of response time, some calculations based on the manufacturer specifications for two analyzers were conducted and results plotted against each other. The calculations were performed for CL17 (DPD colorimetric) and CLT10sc (amperometric) analyzers chosen as model instruments and the resulting graphs are presented in Figure 1. Although the study involved Hach’s previous CL17 model, the conclusions remain applicable to the CL17sc, as both use the same DPD method and chemistry.

It is seen from Figure 1 that absolute accuracy of the response to changing chlorine concentration is achieved at approximately the same time by both instruments. However, the amperometric instrument built on continuous measurement principle, starts providing the response instantaneously and therefore it can be configured for tighter control of the feed pumps. Moreover, if the sample was taken by a colorimetric analyzer (whether online or handheld) little earlier than the dosage change happened, the accurate concentration reading becomes available only after two cycles of measurement (Fig. 1). In this case, the continuous amperometric analysis will provide benefit of fast response and trending even if the final accurate response time is comparable to the colorimetric method.

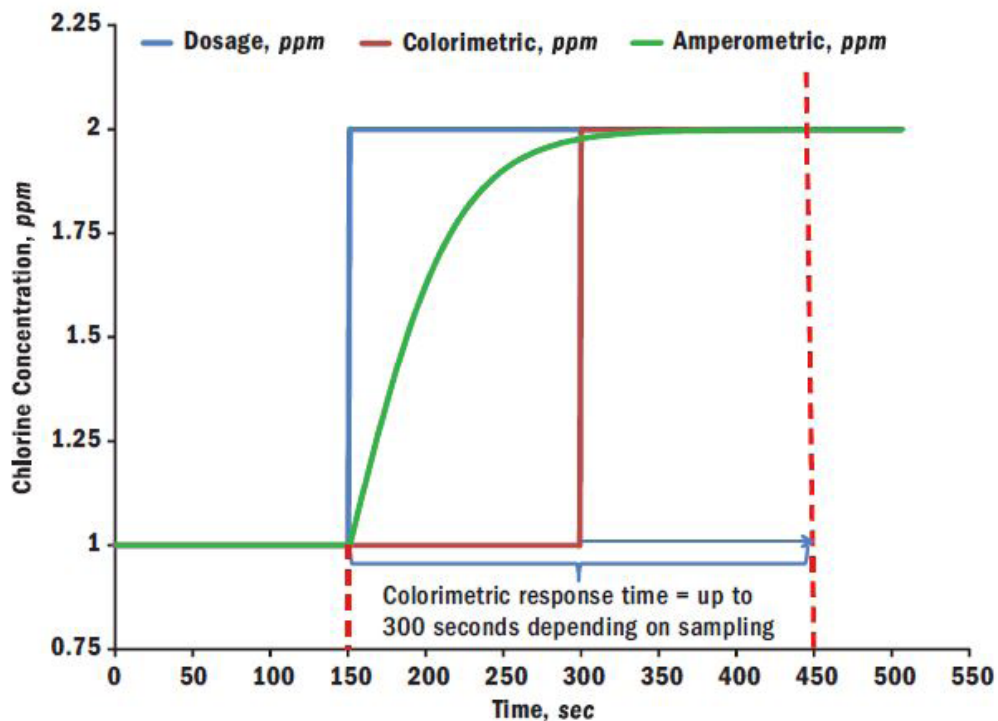


Figure 1. Graphical expression of calculated responses of the analyzers built on two different monitoring technologies to chlorine dosage change (based on the specifications provided in Table 3).

Drinking Water Disinfection Applications

What you really want to know

Applications within disinfection of drinking water can be arranged around regulatory reporting requirements and the desire to use the instrumentation for better disinfection process control. This may be final water discharge into the distribution system and monitoring in the system (booster stations), as well as the samples after mixing the chemicals in, various water disinfection loops, etc. From the application standpoint, it is important to understand the interferences affecting accuracy of the analysis and therefore suitability of corresponding analytical methods for the task. There have been a few recent studies^{4, 5} focused on the analysis of such suitability for the two major technologies discussed above.

When amperometric sensors are used for continuous online process measurements, several variables present limitations. Some of them are based on sample and sampling conditions and related to changing chlorine concentration, pH, temperature, sample flow, and pressure; and some are application-based involving ease of use, sensor fouling, chemical interferences and calibration requirements. In contrast, the DPD colorimetric method (Standard Method 4500G) accuracy is independent of sample temperature, pH, chlorine, and flow/pressure fluctuations.

Table 1 illustrates major differences between amperometric and colorimetric methods and Table 2 summarizes application characteristics.

Table 1. Summary of What Each Online Chlorine Analysis Method IS and IS NOT	
Amperometric Instrumentation (e.g. Hach CL10sc)	Colorimetric Instrumentation (e.g. Hach CL17sc)
<p style="text-align: center;"><u>IS</u></p> <ul style="list-style-type: none"> • Continuous measurement (fast response to changes in Cl₂ concentration) • Reagentless (no reagents in waste stream) 	<p style="text-align: center;"><u>IS</u></p> <ul style="list-style-type: none"> • Accurate without calibration • Independent of changes in sample pH, Cl₂ concentration, temperature, flow/pressure
<p style="text-align: center;"><u>IS NOT</u></p> <ul style="list-style-type: none"> • Accurate without calibration • Independent from changes in sample pH, Cl₂ concentration temperature, flow/pressure 	<p style="text-align: center;"><u>IS NOT</u></p> <ul style="list-style-type: none"> • Reagentless • Continuous

Table 2. Classification of Major Drinking Water Applications	
Application Type & Regulatory Expectations	Main Characteristics
<p><u>Stable Finished Water Applications:</u> Mainly Reportable, Sometimes Process Control</p>	<p>Very stable sample conditions (pH, Temp, Flow, Chlorine concentration): post-clearwell, final discharge, POE, distribution system</p>
<p><u>Quasi-Stable Applications:</u> Mainly Process Control, Sometimes Reportable</p>	<p>Relatively stable sample conditions: settled water, pre-clearwell</p>
<p><u>Dynamic Applications:</u> Mainly Process Control, Possibly Reportable</p>	<p>Constantly changing sample conditions: flash mixers, backwash loops, disinfection loops, etc.</p>

Selecting a Technology

The information from Tables 1 and 2 may help utility managers answer some basic questions:

- What is more important in my specific case - fast response or accuracy of the measurement?
- What gives me more problems – managing the waste stream or frequently calibrating the analyzer?
- What is my application? What is more important for me in this specific application – measurement accuracy or better process control?

Based on the accumulated knowledge and extensive hands-on experience, the Online Chlorine Monitoring Instrumentation Selection Guide (Table 3) is suggested in order to help the utilities to make the right choice. The analyzers presented in the guide are models of typical instruments built upon the two major technologies. The principles and approaches detailed in the guide can be used to select the right analyzer solution for your application based solely on comparison of the technologies and regardless of brand name of the instrumentation.



Table 3. Online Chlorine Monitoring Instrumentation Selection Guide



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Online Chlorine Monitoring Instrumentation Selection Guide	CL17sc Free or Total Chlorine Analyzers	CLF10sc Free, CLT10sc Total Chlorine Analyzers
		
Step 1. BASIC SPECIFICATIONS		
Does the technology range cover your expected values?		
Chlorine Concentration Range	0 - 10 mg/L	0 - 20 mg/L
Sample pH range (w/o buffering)	N/A	pH 4 - 9
Step 2. KEY DIFFERENTIATORS		
Which is preferred for your application?		
Sample pH, chlorine concentration, temp, flow and/or pressure changes	No impact on readings.	Readings may be impacted. Adjustment to calibration may be needed.
Calibration	Calibration not needed.	Yes. Frequency based upon the application.
Average Routine Maintenance	Tubing replacement every 6 months	Membrane and electrolyte replacement every 3-6 months
Reagents	Reagent replacement every 30 days	N/A
Reagent in Discharge?	Yes	No
Multi-parameter	Single parameter	Optional pH and Temperature
Step 3. INSTRUMENT SPECIFICATIONS		
Which nuances are most suitable for your application?		
Accuracy	± 5% or 0.04 mg/L whichever is greater	CLF10sc: ±3% at pH<7.2 (±0.2 pH unit), ±10% at a pH<8.5 (±0.5 pH unit) CLT10sc: ±10% at a pH<8.5 (±0.5 pH unit)
Limit of Detection (LOD)	30 ppb	30 ppb (or less)
Response Time	Batch analysis, 150 seconds	Continuous, CLF10sc T ₉₀ = 140s CLT10sc T ₉₀ = 100s
Technology	DPD Colorimetric Method	Amperometric Method
Regulatory Method	SM 4500 CLG, 40CFR 141.74, EPA Method 334.0	EPA Method 334.0
Automated Cleaning	No	Yes

Table 3. Online Chlorine Monitoring Instrumentation Selection Guide

Step 4. KEYS TO APPLICATION SUCCESS		
Can your utility meet these requirements?		
Appropriate Applications (Requirements)	<ul style="list-style-type: none"> • Must be able to replace reagents monthly • Must have a system to manage the waste stream (if required) 	<ul style="list-style-type: none"> • Must have uninterrupted sample flow • Must have uninterrupted power • Sample pH should be stable within ± 0.5 pH unit from the average value • Chlorine concentration should be stable within $\pm 20\%$ from the average value

Based on this guide, one can define the preferred method for online monitoring of drinking water disinfection. For example, complex accuracy specifications established for amperometric instruments clearly indicate a dependency on sample pH even in the case of available pH compensation (i.e. the utility personnel must be willing and able to adjust calibration of the amperometric analyzers as necessary and it may happen frequently depending on the sample conditions.)

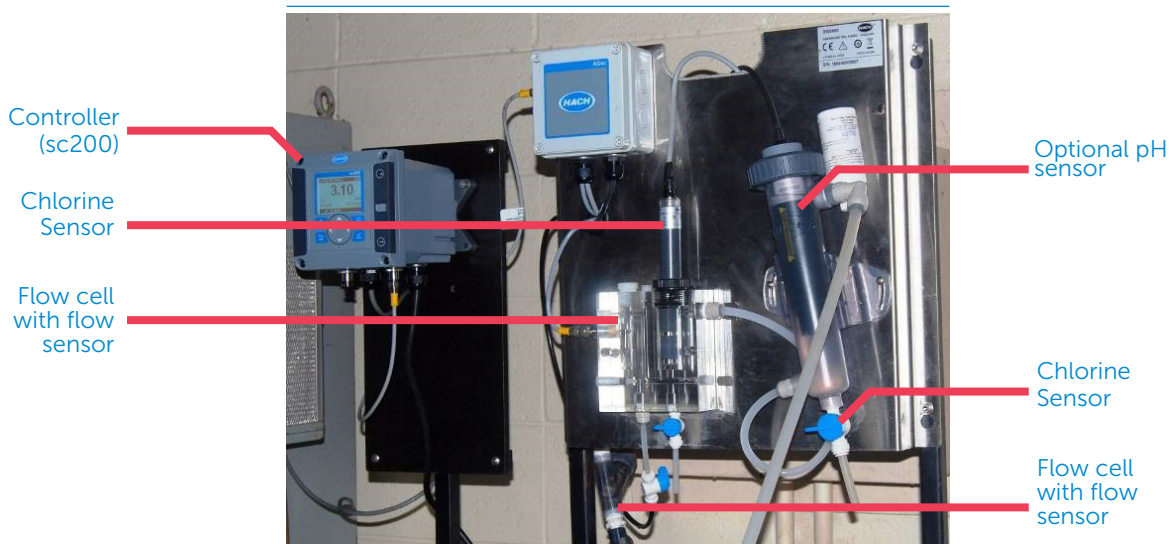
Case Study

To compare the two methods, a field study was conducted at a large surface water treatment facility in South Carolina. The facility measures total chlorine concentration in its final treated water with online colorimetric analyzers, but plant personnel wanted to minimize ongoing analysis costs by using a reagentless method. As shown in the photograph (Fig. 2), an amperometric analyzer equipped with an optional differential pH electrode was used for the demonstration study.

System Installation

The water sample containing free chlorine residual undergoes post-treatment pH adjustment and ammonia injection for chloramination before the product is discharged into the distribution system. Collecting samples from the location of the colorimetric analyzer allowed for about 15 min of mixing and reaction time after the last chemical addition. Mixing time varied with plant production flow. Flow to the analyzer also varied and may have presented challenges for the amperometric method because of its sensitivity to the sample pressure.

Figure 2. Installed CLT10sc with optional pH sensor and sample conditioning kit (pressure regulator and strainer)



Application Note: Amperometric vs. Colorimetric Comparison

Data Analysis

Signal outputs from the colorimetric and amperometric analyzers were connected to the plant's supervisory control and data acquisition (SCADA) system. Primary comparative analysis was performed based on recorded values of chlorine concentration measured by the instruments and collected by the SCADA system (Figure 3).

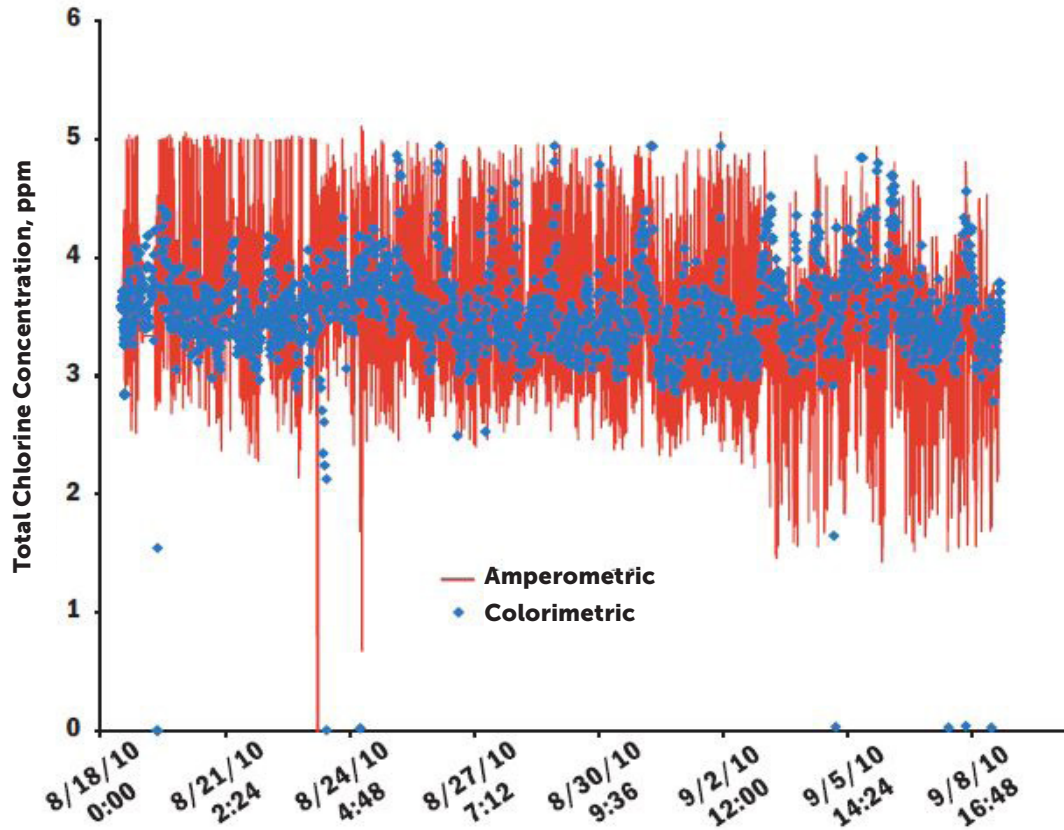


Figure 3. Total chlorine concentration trending from the SCADA. The results were considered satisfactory in terms of trending, but the amperometric analyzer showed more interference.

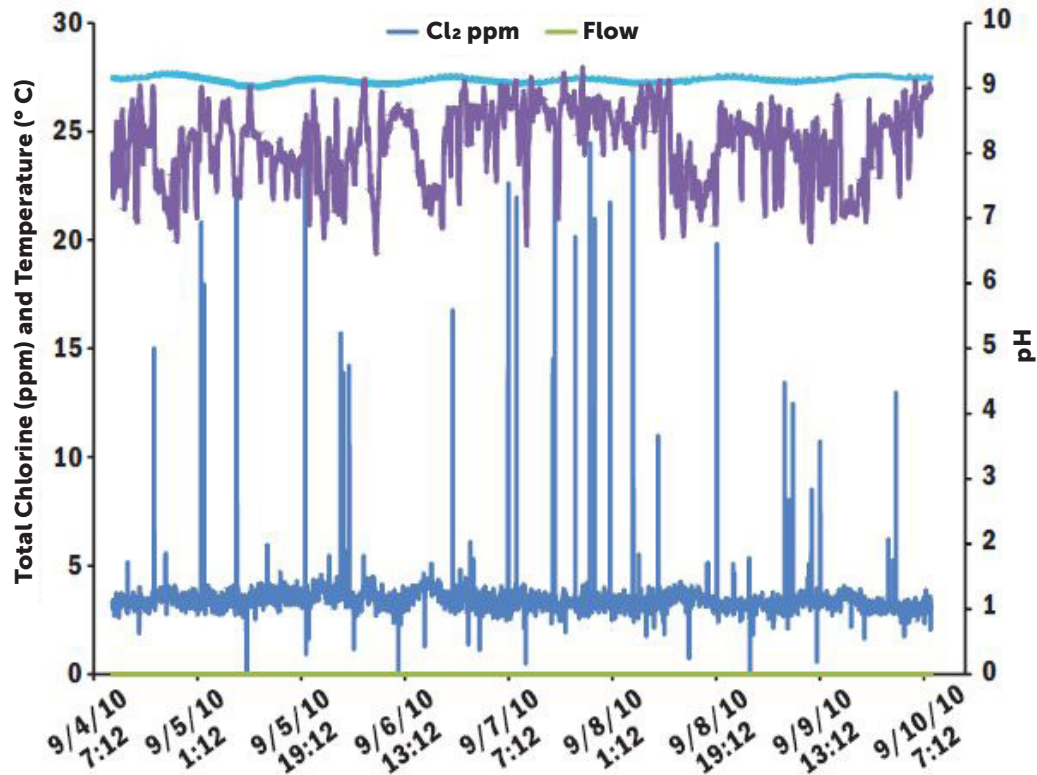


Figure 4. The data recorded by internal data logger: sample chlorine concentration, pH, temperature, flow

In order to understand the root cause of the interference, internal data logging was activated in the amperometric analyzer to collect more comprehensive data to analyze interferences. Figure 4 displays four of five parameters collected by the instrument in its internal data log. The optional pH sensor helps to determine and register critical fluctuations in the sample pH and temperature as well as allows for extended diagnostics and troubleshooting.

The continuous nature of the amperometric technology allowed a better understanding of the factors influencing the chlorine readings, unlike analyses based on batch and grab samples.

In this case study, the pH swings could have been interpreted as causing interference in the chlorine readings. Although facility personnel had never thought about pH being unstable in finished water, they were satisfied with some swings in chlorine readings displayed by the colorimetric analyzer, which could be negated by applying the signal averaging function. In addition, having the entire picture with all relevant parameters—including pH and chlorine concentration on the same time scale — triggered a thought process leading to the right conclusions.

Application Note: Amperometric vs. Colorimetric Comparison

Assumptions and Performance Validation

The main assumption was based on the fact that pH swings alone shouldn't have caused such noise in the chlorine readings because of viable internal compensation. Due to potentially insufficient chemical mixing after post-treatment (pH adjustment and ammonia addition) as indicated by unstable sample pH and relatively high temperature, total chlorine concentration was also unstable, possibly because of incomplete conversion of free chlorine into monochloramine⁶. This would provide a constantly changing mix of chlorine species at the sampling point resulting in unstable readings.

To validate performance, the instrument was placed at a remote pump station (about 12 miles downstream of the plant) and tested for several weeks. Figure 5 shows that the instrument registered no spikes in either sample pH or chlorine concentration at that location. The results represent good sample consistency and indicate an appropriate application for the amperometric technology.

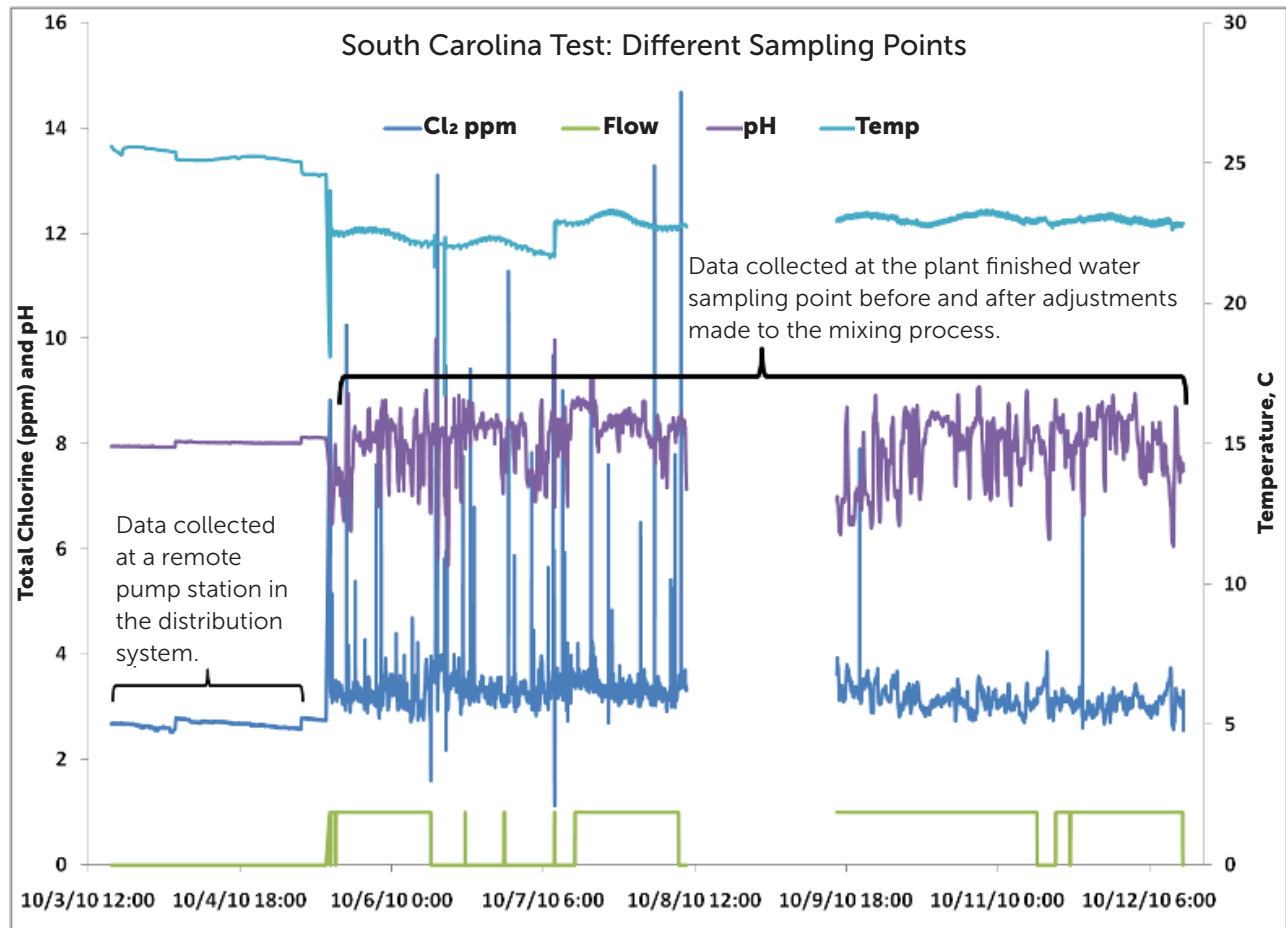


Figure 5. Data collected at different locations: in the distribution system and at the plant before and after the adjustments made to the chemicals mixing

When the analyzer was moved back to the original plant location, the spikes returned (Figure 5). After a few days, some improvements to the chemical mixing process resulted in less pronounced pH swings and much more stable chlorine readings, even with sometimes insufficient sample flow (Figure 5, last portion of the chart).

Results and Conclusion

- New amperometric total chlorine continuous analyzer helped to reveal issues with finished water and showed excellent performance in applications where the sample matrix was consistent from the pH and chlorine concentration standpoint. Based on the test results, the facility has acquired several CLT10sc analyzers to place at remote pump stations in the distribution system.
- The unexpected problem uncovered in this case study may be very common for many drinking water treatment facilities⁶ and can potentially affect quality of the water entering the distribution system.
- The continuous online chlorine analysis can provide an exceptional value for the customers in addition to the batch-type online chlorine analysis, let alone the grab sample laboratory analysis. The value is not only in better process control that continuous methods provide by definition, but also in ability to learn more about the treatment process when using more real-time data.
- Both laboratory and online methods based on batch analysis (i.e. DPD colorimetric) provide the customers with great value of accurate results that may be used for regulatory reporting, while an amperometric-based online technology can provide additional benefits when it is used properly.

References

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