Disinfection

Discovering the Unexpected in Disinfection Applications

An amperometric analyzer equipped with flow sensor and optional pH probe was installed side by side with a colorimetric process instrument in a finished drinking water disinfection study to compare the two technologies. BY VADIM B. MALKOV AND GARY R. VISSER

Operators at a large surface water treatment facility in South Carolina compared their DPD colorimetric method with a reagentless amperometric analyzer (shown here) equipped with an optional pH sensor.

Controller

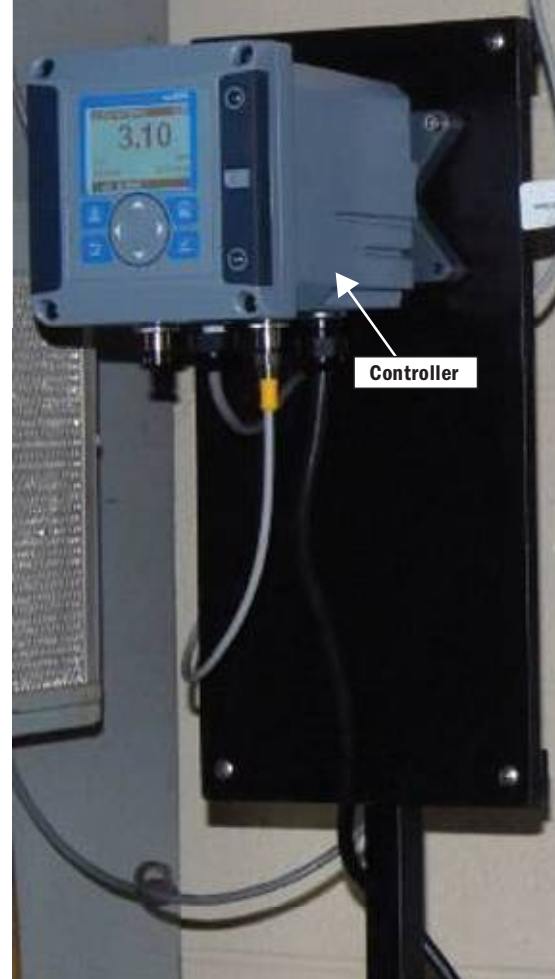CONTINUOUS ONLINE chlorine monitoring is used extensively at the point of distribution in water treatment to ensure disinfection and regulatory compliance. The Surface Water Treatment Rule suggests continuous monitoring of residual chlorine in distributed water for systems serving more than 3,300 people. The new Ground Water Rule has similar monitoring requirements.

The two most common methods for online chlorine analysis are colorimetric and amperometric detection. N,N-Diethyl-p-Phenylenediamine (DPD) colorimetric detection is a method based on DPD reaction with active halogens. The reaction is a standard approach for analyzing residual chlorine and other chlorine oxidants and is based on formation of colored products with DPD. Approved by the US Environmental Protection Agency (USEPA) for online analysis of chlorine residual, the DPD method is a widely used reference method.

Amperometry is an electrochemical technique that measures the change in current resulting from chemical reactions as a function of 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

Table 1. Amperometric and Colorimetric Analysis
Weigh the pros and cons of both chlorine analysis methods to decide which to use.

Amperometric	Colorimetric
Pros	**Pros**
■ Fast response to changes in Cl_2 concentration ■ Reagentless ■ No waste stream	■ Accuracy (no calibration needed) ■ Unattended operation for up to 30 days ■ Predictable and simple maintenance ■ Results independent of changes in sample pH, temperature, Cl_2 concentration, etc.
Cons	**Cons**
■ Greater interference from sample pH, temperature, pressure, Cl_2 concentration	■ Reagents and waste stream management

Optional pH Sensor

Chlorine Sensor

Flow Cell with Flow Sensor

Grab Sample Port

Sample Conditioning Kit

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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.

Electrodes are usually covered with a membrane, providing for better analysis selectivity. In addition, a small electrical voltage (potential) is applied across the electrodes. In the case of no membrane, the system is called bare-electrode amperometric; in the case of no applied voltage, the system is called galvanic. From a technical standpoint, many electrochemical methods fall under the amperometric measurement category.

There are pros and cons to each method (Table 1). Currently, no ideal method to quantify chlorine and chloramines in water exists. All common methods of chlorine analysis display some lack of specificity and aren't selective enough to be

interference free. However, most limitations associated with traditional DPD chemistry (e.g., calibration linearity, reagent stability, reaction product stability, etc.) have been addressed. New
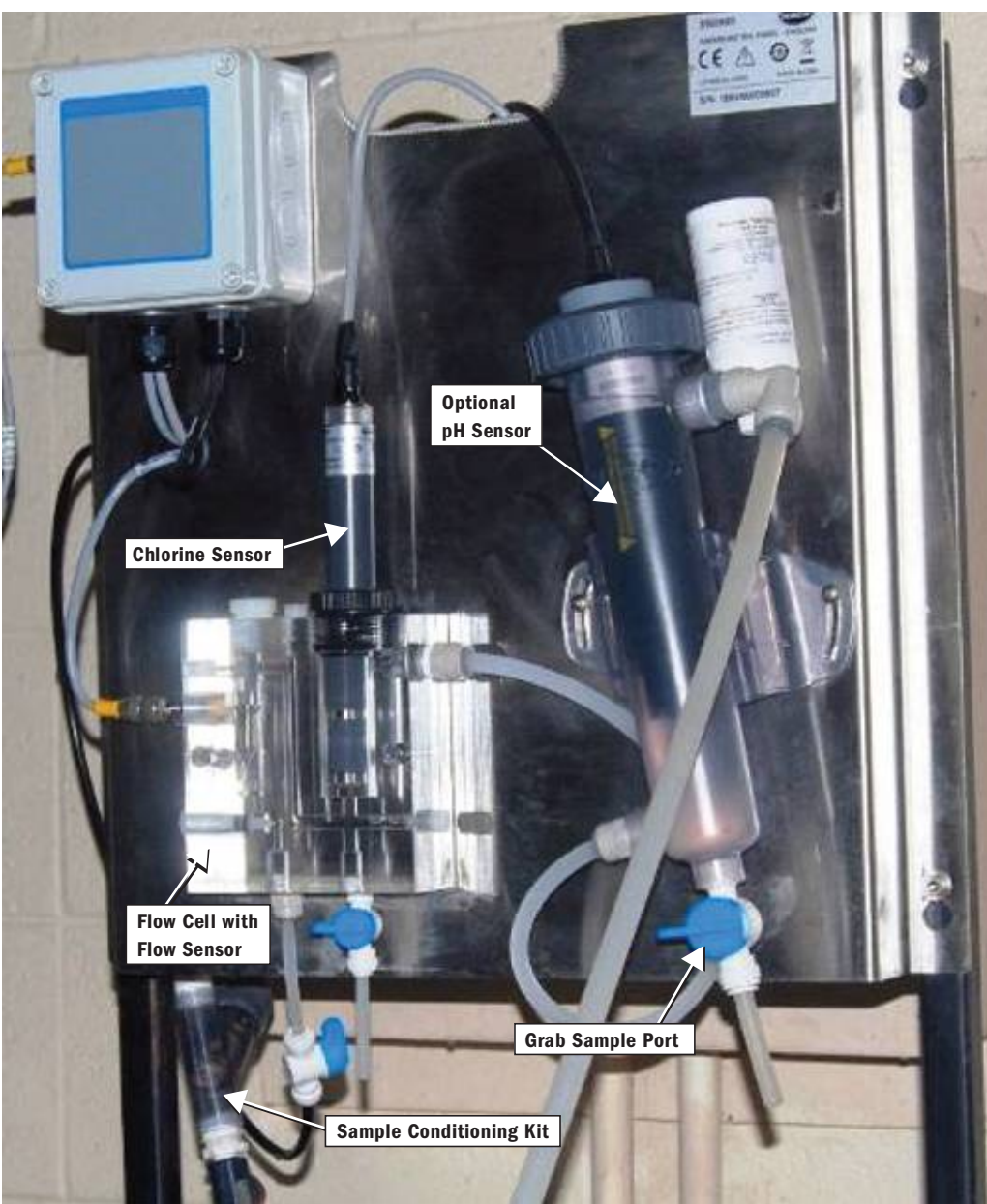
methods—including online amperometric chlorine determination—should be characterized with respect to interference. When the methods are well understood, especially in terms of application specifics, they can be used successfully for online chlorine monitoring and may provide additional customer benefits.

APPLICATIONS

For better disinfection process control, drinking water disinfection applications can be arranged around regulatory reporting requirements and internal concentration monitoring (Table 2), which may include final water discharge into the distribution system, booster stations, samples after mixing chemicals, and various water disinfection loops. From an application point of view, it's important to understand interferences that can affect analysis accuracy.

When amperometric sensors are used for continuous online process measurements, several variables present limitations, most notably those based on sampling environments with changing chlorine concentration, sample pH, temperature, flow, and pressure. Some are application-based interferences involving ease of use, sensor fouling, chemical interferences, and calibration frequency.

Table 2. Classification of Major Drinking Water Applications
Consider application type and regulatory expectations before selecting a chlorine analysis method.

Application Type and Regulatory Expectations	Main Characteristics
■ Stable finished water applications: reportable, sometimes process control ■ Quasi-stable applications: mainly process control, sometimes reportable ■ Dynamic applications: mainly process control, possibly reportable	■ Very stable sample conditions (pH, temperature, flow, Cl_2 concentration): final water discharge, distribution systems ■ Relatively stable sample conditions: pretreated water at a drinking water treatment plant ■ Constantly changing sample conditions: flash mixers, backwash loops, disinfection loops, etc.

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Table 3. Online Chlorine Monitoring Instrumentation Selection Guide
Consider key differentiators and specifications to help determine suitability.

	DPD Colometric Method	Amperometric Method
Basic Specifications		
Chlorine concentration range	0–5 mg/L	0–10 mg/L
Sample pH range (without buffering)	NA	pH 4–9
Key Differentiators		
Sample pH, chlorine concentration, temperature, flow and/or pressure changes	No impact on readings	Readings may be affected; adjustment to calibration may be needed
Calibration	Calibration not needed	Yes. Frequency based on the application
Routine maintenance	Tubing replacement every 6 months	Membrane and electrolyte replacement every 3–6 months
Reagents	Reagent replacement every 30 days	NA
Reagent waste stream	Yes	No
Regulatory method	SM 4500 CLG, 40CFR 141.74 or USEPA Method 334.0	Only USEPA Method 334.0
Multi-parameter	Single parameter	Optional pH and temperature
Instrument Specifications		
Accuracy	±5% or 0.035 mg/L, whichever is greater	Free: ±3% at pH < 7.2 (±0.2 pH unit), ±10% at a pH < 8.5 (±0.5 pH unit) Total: ±10% at a pH < 8.5 (±0.5 pH unit)
Limit of quantitation	35 ppb	90 ppb (or less)
Response time	Batch analysis, 150 seconds	Continuous, Free T_{90} = 140 seconds, Total T_{90} = 100 seconds
Automated cleaning	No	Yes
Keys to Application Success		
Appropriate applications (requirements)	■ Must be able to replace reagents monthly ■ Must have a system to manage the waste stream (if required)	■ 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 ±20% from the average value

In contrast, the USEPA-approved DPD colorimetric method is independent of sample temperature, pH, flow, and pressure fluctuations. Information provided in Table 3 can help plant personnel make the right choice when considering each method for chlorine analysis.

Choosing the correct analyzer for your application starts with these simple steps:

■ Base your initial decision on the instrument's specified chlorine concentration and sample pH measurement ranges. If the measurement range isn't definitive, proceed to the next step.

■ Consider each technology's key differentiators to determine which technology is preferred for your application.

■ Consider other specifications to understand nuances that can help you determine suitability.

■ Consider the keys to application success to ensure choosing the correct instrument for your application.

Based on this guide, 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 readings, even in the case of available pH compensation.

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Figure 1. Responses of Amperometric vs. Colorimetric Methods to Process Chlorine Concentration Change

The response time to a change in chlorine concentration varies with the method used.

Colorimetric response time = up to 300 seconds depending on sampling
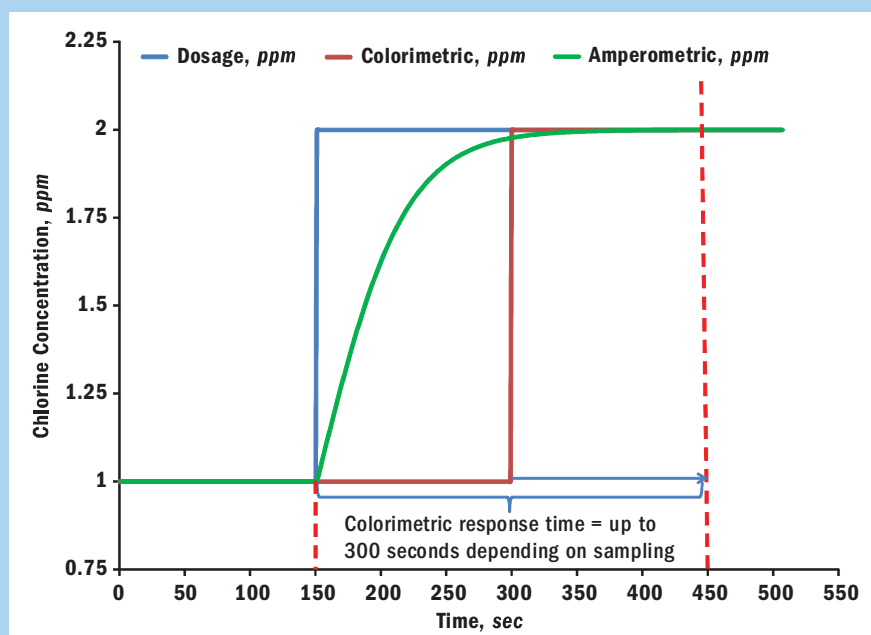
However, the most difficult aspect to understand may be the specified response time—expressed in seconds—to reach a certain level of chlorine concentration. In this case, assuming the concentration reached its final level at the time of the reading, it's 100 percent for a batch method or 90 percent (T_{90}) for continuous analysis. To explain the difference, calculations for the two methods were plotted against each other; Figure 1 presents the results.

For example, in an ideal situation, absolute accuracy of the response to changed chlorine concentration is reached in about the same time by the colorimetric analyzer as the amperometric analyzer. However, an amperometric instrument that's built on the continuous measurement principle starts providing the response instantaneously and can be better configured for tighter feed pump control.

In addition, if the sample was taken by the colorimetric analyzer before the dosage change occurred, the accurate concentration reading becomes available after only two cycles of measurement, which may be exacerbated by using a signal-averaging function. This function, which is useful for stable chlorine concentration conditions, helps to avoid false-positive responses caused by unexpected events—mostly air bubbles in the sample. However, when activated, the feature will extend the time for receiving accurate readings should the chlorine concentration change rapidly and substantially. In this case, the continuous amperometric analysis provides fast response and trending, even if the final accurate response time is comparable to the colorimetric method.

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 on pages 24 and 25, an amperometric analyzer equipped with an optional differential pH electrode was used for the demonstration study.

The water sample containing free chlorine residual undergoes posttreatment 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.

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 2).

The results were considered satisfactory in terms of trending, but the amperometric analyzer showed more interference. As shown in Figure 2, the colorimetric readings were about 3.5 (±0.5 ppm), and readings from the amperometric analyzer showed a span of more than ±1 ppm from the mean value. Because the interference was considered excessive, some standard troubleshooting actions—including sample flow stabilization with a sample conditioning kit—were undertaken to ensure analyzer performance. The idea was to remove all sources of unstable readings to understand the root cause.

Therefore, internal data logging was activated in the amperometric analyzer to collect more comprehensive data to analyze interferences. Data logged by the analyzer (Figure 3 on page 32) display four of five parameters collected by the

instrument in its internal data log. The amperometric analyzer was equipped with an optional pH sensor that also measured temperature. The chlorine amperometric sensor has an internal thermometer, which allows for sample temperature compensation, and the electrolyte where electrodes are immersed is highly buffered to provide internal pH compensation. Nevertheless, the optional pH sensor helps determine and register critical fluctuations in the sample pH and temperature and allows for extended diagnostics and troubleshooting.

This optional equipment allowed researchers to note that the sample pH was extremely unstable for the finished water application. 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. Therefore, in many cases, the DPD method's insensitivity to pH change is a positive trait; however, the intermittent nature and trait of DPD-based methods sometimes wouldn't allow problems associated with the treatment process to be visualized.

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.

The main assumption was that, because of potentially insufficient chemical mixing after posttreatment (pH adjustment and ammonia addition) indicated by unstable pH, total chlorine concentration was also unstable, possibly caused by incomplete conversion

Figure 2. South Carolina Total Chlorine Comparison, Amperometric vs. Colorimetric

The amperometric analyzer showed more interference, so troubleshooting actions were taken to ensure performance.
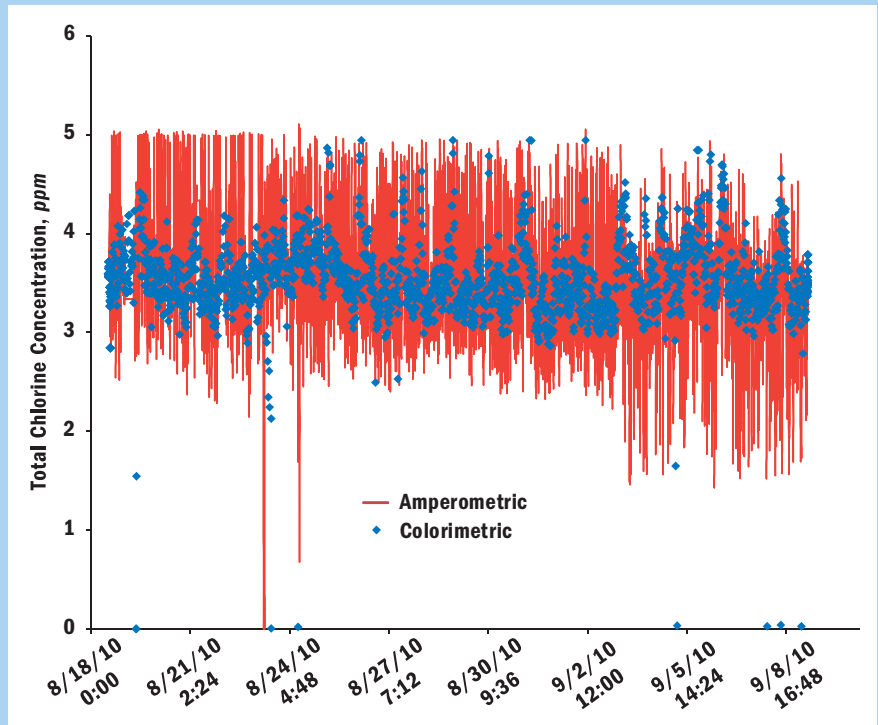
of free chlorine to monochloramine. This would cause a changing mix of chlorine species—free chlorine and monochloramine—at the sampling point. This assumption was based on the fact that pH swings alone shouldn't have caused such noise in the chlorine readings because of internal compensation. Relatively high sample temperature and literature data supported the hypothesis. To verify the assumption, the instrument was placed at a private residence with tap water provided by the facility.

After necessary conditioning (establishing equilibrium) in the new sample, responses to chlorine concentration and pH were found to be stable at that location. This test served as a verification of the analyzer's performance. Based on collected data, it was recommended that the analyzer be placed at a distribution

system sampling location that received water produced at the plant.

To validate performance, the instrument was placed at a remote pump station (about 12 mi downstream of the plant) and tested for several weeks. The location was a remote groundwater storage site with high-service pumping where total chlorine and pH are usually monitored but not adjusted. Because of the station's remote location, it was difficult to collect data, so only the last portion of data collected before the system was moved back to the plant is presented in Figure 4 on page 32, which 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.

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Figure 3. South Carolina Data Logged by Amperometric Analyzer

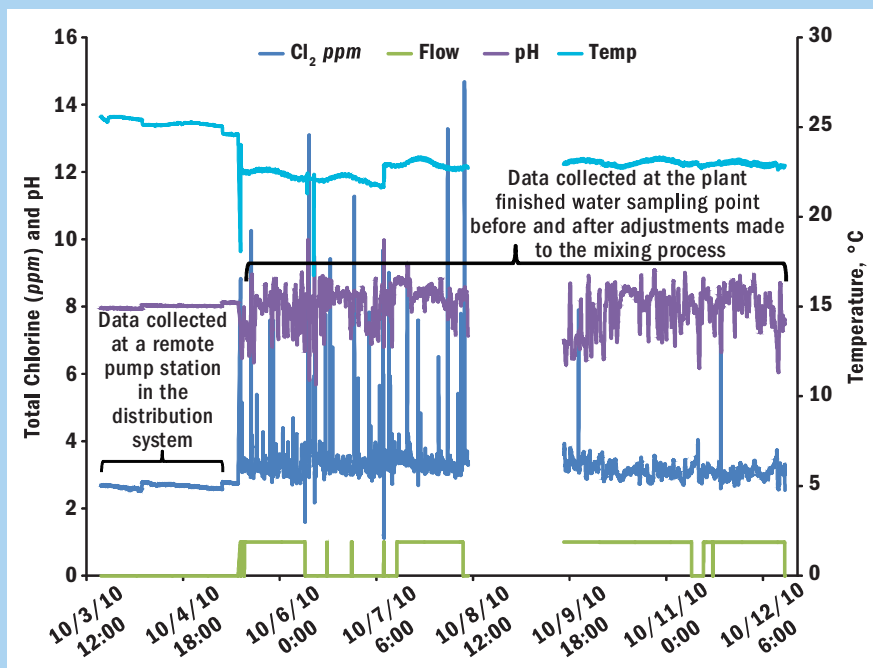Internal data logging was activated to help analyze interferences.
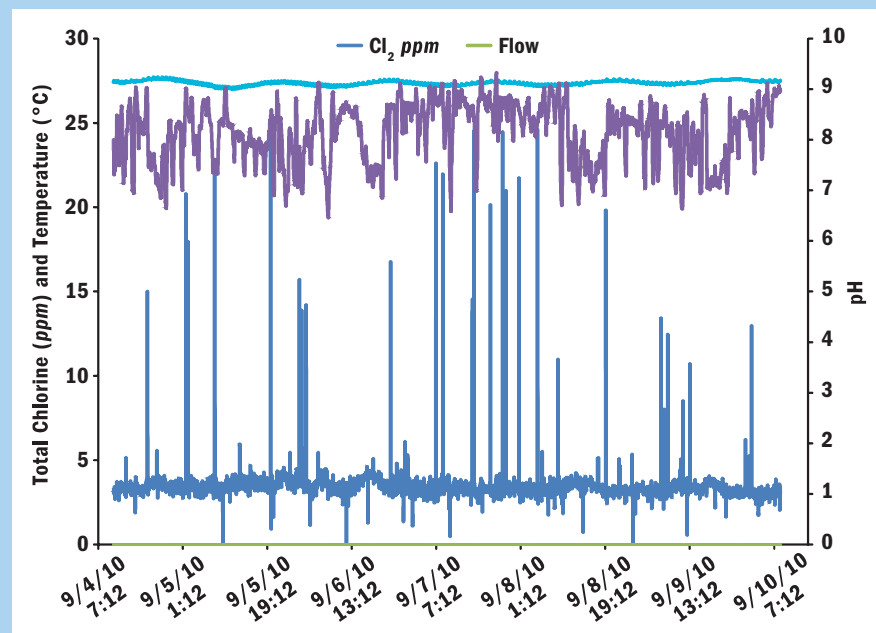
When the analyzer was moved back to the original plant location, the spikes returned (Figure 4), another indication of sample inconsistency. After a few days, some improvements to the chemical mixing process resulted in less pronounced pH swings and more stable chlorine readings, even with sometimes insufficient sample flow (Figure 4).

RESULTS

The demonstration test helped reveal problems with finished water, and the amperometric analyzer performed well in applications in which the sample was consistent regarding pH and chlorine concentration. The facility plans to place several amperometric analyzers at remote distribution system pump stations. The unexpected problem uncovered in this case study may be common at other drinking water treatment facilities, potentially affecting the quality of water entering the distribution system.

Figure 4. South Carolina Sampling Points

The results represent good sample consistency between the analyzer's locations.

Data collected at the plant finished water sampling point before and after adjustments made to the mixing process

Data collected at a remote pump station in the distribution system

RESOURCES

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