Comparison of On-line Chlorine Analysis Methods and Instrumentation Built on Amperometric and Colorimetric Technologies

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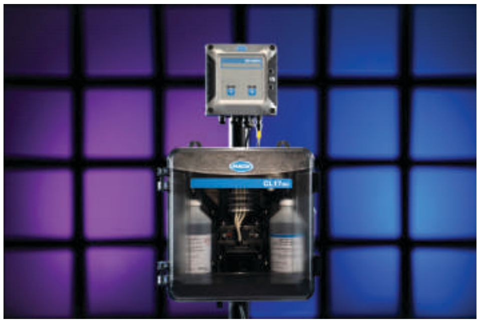
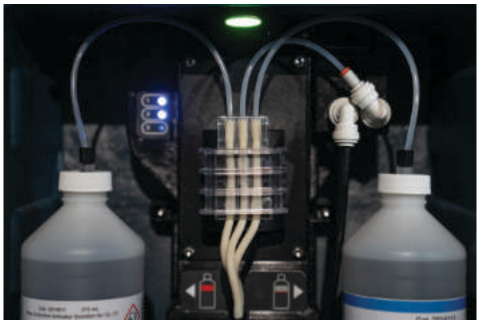
Preface

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 the USEPA Method 334.0, which added the amperometric chlorine monitoring to the list of approved methods, even though with significant stipulations. Also, additional Hach experience with the reagentless sensors allowed us to develop a practical guide to choosing the right technology for online chlorine monitoring. Therefore, some statements regarding amperometric measurements made in this study published in 2009, may sound outdated. For the most current information regarding chlorine monitoring technologies and instrumentation, visit http://www.hach.com/chlorine.





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

Historically, both amperometric and colorimetric technologies have been widely used for monitoring free and total chlorine residual concentrations within water treatment processes and distribution systems. However, the accuracy of the amperometric sensors and the necessity to routinely calibrate them against accepted methods brings into question their suitability for regulatory reporting, which has been debated within the industry. The goal of this study is to objectively evaluate the accuracy of the amperometric technology for measuring chlorine residual concentrations in practical applications relative to the reference colorimetric method.

Introduction

Continuous on-line chlorine monitoring is used extensively at the point of distribution in water and wastewater treatment to ensure disinfection and regulatory compliance. Membrane systems ranging from reverse osmosis to micro filtration make use of monitored chlorine residual to clean and preserve a variety of membrane filtration media. The Surface Water Treatment Rule[1] suggests continuous monitoring of residual chlorine on distributed water for systems serving more than 3,300 people. Similar monitoring is required in the new Ground Water Rule[2], to be in effect December, 2009.

The two most common methods for on-line chlorine analysis are amperometric and colorimetric 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 USEPA for online analysis of chlorine residual and therefore is widely used a reference method.

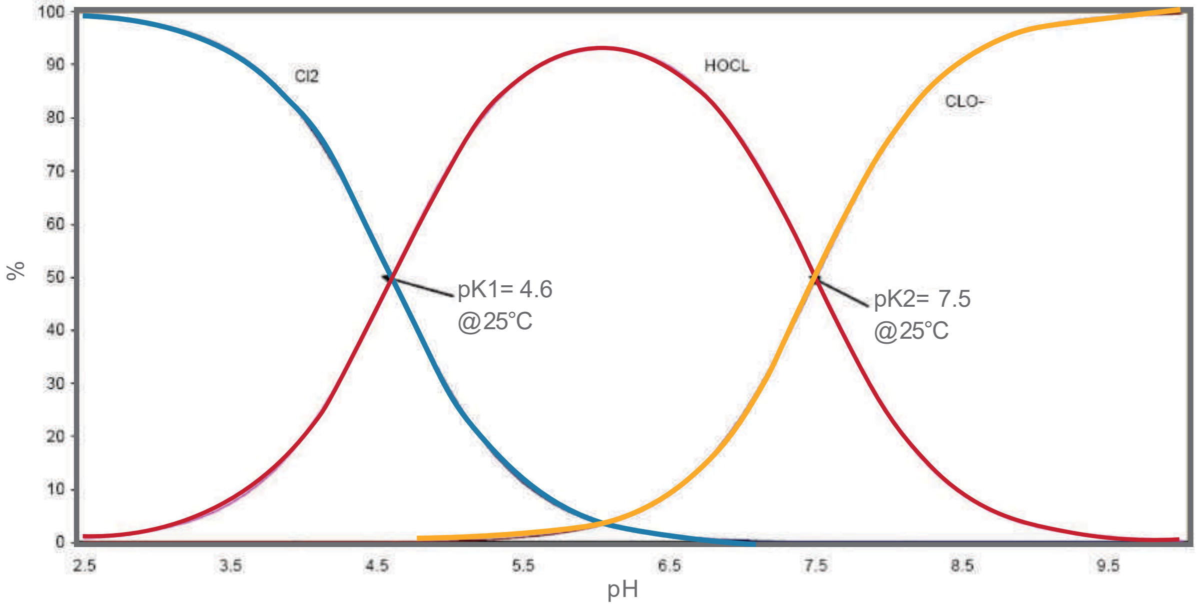
Amperometry is an electrochemical technique that measures the change in current resulting from chemical reactions as a function of the analyte concentration. A typical amperometric sensor consists of two dissimilar electrodes – an anode and a cathode (i.e. silver/platinum or copper/gold). Below is a general scheme of the oxidation-reduction reaction occurring in the amperometric systems:

Cathode (working electrode):
$HOCl + H^+ + 2\bar{e} \rightarrow Cl^- + H_2O$ (reduction of hypochlorous acid)

Anode (reference electrode):
$Cl^- + Me \rightarrow MeCl + \bar{e}$ (oxidation of anodic material)

The anode may be 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 electrodes are covered with a membrane, providing for better selectivity of the analysis. Additionally, a small electrical voltage (potential) is applied across the electrodes. In the case of no membrane, the system is called bare-electrode amperometric and 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, including bare-electrode and galvanic systems, which are sometimes wrongly referred to as polarographic.

Figure 1 - Free Chlorine Dissociation Curve



It is important to note that amperometric sensors do not use the same methodology as the laboratory amperometric titration apparatus and have to be calibrated against a reference measurement in order to display accurate results. Additionally, it should be considered that the DPD methodology and amperometric titration are standard analytical methods that provide adequate accuracy throughout the entire measurement range. Currently, no “ideal” method exists for quantifying chlorine and 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 addressed sufficiently through procedures and reagent formulation advanced by Hach since it introduced its first chlorine test kit based on the DPD chemistry in 1973.

Several interferences have been identified that can present limitations when amperometric sensors are used for continuous on-line process measurements. Some of the more noted variables providing interference are based on sample and sampling environments with changing chlorine concentration, pH, temperature, sample flow, and pressure; and some are application-based involving ease of use, sensor fouling, interferences and calibration. In contrast, the EPA-approved DPD colorimetric method (SM4500G) is independent of temperature, pH, and sample flow/pressure fluctuations.

There have been attempts to objectively evaluate performance of instrumentation representing these two technologies[3] and a recent study[4] conducted in Australia is worthy of a special notice. The authors[4] analyzed responses of several colorimetric and amperometric analyzers to changes introduced to the same sample. The comparison was conducted anonymously, the sample conditions were tightly controlled, and the tests included but not limited to the following parameters: response time, LOD/LOQ, short-term and long-term repeatability, pH and conductivity dependence. The study was conducted according to the guidelines of the ISO method for process analyzers evaluation (ISO 15839:2003). In the course of presenting the study results and discussion, the authors made several observations indicating that performance specifications of online amperometric analyzers are often overstated by the manufacturers. The main conclusion of the study read that “in general, colorimetric systems performed better compared to amperometric/polarographic systems.”[4]

Laboratory Study

In order to illustrate the differences in response to key water parameters, such as pH, temperature, and chlorine concentration, a laboratory evaluation of several representative amperometric sensors was conducted prior to and in parallel with the field study. The aforementioned parameters are those that are most likely to fluctuate in the real life. Therefore it seemed appropriate to evaluate the amperometric system’s response to these characteristics of water. The tested amperometric probes were examples of the most advanced and widely used membrane-based 3-electrode sensor built upon a Au/Ag-AgCl electrode system with a stainless steel counter electrode. The tested probes were designed for Free and Total chlorine residual measurements and five sensors of each type were evaluated side-by-side with two DPD colorimetric analyzers (Hach CL17). The chlorine concentration in the samples was also verified by a grab sample analysis (DPD colorimetric method).

pH test

The most prominent influence on chlorine concentration readings by amperometric analyzers is caused by the sample pH, therefore, the objective of the first experiments was to identify and quantify this influence. It is well known, that in free chlorine applications, a pH of 5.0 to 7.0 is the ideal operation range for an amperometric sensor due to the high percentage of hypochlorous acid (HOCl) (>80%) in the sample and the steepness of the Free Chlorine Dissociation Curve (Fig. 1) in this range. The pH can move within this range without significantly diminishing the accuracy of the instrument. However, the majority of drinking water facilities do not operate in this range.

A pH of 7.0 to 8.0 is the normal operating range for many drinking water facilities. The HOCl concentration is much lower versus the OCl- (hypochlorite ion) in this range. Amperometric free chlorine sensors directly measure only HOCl, not OCl- or Cl2, so any change in pH within this range may substantially affect the accuracy of the on-line unit (Table 1).

Table 1 - Example: DPD vs. amperometric in the case of no pH compensation (calculated based on the dissociation curve)

Free Chlorine = 1.0 ppm	Concentration Readings		
	pH = 7	pH = 7.5	pH = 8.0
DPD	1.0 ppm	1.0 ppm	1.0 ppm
Amperometric	1.0 ppm	~0.6 ppm	~0.2 ppm

At a pH 8.0 or greater (often the operating range for facilities experiencing problems with DBPs), the HOCl part of free chlorine concentration is very low (<20%), therefore accuracy of the amperometric probe suffers significantly with any slight changes in pH or chlorine concentration. When pH influence is mathematically compensated, the instrument reads more consistently, however, the possibility of drift always exists. In contrast, the DPD method is equally sensitive to all present species, plus, it is pH independent because the sample is buffered and the pH of the reaction is controlled.

There are technologies allowing for either external or internal control of pH influence by conversion of hypochlorite ions (ClO^-) into HOCl molecules either inside the sensor cap with highly buffered electrolyte (internal pH compensation) or in the flow cell by injecting an acidic buffer. It has been demonstrated in the field that pH compensation greatly improves the potential accuracy of on-line amperometric sensors.

The sensors selected for this study were most widely used membrane-covered 3-electrode amperometric systems. The Free Chlorine probes had reduced pH dependency as claimed by the manufacturer by employing the internal pH compensation. Along with the Free Chlorine sensors there were several Total chlorine sensors from the same manufacturer built upon the same technology. Both types of sensors underwent the same set of laboratory and field tests with constant comparison to the DPD colorimetric method.

The performance of the amperometric probes was considered to be acceptable if the results fell within 10% of the reference method results. The sensors were allowed to equilibrate in tap water for several days prior to the test. All signals generated by chlorine, temperature, and pH probes were collected at 30-sec intervals using OPC Data logger.

Figures 2 (a, b) and 3 demonstrate response of the tested Free and Total chlorine sensors respectively to varying sample pH and introduction of ammonia changing the analyte from combination of free chlorine species to monochloramine (Fig. 2b - the sample pH was adjusted accordingly). The results were then quantified and tabulated (Tables 2, 3) with statistical data representing accuracy of the online amperometric sensors against colorimetric analysis.

It was very interesting to observe the response of two Free Chlorine CL17 analyzers vs. the response of the free chlorine amperometric sensors to the introduction of ammonia into the sample containing free chlorine (Fig. 2b). As seen from this chart (Fig. 2b), the pH of the solution was adjusted to provide for stability of monochloramine formed after introduction of an ammonium salt solution. The amperometric sensors responded slightly to disturbance of the pH, however, did not see any difference in the analyte. At the same time, the colorimetric instruments responded promptly by changing the readings to almost zero that reflected concentration of free chlorine in the sample. Thus the amperometric sensors demonstrated no selectivity to chlorine species in the sample and interference from monochloramine may be considered 100%.

As seen from the charts in Figures 2, 3 and Tables 2, 3, the response of the sensors to changing pH of the sample (Fig. 2a) was found to be within ~20% per one pH unit. A positive result was that the readings returned to an acceptable level of accuracy once the pH was adjusted to the same level as at the sensor calibration.

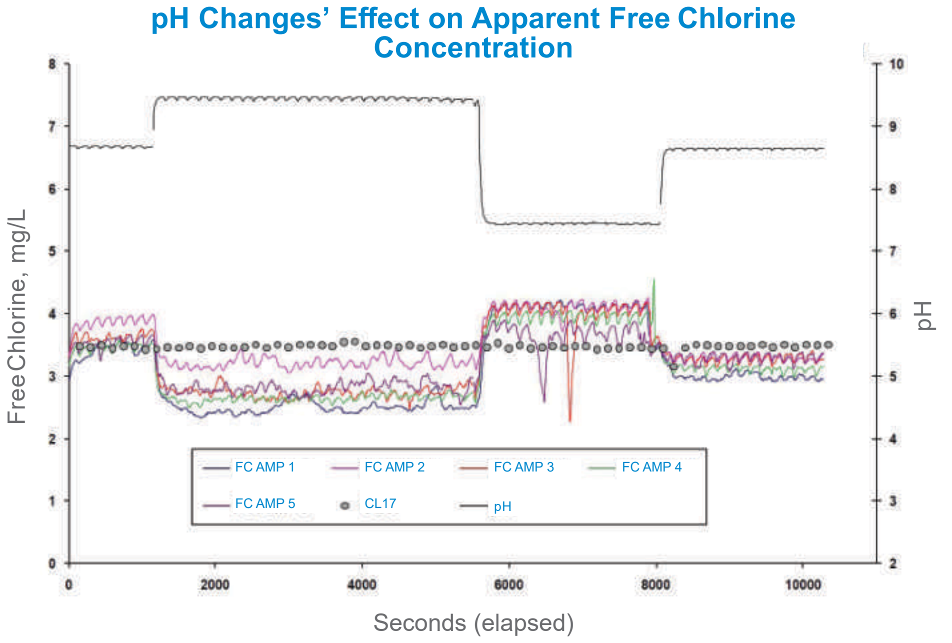


Figure 2a - Free Chlorine Amperometric Sensors' Response to the Sample pH Changes

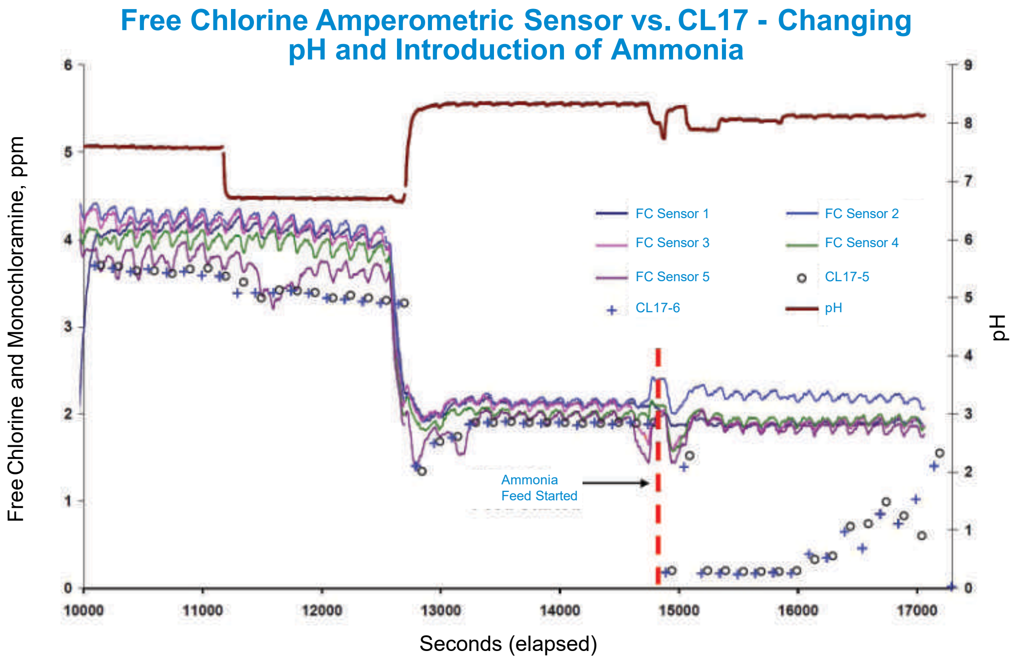


Figure 2b - Free Chlorine Sensor's Response to Monochloramine in the Sample

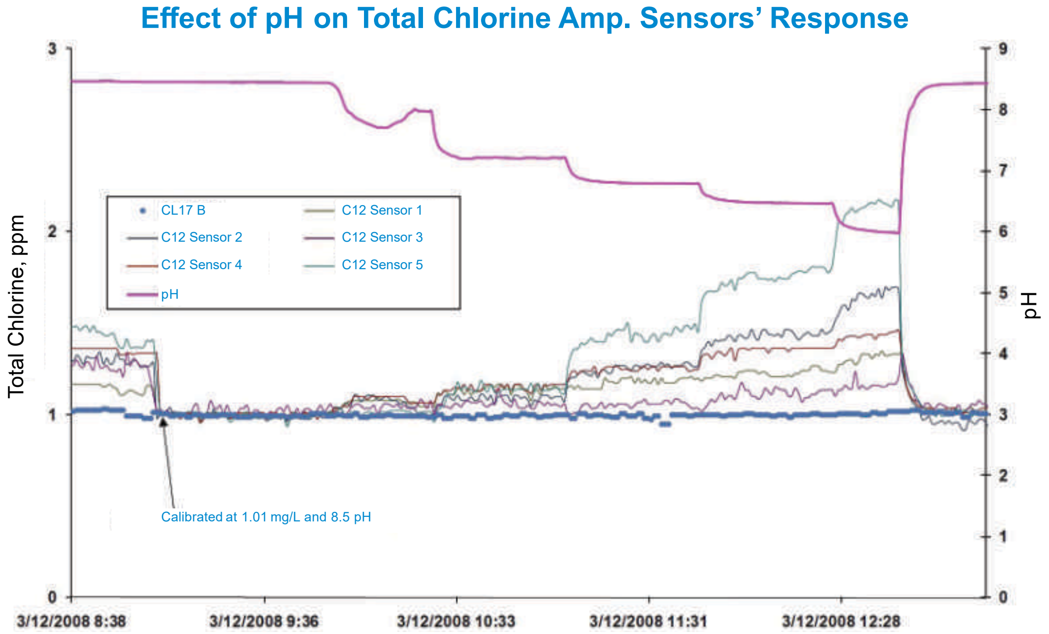


Figure 3 - Total Chlorine Amperometric Sensors' Response to the Sample pH Changes (Analyte = Monochloramine)

The major take away from the pH test was that the free chlorine sensors designed for lower pH dependency demonstrated approximately the same response to changing acidity of the sample as the total chlorine sensors. However, it is necessary to mention that the pH was adjusted to different values in the Free and Total chlorine experiments, which was justified by modeling the most probable applications for respective sensors.

Changing pH may sometimes be the reason for the change from free to total chlorine species and the tested amperometric sensors, both free and total, demonstrated no ability to distinguish between hypochlorous acid/hypochlorite and monochloramine.

Table 2 – pH dependency of the free chlorine amperometric sensor (five sensors tested). The highlighted numbers illustrate the accuracy results: green – acceptable, red – unacceptable.

Test Steps	**pH**		**Average for Amperometric Sensors**	
	Mean pH	**Std Dev**	**Mean, mg/L**	**Difference**
Step 1 (calibrated)	8.67	0.010	3.56	2.6%
Step 2	9.45	0.021	2.78	20%
Step 3	7.44	0.008	4.01	16%
Step 4 (same pH as calibrated)	8.64	0.009	3.20	7.8%

Table 3 – pH dependency of the total chlorine amperometric sensor (five sensors tested). The highlighted numbers illustrate the accuracy results: green – acceptable, red – unacceptable.

pH	**CL17, ppm**	**Average Amperometric, ppm**	**Average Amperometric, ppm**
8.44	0.99	1.00	1.1%
7.85	0.99	1.06	6.5%
7.21	0.99	1.12	13%
6.80	0.99	1.24	25%
6.48	1.00	1.38	39%
6.01	1.01	1.55	54%
8.42	1.00	1.01	0.36%

Temperature Test

Amperometric sensors are always sensitive to temperature changes. Three main areas affected by temperature are the membrane permeability rate, conductivity of the electrolyte, and the sample pH. The temperature compensation is always done by calculation; however, no mathematical algorithm can accurately reflect all changes in the water matrix or the response of chlorine to those changes.

The data presented in Figure 4 were obtained at Hach Company during testing of various amperometric systems and reported earlier[3]. The chart illustrates general temperature dependency of a membrane-based amperometric probe. The graph demonstrates absolute necessity of a well-developed temperature compensation algorithm based on multi-parameter equation taking into account all major factors listed above. An algorithm developed for one amperometric sensor will not work for other sensors due to potential differences in membrane material, geometry of the electrodes, placement of the thermistor, etc. The development of such algorithm and its implementation through firmware is a very challenging task and is not always conducted properly. Therefore, amperometric sensors with announced internal temperature compensation may not always perform very well in samples with varying temperature.

Any deficiency in temperature compensation may be exacerbated by unstable pH and the only solution available to end users is recalibration of the sensors in current conditions against a reference method. However, this option may not be appropriate in dynamic conditions of the analyzer application. Another example of dynamic conditions is the changing chlorine concentration and evaluation of this factor was undertaken in the next test.

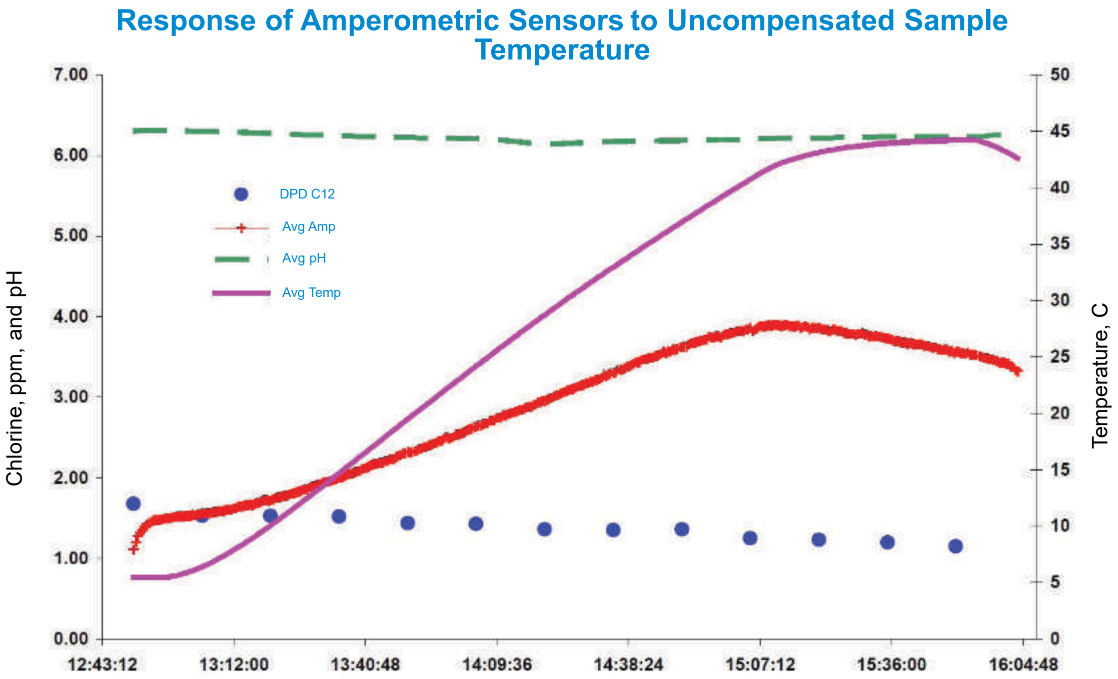


Figure 4 – Averaged Response of Five Free Chlorine Sensors to Changing Temperature of the Sample

Chlorine concentration test

A series of experiments was conducted to quantify response of the amperometric systems to varying chlorine concentration and dependency of sensor accuracy on the calibration set point. The data collected in Table, 4, Figures 5, and 6 below show the response of the Free and Total chlorine sensors to varying chlorine concentrations.

The test results collected in the table above along with some statistical material demonstrate very solid performance of the five tested sensors in the varying free chlorine concentration conditions. A graphical expression of the results is presented in Figure 5 below.

Table 4 – Response of Free Chlorine Amperometric Sensors to Chlorine Concentration (calibrated at 2.02 ppm vs. DPD reference method – CL17)

Average CL17	Amp 1		Amp 2		Amp 3		Amp 4		Amp 4		Average AMP	RSD %
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD		
4.61	4.57	0.05	4.65	0.07	4.78	0.07	4.68	0.08	4.71	0.07	4.68	1.52
3.67	3.62	0.57	3.64	0.57	3.66	0.55	3.61	0.59	3.67	0.60	3.64	-0.78
2.60	2.69	0.04	2.70	0.04	2.81	0.04	2.56	0.08	2.70	0.05	2.69	3.33
2.02	2.06	0.02	2.06	0.04	2.11	0.05	1.99	0.07	2.10	0.04	2.07	2.16
0.73	0.77	0.02	0.78	0.02	0.79	0.03	0.75	0.02	0.78	0.02	0.77	5.41

As seen from Table 4 and Figure 5, the Free Chlorine sensor demonstrated an accurate response to the chlorine concentration within approximately a 4 ppm range (± 2 ppm from the calibrated concentration). This accuracy is considered to be very good versus the results demonstrated by Total Chlorine sensors presented in Figure 6. Total chlorine test results presented in the chart in Figure 6 are very much self-explanatory – the accuracy was considered sufficient (± 10% of the reference) only within 2 ppm range (±1 ppm from the calibrated concentration). The sample pH was maintained at 8.6±0.05 to provide stability for created monochloramine; sample temperature was maintained at 11 ± 0.5ºC. Based on the conducted tests, the total chlorine amperometric sensor was concluded to produce accurate readings within ± 1 ppm or ~20% (whichever is greater) of the calibrated set point.

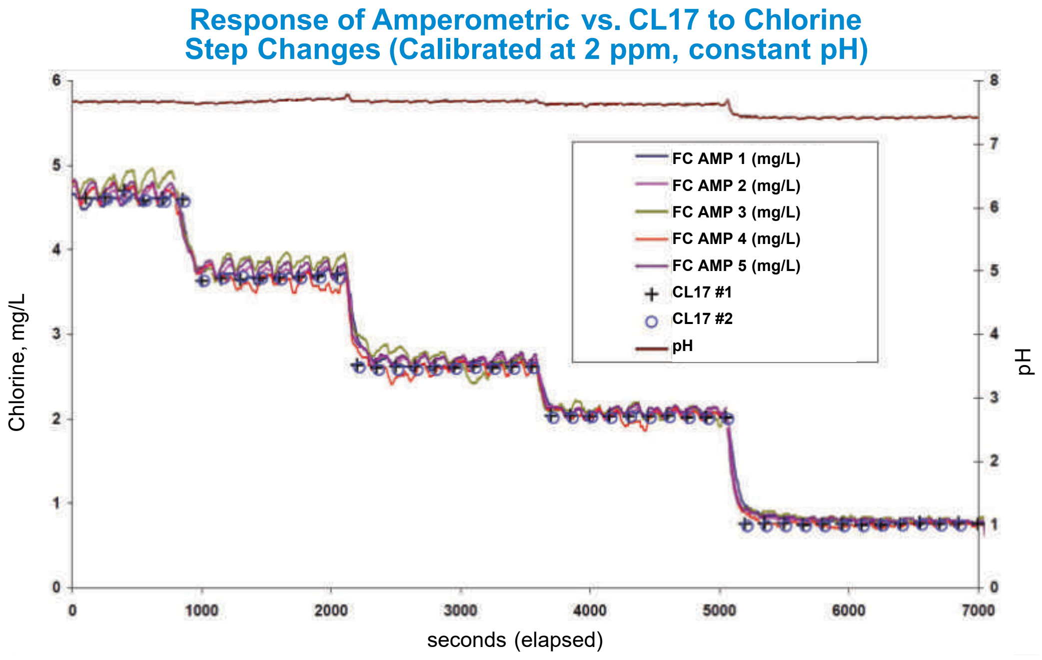
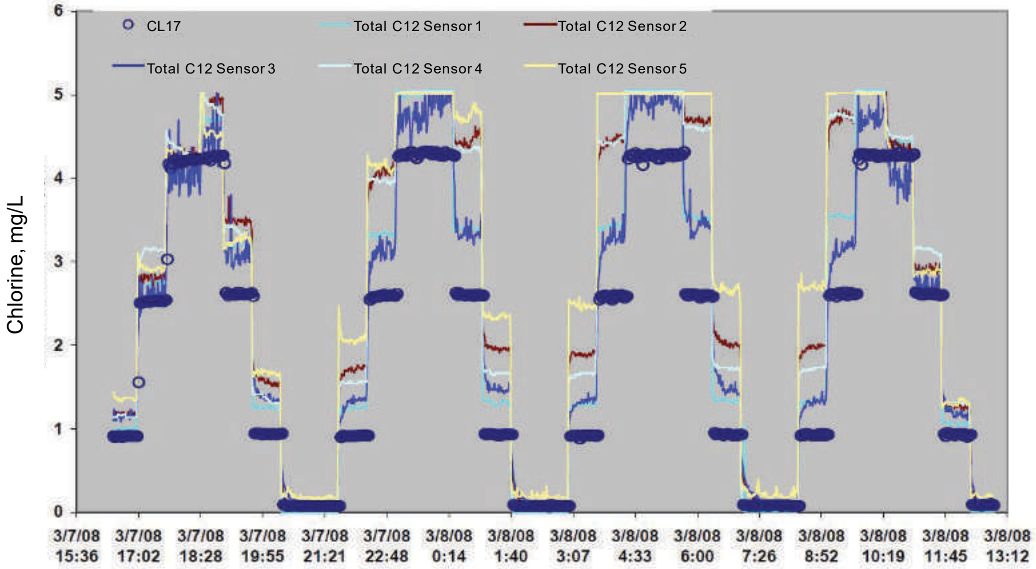


Figure 5 – Response of free chlorine amperometric sensors to changing chlorine concentration vs. CL17 (reference)



Response of Total Chlorine Amperometric Sensors to Chaning Chlorine Concentration

Figure 6 – Response of total chlorine amperometric sensors to changing chlorine concentration vs. CL17 (reference). Five sensors were calibrated at 3.6 ppm total chlorine immediately prior to testing.

In addition to the tested situations, any essential changes to the water sample matrix will require recalibration of the amperometric sensor. When the water characteristics are constantly changing, this will often require weekly and sometimes daily calibration of the instrument to retain overall accuracy. In contrast, DPD technology does not require calibration due to the established consistent proportionality between chlorine concentration and the light absorbance.

Other Considerations

Both chemical (DPD) and amperometric methods suffer from interferences due to presence of some specific compounds. For example, there is well known sensitivity of DPD analysis to the presence of certain iron and manganese species in water. Chemically, the amperometric method is free of this interference, however amperometric sensors are more prone to fouling with the presence of iron or manganese compounds in the sample (as well as in the presence of high turbidity), and this will result in increased cleaning and calibration frequency.

The simplest way to address pH dependency is external compensation where a buffer from an external reservoir is added to the sample to adjust and control the pH. Although this approach provides improved accuracy, the on-line instrumentation often loses its “reagentless” appeal due to additional ongoing expenses and a waste stream containing chemicals (buffer).

The waste stream generated by the DPD-based analyzers has been considered a major drawback of such systems. The chemicals present in the analyzer discharge are perceived to be harmful to the environment. The authors of this study conducted a comprehensive analysis of the discharge generated by the Hach CL17 analyzer – by far the most popular on-line analytical system. Due to the absence of federal regulations (RCRA) for this kind of discharge, the analyses were performed in accordance with the EPA methods[5] to identify compounds regulated for Drinking Water[6] and the results were compared with Maximum Contamination Levels (MCL) listed for those chemicals. In order to identify chemicals produced by the reagents and analyzer, additional analyses of the sample matrix and pure reagents were also conducted. Obviously, comparison to drinking water standards is a very stringent test to apply to a discharge sample that is considered wastewater. The results of the analyses are presented in Table 5.

The experiment was conducted on the most common setup of the CL17 analyzer involving a stand pipe providing steady sample flow/ pressure to the analyzer. Two regular analyzers – one with Free and another with Total Chlorine reagent sets – were used in the study. The discharge samples were collected in glass containers and analyzed by an independent certified laboratory immediately after the grab samples were taken.

Table 5. Summary of Analysis of CL17 discharge (Deionized water)

Sample ID	Analyte	Method	Result	Units	MDL[a]	MCL (DW)[6]	CAS
TC	Bis(2-ethylhexyl) phthalate [DEHP]	M8270C GC/MS	12	µg/L	4	6	117-81-7
TC	Chloroform	M8260B GC/MS	15.7	µg/L	0.5	80	67-66-3
TC	Aluminum, total	M200.8 ICP-MS	5	µg/L	1	50-200[b]	7429-90-5
TC	Boron (dissolved)	EPA-6010B	0.043	mg/L	0.006	1[c]	7439-92-1
TC	Potassium, total	M200.7 ICP	3.2	mg/L	0.3	NA	7440-09-7
TC	Sodium, total	M200.7 ICP	13.1	mg/L	0.3	20[d]	7440-23-5
TC	Zinc, total	M200.8 ICP-MS	3	µg/L	2	5000[b]	7440-66-6
TC	Chloroform	EPA8260B GC/MS	5.1	µg/L	0.5	80	67-66-3
TC	Al (dissolved)	EPA6010B ICP	20	µg/L	10	50-200[b]	7429-90-5
TC	Zn (dissolved)	EPA6010B ICP	5	µg/L	2	5000[b]	7440-66-6
TC	Chloroform	EPA8260B GC/MS	13.9	µg/L	0.5	80	67-66-3
TC	Zn (dissolved)	EPA6010B ICP	4	µg/L	2	5000[b]	7440-66-6

[a] Method Detection Limit; [b] Secondary DW Regulations; [c] Lifetime level (Health Advisory); [d] DW advisory, health-based value

As seen from Table 5, there was only one regulated compound exceeding the limits for DW samples – DEHP, which is a common plasticizer leaching out of various polymeric materials (pipes, tubing, etc.). It caused a concern when this compound was discovered in the discharge of only a CL17 equipped with Total Chlorine reagents, but not with the Free Chlorine set. After additional testing, the source of DEHP in the CL17 discharge was identified to be a plastic drain tube, which is an optional accessory and is not supplied as a part of the analyzer.

A very important point is that the analysis of pure reagents (both for Free and Total chlorine) revealed no DEHP presence. Obviously, DPD was found in the discharge, however, this chemical is not reportable according to the current EPA methods and regulations; therefore, it did not even appear on the official laboratory reports. The analyses were conducted by two different laboratories with different equipment providing slightly different MDL (Table 5).

Thus, it is concluded that the Hach CL17 produces no regulated compound at concentrations exceeding the federal drinking water regulations.

Field Testing

Based upon all accumulated knowledge about the amperometric sensor performance, several field sites were identified to conduct the field testing. The sites were located in several US regions including the South (Texas), Southeast (Florida), and West (Colorado). The objective of the field tests was to place the sensors in the applications where water conditions can be described as static or dynamic, based on the key sample characteristics such as chlorine concentration, pH, and temperature. The applications with constantly changing sample conditions were considered dynamic and those with relatively stable conditions – static. Another major field test condition was to evaluate both free chlorine and total chlorine (monochloramine) applications. The tested amperometric sensors represented the most common 3-electrode system described above.

One more requirement for the field studies was the availability of a DPD on-line analyzer at the test site, and existence of valid and active verification and maintenance protocols established by the utilities. All facilities where the study was conducted performed periodic maintenance of the on-line analyzers and had verification procedures involving a daily, grab sample analysis in place. The accuracy criterion applied throughout the field test was the same as for the laboratory testing – being within ±10% of the readings provided by the reference method. This criterion was adopted from discussions among the members of the AWWA Online Chlorine Standard Committee representing all aspects of the water treatment process. This team unanimously agreed on applying the above-mentioned accuracy criterion to verify performance of on-line chlorine instrumentation.

Case Study 1 – City of Westminster, CO

The first case study was conducted at two facilities in Westminster, CO – the tested applications represented both relatively stable and highly dynamic situations. The sensors tested at these facilities were amperometric units randomly selected from the five Free and five Total chlorine instruments previously tested in the laboratory. All sensors were installed according to the manufacturer recommendations.

Semper Water Treatment Plant – Conventional Filtration

The first test plant's raw water source is a high quality, snow-melt-supplied surface reservoir with TOCs below 2 mg/l and turbidities ranging from 2 to 20 NTU. The 48 MGD conventional treatment plant employs coagulation with ferric chloride, flocculation/sedimentation, sand and anthracite dual media filtration; hardness and pH control are achieved using calcium hydroxide (lime). Sodium hypochlorite (12% bleach), provides primary disinfection.

As seen from the general schematic presented in Figure 7, the raw lake water containing the mixed coagulant, bleach, and lime from the flash mixer travels several hundred feet through a pipeline where it is thoroughly mixed and reacted to provide early stage flocculation and depletion of the initial chlorine demand. After leaving a splitter box the water is diverted into 2 sedimentation basin, influent chambers. Here the water is continuously sampled and monitored for pH and free, breakpoint, chlorine residual via a Hach CL17 colorimetric (DPD) analyzer.

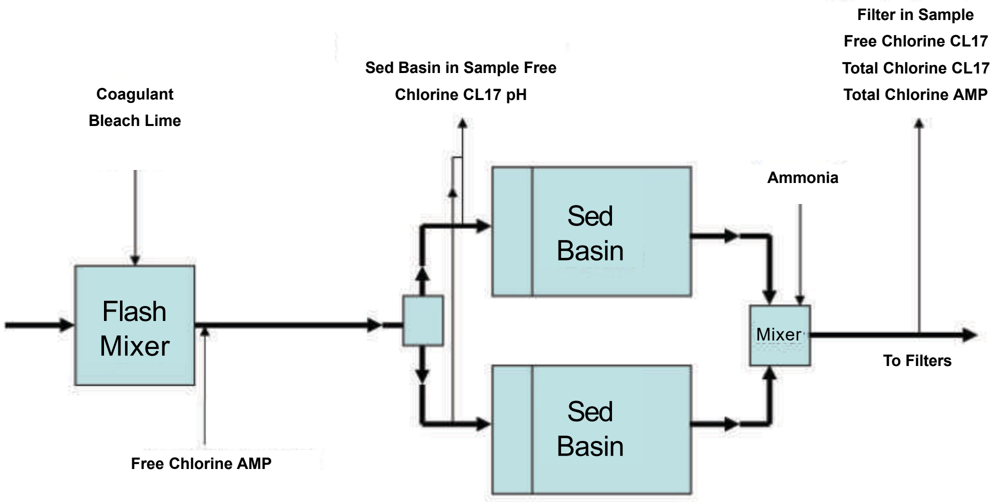


Figure 7 – General schematic of the conventional Semper WTP where the testing occurred

Proportional flow pacing, combined with PID controlled metering of the bleach dosage, as determined by the CL17 measured residual, is used to provide a consistent, free chlorine residual, typically 2.5 mg/l. This application is well suited to testing by free chlorine amperometric membrane analysis. The chemical additions (and subsequent floc formation) in the water, prior to sedimentation, provides an opportunity to test the ability of the membrane analyzer to withstand a challenging analytical environment.

Immediately after passing through the sedimentation basins (Fig. 7) the settled water undergoes addition of ammonia hydroxide to convert the remaining free chlorine into a more stable monochloramine residual. This conversion process is almost instantaneous. Proportional flow pacing, and a calculation based on the level of both the total and free chlorine residuals is used to continually meter a varying, optimized dosage of ammonia using a 29% solution of ammonium hydroxide. Both the free and total residuals are measured using separate free and total chlorine Hach CL17 analyzers. Total chlorine at this point in the treatment process (just prior to final filtration) is maintained at approximately 2 mg/l as monochloramine. This application is well suited to parallel testing by amperometric membrane chlorine analysis for total chlorine. The time-tested Hach CL17 would provide an ideal verification of the amperometric membrane analyzer's performance by direct comparison of their almost simultaneous measurements for total chlorine. The result of the above comparative analyses is presented in Figure 8 below.

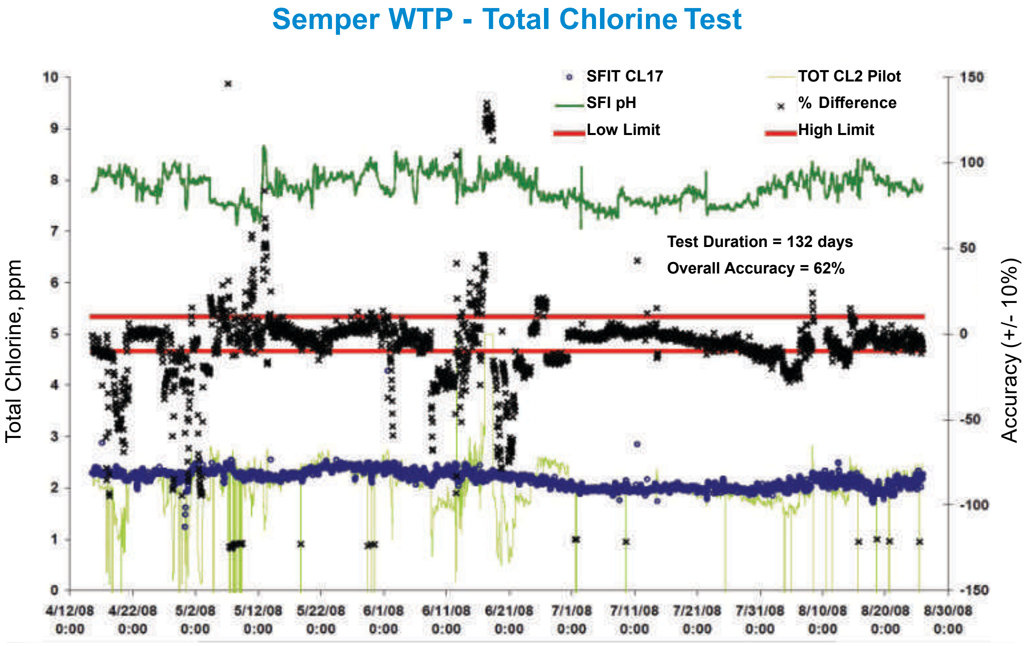


Figure 8 – The Entire Test Conducted at Semper WTP, Total Chlorine Sensor, Static Application

As seen from Figure 8, the sample pH was ~8±0.5 unit and the chlorine concentration was stable as described above thus confirming the static nature fo this application. It must be mentioned that the readings from both analyzers were recorded by SCADA system with 1-min interval and only selected data points (every 10 minutes) are presented in the chart (Fig. 8). The overall accuracy of the amperometric sensor during the longer-than-four-month test was 62% of the reference method in most cases due to unstable readings of the sensor (Fig. 8). Most of the time it happened due to insufficient or unstable sample flow through the amperometric cell, especially in the beginning of the test (Fig. 8). After the flow was increased and calibration/cleaning procedures established the situation improved. The longest period of acceptable performance without calibration was found to be one month. To the surprise of plant personnel, the sensor continued to demonstrate acceptable readings even when heavily fouled with iron and manganese compounds. The key to success was identified to be timely calibrations and daily visual inspection of the sensor along with adequate maintenance involving membrane cap cleanup and electrolyte change.

North West Water Treatment Plant – Membrane Filtration

The second, 12MGD, test plant, uses the same source water but employs micro membrane rather than conventional filtration. The pretreatment is similar to the first plant with one exception. Because no chlorine is fed across the sedimentation basins and the membranes are able to filter raw water without any pretreatment if desired (however almost never used), CT requirements for chlorine residual are met by maintaining a breakpoint, free chlorine residual through the clear well. Ammonia addition for conversion to a monochloramine residual takes place in the clear well effluent. The plant's general schematic is presented in Figure 9 below.

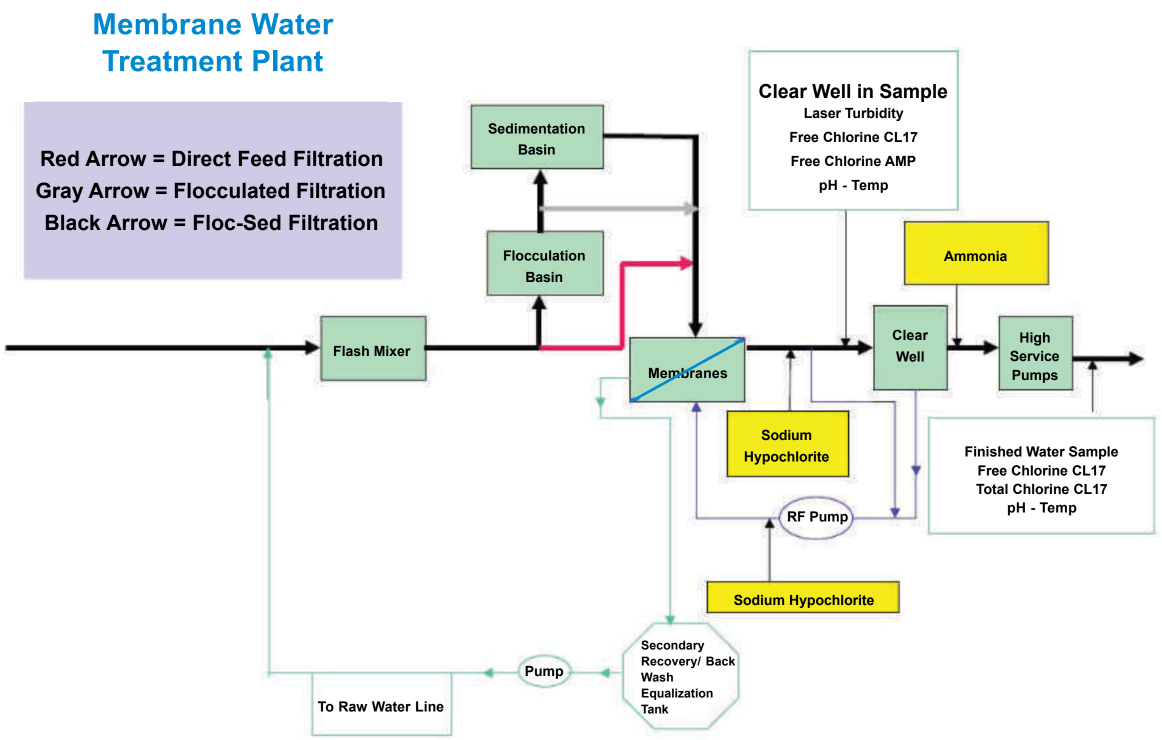


Figure 9 – General schematic of the treatment process at the Membrane filtration WTP

The baseline chlorine residual for disinfection is provided by a metering pump which continually pumps, and maintains, approximately 2 to 2.5 mg/l of free chlorine into the clear well influent pipeline downstream from the membrane effluent. Free chlorine in the form of a 10% bleach solution is also injected into the membranes as part of the reverse flush process to remove organic fowling from the membranes on an ongoing basis. A reverse flush (RF) occurs on each one of the 8 membrane racks after every 20 to 30 thousand gallon filtration run. The RF water is recycled back to the head of the plant and combined with the plant influent raw water. After an RF is complete the rack goes back into forward flow (filtration mode) and any chlorinated solution remaining in the membrane modules is micro filtered into the clear well influent flow. This process provides a second portion to the chlorine residual; it is fairly consistent and occurs at regular intervals. This additional free chlorine residual can be measured as a short term spike above the "baseline" chlorine residual in the clear well influent piping. A free chlorine CL17 analyzer downstream of both processes is used to monitor both processes, and verifies proper metering of both the reverse filtration chlorine dosage for organic removal, and the clear well influent, baseline, disinfection residual.

This process is fairly well suited to parallel testing by amperometric membrane chlorine analysis for free chlorine. The measuring challenge here is different than the previously discussed total chlorine analyzer. In this instance there are no contaminants to interfere with the instrument's operation (chemical floc and turbidity). The test water in this case is post micro membrane filtration and has a turbidity that averages below 0.02 NTU. The challenge in this instance is presented by the continually spiking (unstable) chlorine residual above the baseline dosage from the RF process. In order to monitor this process the chlorine analyzer had to be able to measure rapidly changing (both up and down) chlorine residuals. Using direct comparison, the Hach free chlorine CL17 provides only a fair verification of the amperometric membrane analyzer's performance. The CL17 is limited to one analysis every 2.5 minutes and the membrane analyzer measures virtually instantaneously and continuously. The membrane analyzer shows a lot more detail in the residual movement up and down (so long as it is properly calibrated). Results from this comparative performance testing are presented in Figure 10.

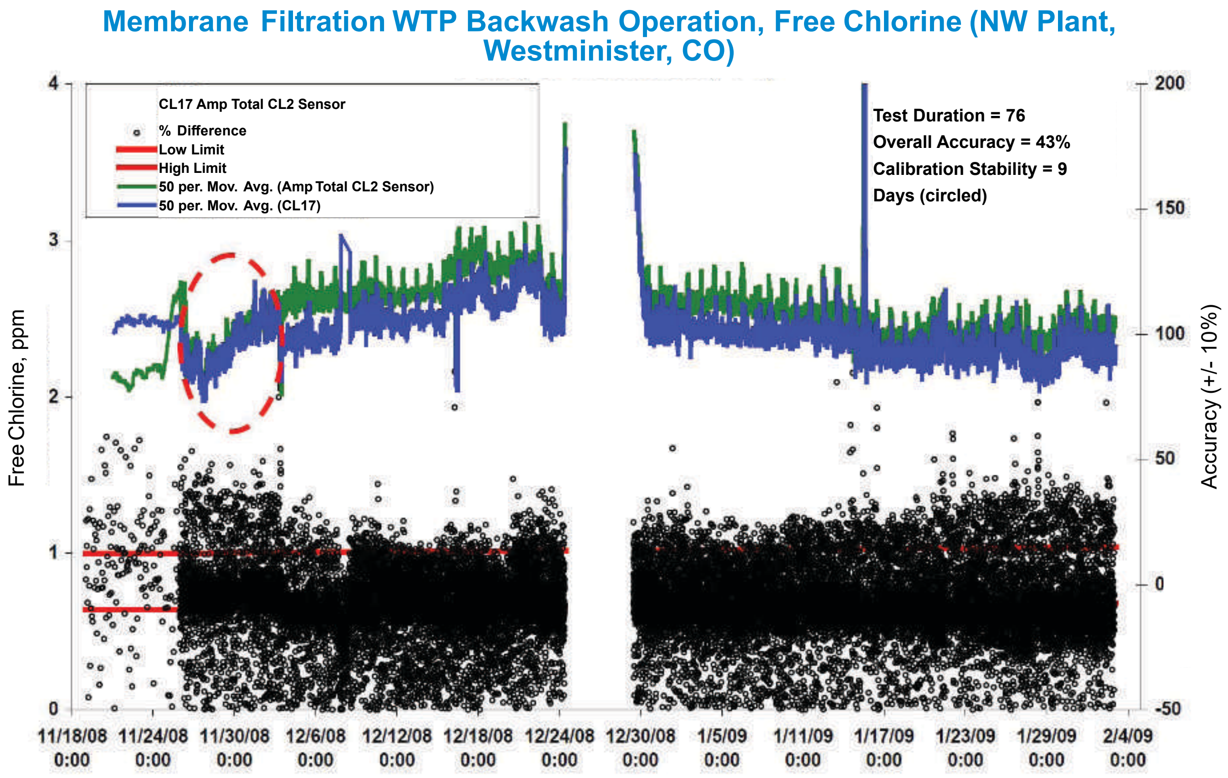


Figure 10 – Reverse Flush (Dynamic Application) at a Membrane Filtration Plant (Free Chlorine Residual, Total Chlorine Sensor)

As seen from Figure 10, the amperometric system and DPD analyzer were tracking each other very well, however, the offset between the readings did not allow for better accuracy. The large discrepancy between the results of two analyzers in the beginning of test was due to calibration of the amperometric unit at too low chlorine concentration (~0.8 ppm). The multiple spikes in the chart reflect the flush cycles in action. The provided chart is presented with a view of moving averages rather than direct data points due to the details overwhelming the picture in this case. The provided graph (Fig. 10) demonstrates that the longest period of relatively accurate readings between calibrations was about 9 days. This may or may not be sufficient for the end user depending on their requirements of accuracy of the residual chlorine concentration measurements. The calibration efficiency was questionable due to very fast change in chlorine concentration when even 2.5 minutes delay can cause an offset between the measurements.

Overall, the fast response to changing chlorine concentration and following the reference method make the amperometric system suitable to this application; however, calibration at a correct set point is required in order to achieve acceptable accuracy.

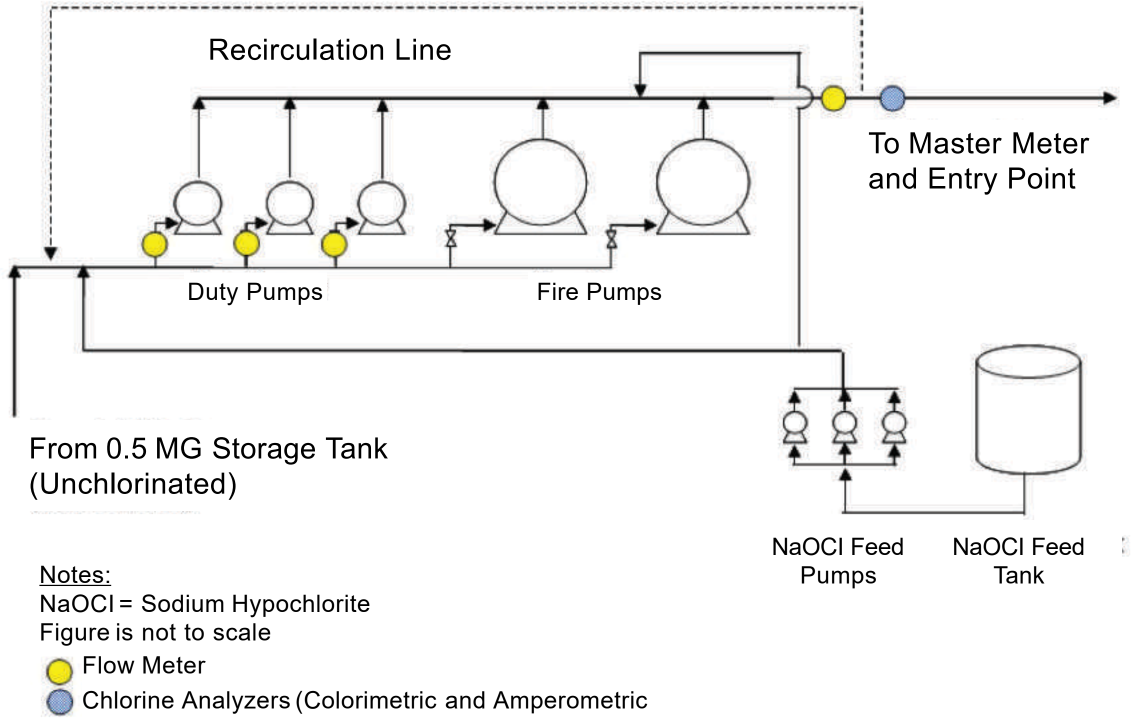
Case Study 2 – City of Aurora, CO

A large part of the field testing was conducted at several facilities in the City of Aurora, CO. The case study included total chlorine testing at Wemlinger WTP in a dynamic application (right after the flash mixer where ammonia is being added) similar to the free chlorine test conducted at Semper WTP as described above. The other parts of testing will be described in greater details below. The City of Aurora currently uses colorimetric chlorine analyzers for all compliance monitoring - both within its treatment facilities and throughout its distribution system. Nonetheless, the City is dedicated to proactively assessing other available or competing technologies that may have distinct advantages over the colorimetric analyzers. Since the amperometric technology is reagentless, the City was most interested in performing comparative performance testing at its most remote facilities. For this study, two locations were selected for the comparison: a remote groundwater treatment facility (challenging application in terms of iron and manganese concentration in the water) and a distribution system pumping (booster) station (stable sample characteristics – target application).

Ground Water Station

The City of Aurora owns and maintains a small groundwater station that serves a relatively remote area east of the Denver, CO metropolitan area. The treatment system includes three groundwater wells, a 500,000 gallon raw water storage tank, and a pumping building where chlorination is applied. The groundwater well system has a total capacity to deliver 540 gpm but average flow ranges between 20 to 100 gpm. The system currently serves approximately 100 people. This system is classified as a non-transient, non-community groundwater station.

The existing disinfection system includes three peristaltic chlorine feed metering pumps and sodium hypochlorite storage. The chlorine feed system is flow-paced based on flow measured from an effluent flow meter minus the recirculation flow. The chlorine injection point is on the suction side of the duty pumps, and the chlorine residual is measured on the discharge side of the pumps. A schematic of the treatment process is shown in Figure 11.



Notes:
NaOCl = Sodium Hypochlorite
Figure is not to scale
● Flow Meter
● Chlorine Analyzers (Colorimetric and Amperometric

Figure 11 - Schematic of Water Treatment and Monitoring at the Ground Water Station (Aurora, CO)

The City remotely monitors this treatment station 24-hour a day via a sophisticated flow control center. Operators visit the site daily to perform routine checks and maintain equipment and are on-call 24 hours a day to respond to process upsets, alarms, and emergencies. However, since the site is monitored remotely, it is critical that the chlorine monitoring equipment operate reliably.

The water quality of the ground water treated by the system is consistent and stable throughout the year. Turbidity of the water is less than 1 NTU and TOC values are approximately 1.0 mg/L. The water has moderately high iron and manganese concentrations with approximate values of 500 µg/L and 60 µg/L, respectively.

The City historically utilized an amperometric chlorine analyzer for monitoring chlorine residual at this system. However, due to possible future regulatory issues, ease of maintenance, and operator preferences, the City recently installed a colorimetric analyzer. Nevertheless, the City was interested in performing a comparative analysis of the amperometric and colorimetric chlorine measuring technologies. For this study, an amperometric analyzer was installed next to the existing colorimetric analyzer. Data was collected between october 30th and December 15th, 2008. The results of this comparison are presented in Figure 12.

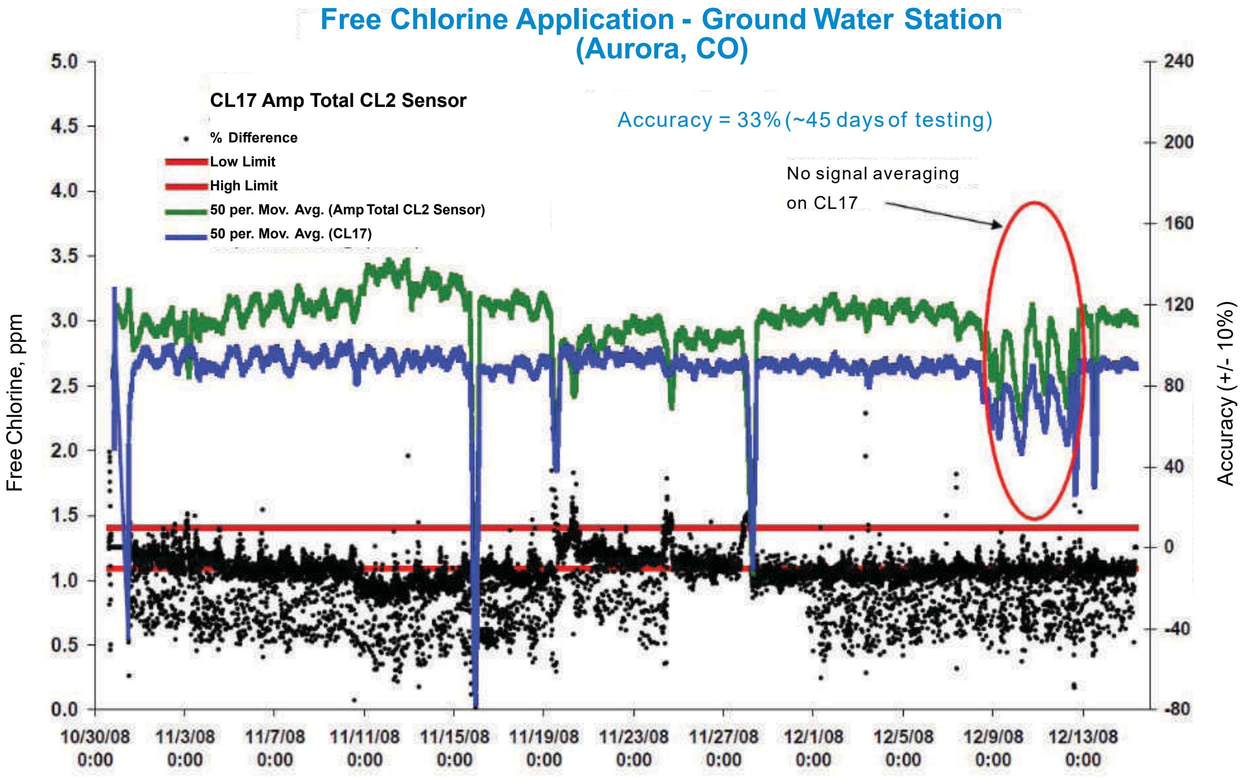


Figure 12 - Dynamic application: Total chlorine sensor in ground water (Aurora, CO

As seen from Figure 12 the situation with accuracy of the readings from the amperometric sensor is similar to the previously discussed dynamic application at NW WTP (Fig. 10). Unlike the latter, the readings were collected every 5 minutes and the sensor was calibrated against the CL17 at the beginning of the test and then two more times when a discrepancy with CL17 in more than 10% was discovered. The chart in Figure 12 shows moving averages for both instruments, because the dynamic nature of the application made the real-time results very difficult to read. Due to the dynamic application as it is, the CL17 used for process control was set to signal averaging and therefore it was difficult to calibrate the amperometric system properly. The initially calibrated amperometric sensor displayed upward drift in the reading during the first three weeks and was recalibrated once the drift was discovered. After that the sensor was showing an agreement with the CL17, however, the accuracy was barely acceptable given the acceptance range. After approximately one month in the test, an experiment was conducted to verify the sensor's ability to follow the chlorine concentration swings. As seen from the chart, the signal averaging function on the CL17 was turned off and the amperometric unit was calibrated again. The circled portion of the chart shows the result of the experiment, which allowed to conclude that the sensor was tracking the chlorine concentration and the CL17's readings satisfactorily overall, however, the accuracy was within the acceptable range for only 33% of all time.

Another comparative test at the same location was conducted using a free chlorine amperometric sensor from the same batch of sensors tested in the laboratory (Figures 2 and 5), and at other DW facilities (Semper WTP, Soldier Canyon WTP). The test was organized in exactly the same manner as the previous trial involving the total chlorine sensor in terms of the sampling point and calibration protocol. Every time when calibration of the amperometric sensor was deemed necessary, the CL17 signal averaging function was turned off and after 10-15 minutes the calibration was conducted. A pH sensor was installed in the drain line of the amperometric sensor and all collected data for this testing are presented in Figure 13. It is necessary to mention that the test was initiated in April 2009 and it was very difficult to achieve stable readings, so, after several weeks of troubleshooting involving multiple calibrations and electrolyte replacements, the sensor was replaced and the test finally started in beginning of June 2009 and lasted for 75 days (Figure 13).

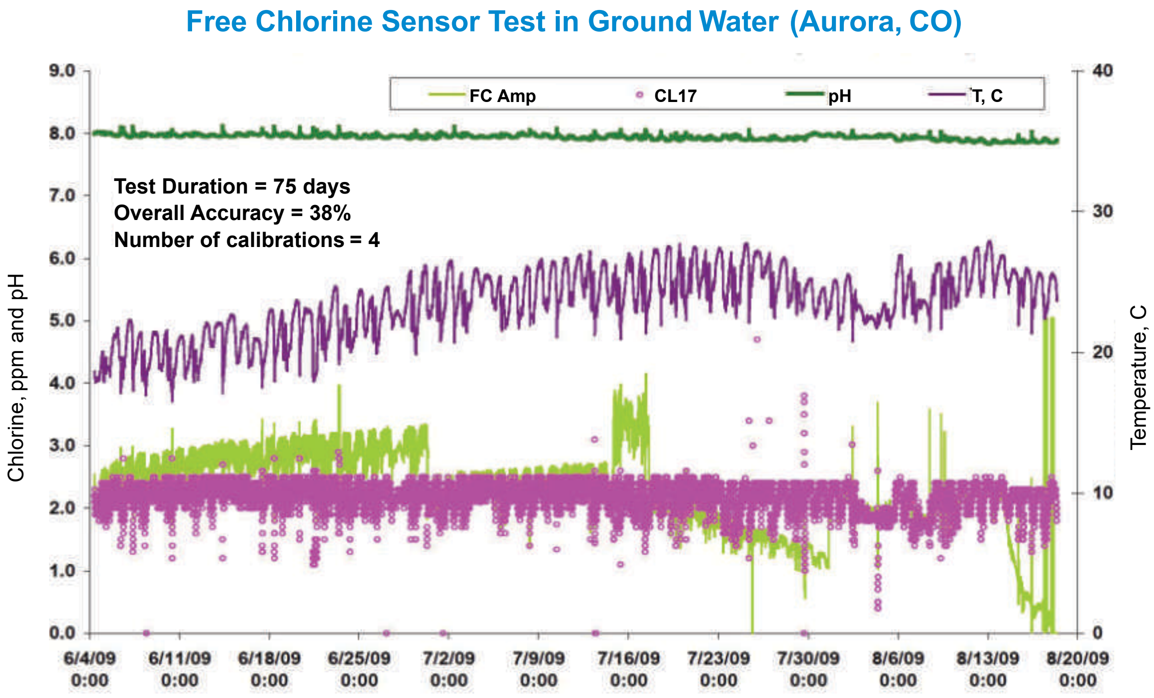


Figure 13 - Free Chlorine Amperometric Sensor Test at the Ground Water Station (Aurora, CO)

This time, no moving average for any readings is presented in the chart displaying also results for sample pH and Temperature monitoring (Fig. 13). As seen from Figure 13, the sensor's performance was not very stable and worsened with time as the probe was exposed to the sample. Since the sample pH and temperature characteristics were found to be relatively stable, only two reasons were identified (other than intrinsic to the probe itself) for the probe's poor performance – swings in chlorine concentration and fouling of the membrane with iron and manganese oxides natural to this ground water. Overall the sensor performed accurately only in 38% of the comparable readings and required frequent calibrations (every two weeks on average). The only maintenance other than the calibrations conducted was the flow adjustments to keep it at above the minimum requirement of 30 L/hr. According to the customer, they routinely perform monthly regular maintenance on the CL17, which involves cell cleaning and reagents replacement. As seen from the chart, no drift on CL17 readings was registered due to the colorimetric cell fouling.

It was concluded that the excessive membrane fouling most likely caused the sensor to perform poorly and, in turn, it promoted more frequent calibrations due to either drift of the zero calibration or faster weakening of the electrolyte capacity.

Distribution System

The City of Aurora's primary water system serves approximately 300,000 people. The system is comprised of two 65-MGD direct filtration surface water treatment facilities. Primary disinfection is performed using a combination of chlorine dioxide and gaseous chlorine. Secondary disinfection is accomplished with the use of chloramines.

The City actively monitors total chlorine residual at numerous locations within its distribution system. Currently, the City uses colorimetric total chlorine analyzers at these remote stations. However, due to the possible elimination of the DPD waste stream generated by the colorimetric analyzers, the City is interested in performing comparative analyses with comparable reagentless technologies. For this study, an amperometric analyzer was installed next to the existing colorimetric analyzer within one of the City's distribution system pump stations receiving and distributing finished water from the Wemlinger WTP. The comparative study at this location was conducted from 6/20/08 through 10/30/08 (more than 4 months). However, some data was lost due to insufficient logger memory and the continuous comparable readings were collected between July 28th and October 30th, 2008. The results of this comparison are presented in Figure 14.

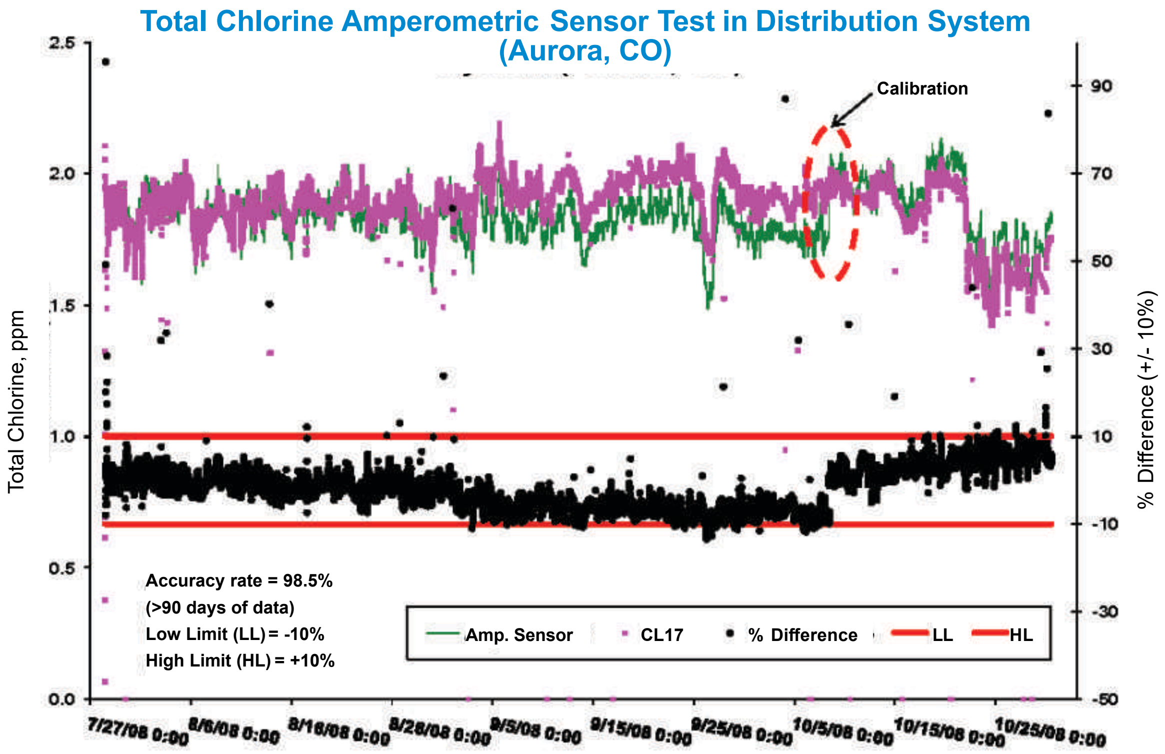


Figure 14 – Test results in the distribution system (Aurora, CO), an example of target application.

The presented chart (Fig. 14) displays only ~90 days of the test, and the accuracy of amperometric system was within the acceptable range throughout the test for more than 98% of all readings. The sample temperature data was also collected during the test and it was found to be fluctuating within 7.8 – 16.9°C tracking the data registered at the Wemlinger plant located approximately 2 miles upstream, where the water was discharged. The sample pH in this application was extremely stable around pH = 8. During the entire test (~130 days) the chlorine and temperature sensors were calibrated three times – at start (6/20/08), on 7/28/08 when the data logging interval was changed to every 5 minutes (from previous 1 minute), and on 10/08/08 when some downward drift was discovered (Fig. 14).

The testing at different facilities and treatment processes of the City of Aurora, CO has confirmed the preliminary conclusion that the most appropriate application for amperometric sensors is on a static sample experiencing no significant swings in chlorine concentration and other characteristics. Therefore, the next case study was conducted to further verify this approach and evaluate different sensors in the same or very similar applications.

Case Study 3 – Soldier Canyon WTP

Soldier Canyon water filtration plant is located in Northern Colorado and is a conventional drinking water facility of 50 MGD capacity receiving the water mainly from the Horsetooth Reservoir and also Poudre River during peak season. The water treatment process scheme is shown in Figure 15.

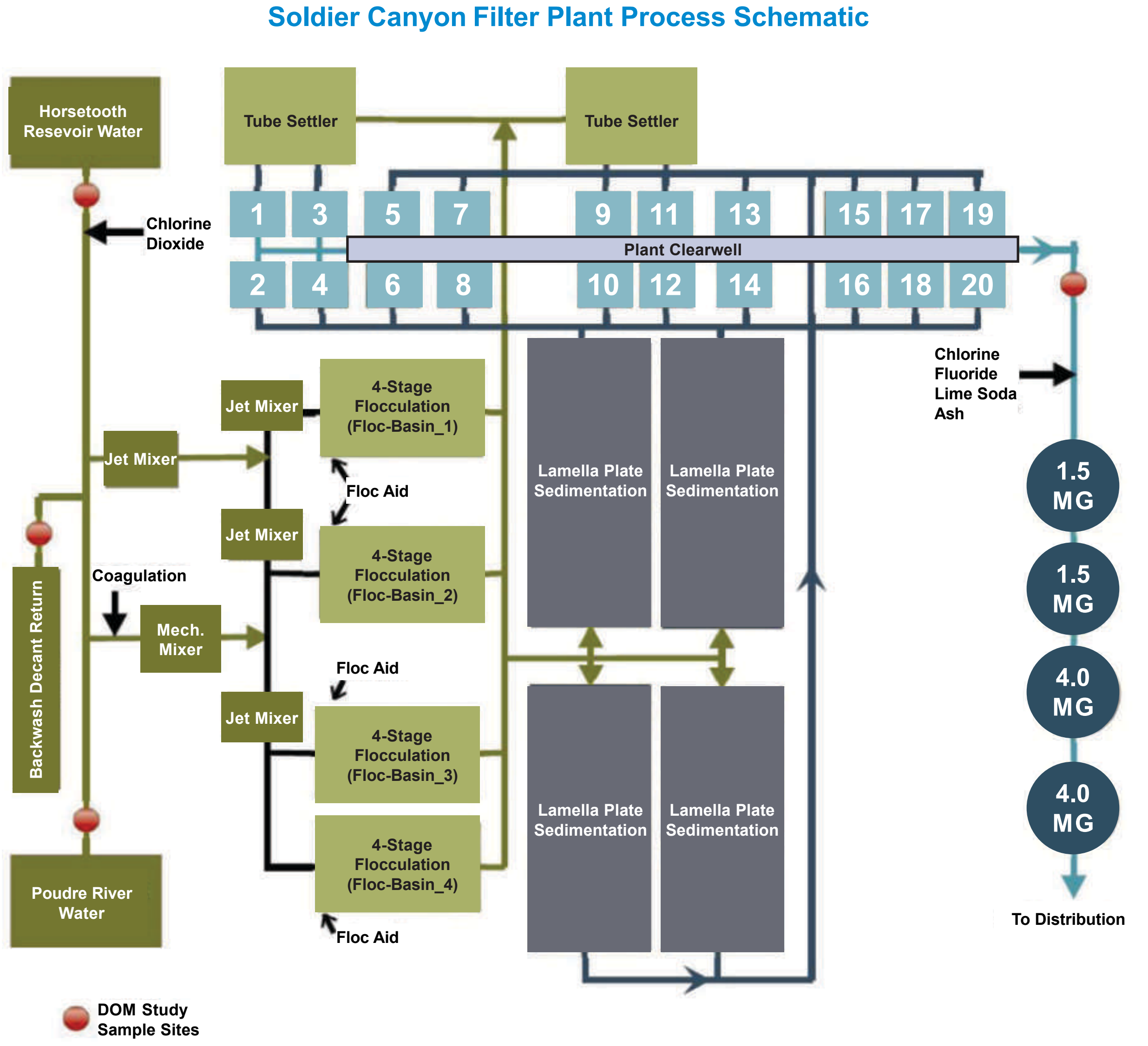


Figure 15 - Soldier Canyon WTP treatment process schematic

As seen from Figure 15, the main water treatment train involves filters 5 through 20 while the older filters 1 through 4 are occasionally used during peak season such as in early summer. The treated water from all filters comes to the same clear well; however, the sampling points for different analyses are located in different places (Fig. 16).

For example, the sampling point for turbidity is located in the clear well prior to the addition of fluoride, soda ash, and lime, while residual free chlorine is tested after all treatment is finished. The sampling for chlorine is conducted before and after the storage tanks and there is always a small difference in free chlorine concentration due to presence of chlorine demand in the tanks. The study was conducted with three amperometric sensors installed at different sampling points – Figure 16. Two total chlorine sensors were tested on the post-tank sample immediately prior to discharge into the distribution system and one free chlorine sensor was tested at two locations – pre-tank sample and in the clear well (turbidity sampling point – Fig. 16). All these applications were considered static and the post-tank test was anticipated to be the most suitable for the amperometric systems. Results of the testing are discussed below.

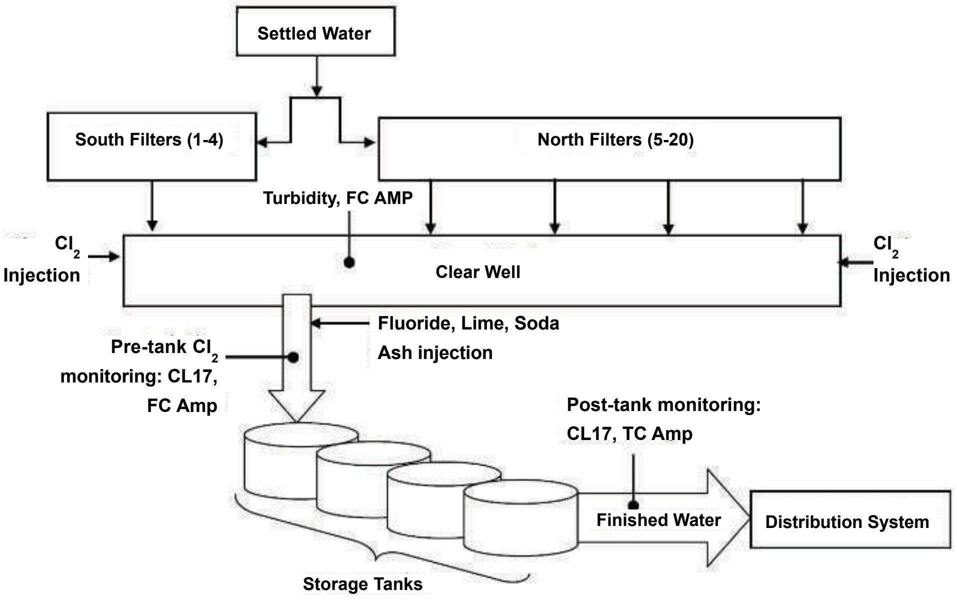
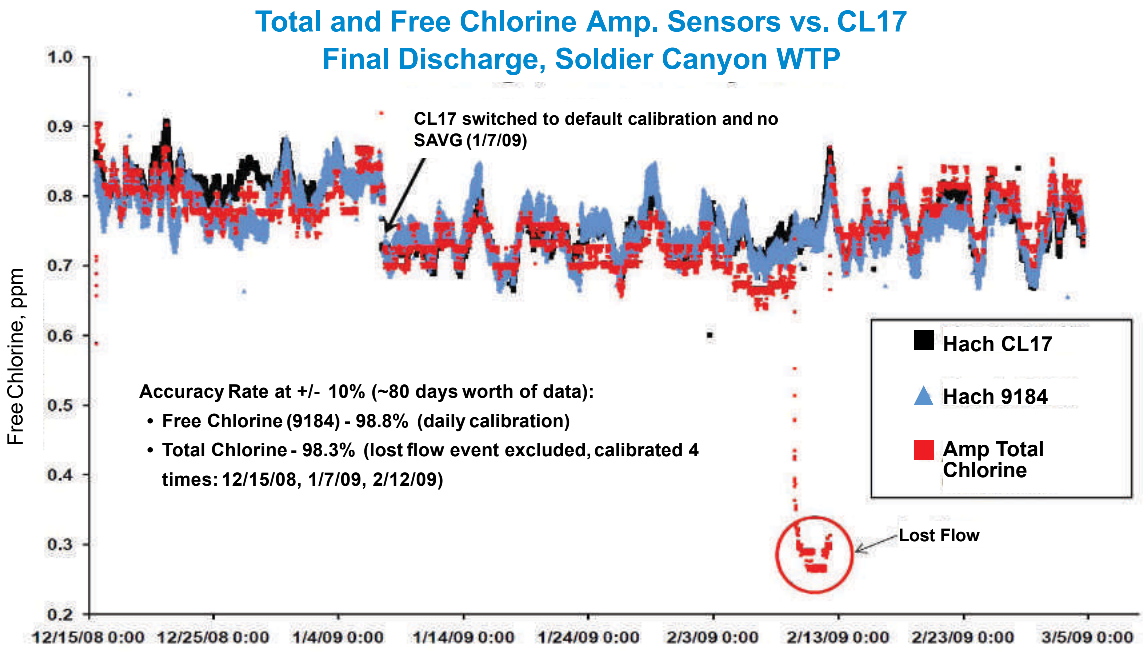


Figure 16 - Soldier Canyon WTP Free Chlorine Residual Monitoring Points

Finished Water Test

The sensors tested in the post-tank application were measured against the existing CL17 and another amperometric analyzer – Hach 9184 (Fig.17).

The residual free chlorine concentration fluctuates between 0.7 and 0.9 ppm, which is approximately 20% lower than the chlorine concentration in the pre-tank sample. The final water is discharged in the distribution system with pH adjusted to 8±0.05 to prevent DBP formation and minimize the corrosion. Due to relatively high sample pH, the Hach 9184 system employs external pH compensation by pumping vinegar into the flow cell to adjust pH to the 5.5-6.5 value. This requires ongoing replenishment of the acid; therefore, the facility is interested in a completely reagentless solution as an alternative to the existing instrumentation.



Accuracy Rate at +/- 10% (~80 days worth of data):
- **Free Chlorine (9184) - 98.8% (daily calibration)**
- **Total Chlorine - 98.3% (lost flow event excluded, calibrated 4 times: 12/15/08, 1/7/09, 2/12/09)**

Figure 17 - Post-tank application immediately prior to the distribution system – target application.

The data presented in Figure 17 demonstrate overall good accuracy of both amperometric systems compared to the CL17. However, the maintenance load on these amperometric instruments was different in terms of frequency of calibrations or minor adjustments required to keep the sensors producing accurate results. For instance, the Hach 9184 required almost daily adjustment of its readings to match the CL17 in addition to the external buffer to compensate for high pH of the sample. In contrary, the tested total chlorine sensor required calibration only every 3-4 weeks and some of the actions were necessary to return the sensor to normal operation. For example, as seen in Figure 17, at one point the flow to the total chlorine sensor was lost and a calibration was conducted after the flow was restored. Another calibration was performed to match the CL17 readings when the DPD analyzer was taken off the signal averaging function and moved to default calibration. The test was conducted to determine the agreement between two technologies in unobstructed conditions. The overall accuracy of both amperometric sensors was found to be very good and the application was confirmed to be the most suitable for this technology. Although this first test went well, another total chlorine sensor failed in this same application – Figure 18. One design difference between the two total chlorine sensors manufactured by the same company was in the signal output format – mV (Fig. 17) and mA (Fig. 18). Since the second sensor was obtained from another vendor it had a different electrolyte and this was considered the most crucial difference responsible for the test results (Fig. 18).

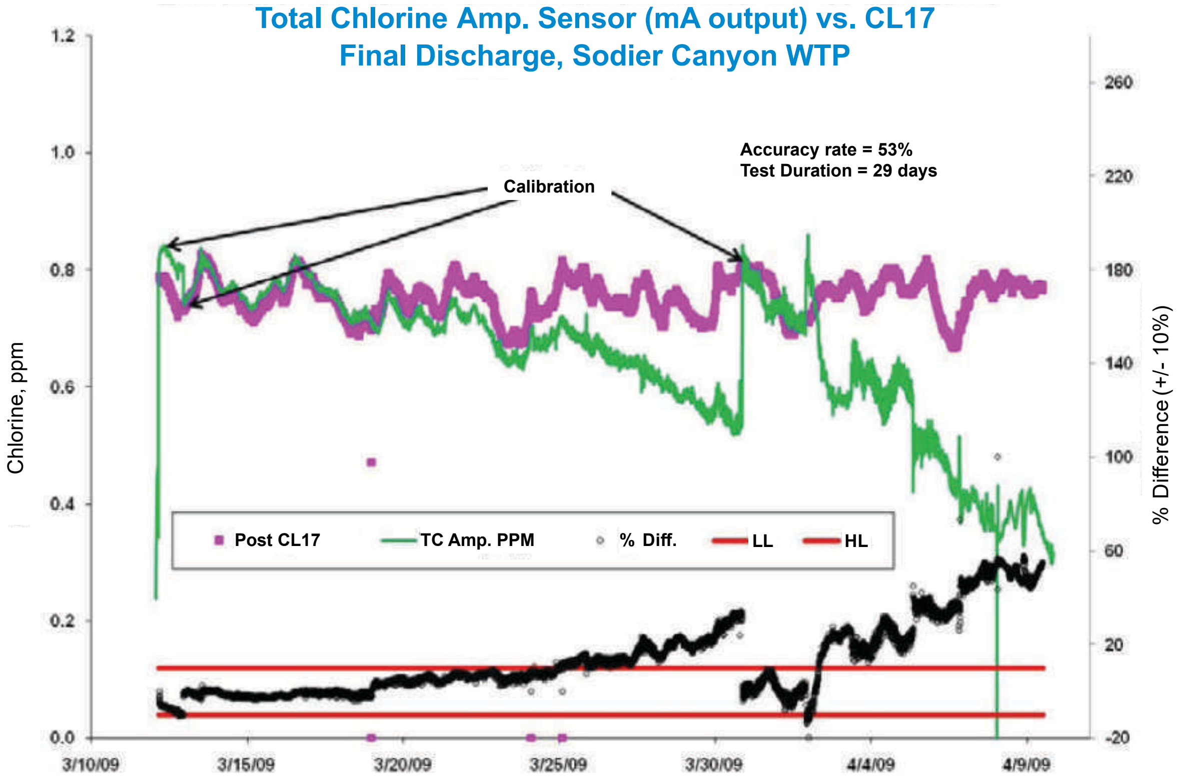
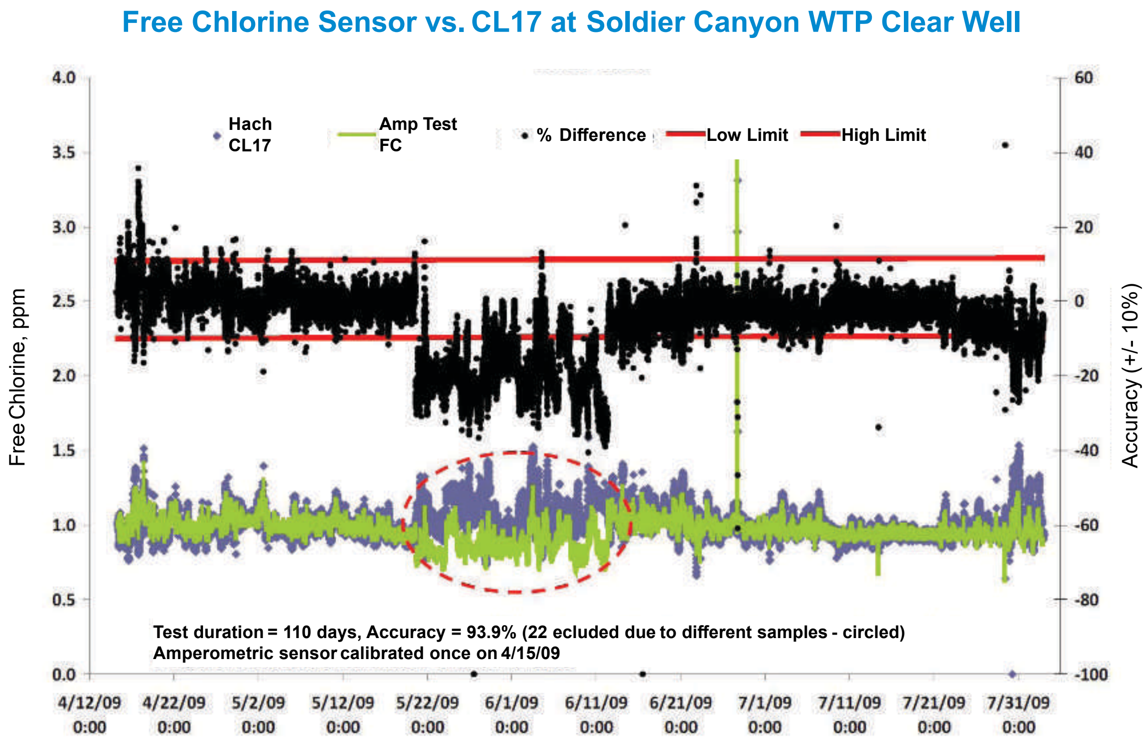


Figure 18 – Total Chlorine Sensor (mA output) test in post-tank application – example of failure.

The data presented in the chart in Figure 18 demonstrate that regardless of multiple calibrations, an amperometric sensor manufactured by the same vendor may fail after a short time in the process. The calculated difference between DPD and amperometric readings was within the acceptable range for only half of the test duration. This is a classical example of the readings drift that can happen at any time and may depend solely on parts of the amperometric system.

Another long-term test was conducted with a free chlorine sensor (randomly selected from the five tested in laboratory) installed before and after addition of lime, soda ash, and fluoride (Fig. 16). The results of this test are presented in Figure 19 below and require special discussion.



Test duration = 110 days, Accuracy = 93.9% (22 ecluded due to different samples - circled)
Amperometric sensor calibrated once on 4/15/09

Figure 19 – Free chlorine sensor in pre-tank application (two sampling points per Fig. 16)

The test results depicted in the chart in Figure 19 was monitored for longer than 110 days and overall accuracy of the free chlorine sensor was considered to be very good (~94% for 87 days). The circled data that showed inadequate variance is explained by the test setup. For the first 35 days the sample to both analyzers came from the same set of filters (5 through 20, Fig. 16). After that point, the CL17 started receiving blended sample from both filter sets while the amperometric unit kept receiving the previous sample due to different sampling points (Fig. 16). The result was obvious – different responses of these two analyzers as reflected in Figure 19. Thus, to make the test results comparable again, the amperometric system was moved to the same sampling point as the CL17 and both systems started analyzing the same sample again for another 52 days of test. What is important, the amperometric sensor used in this test did not require recalibration after switching the lines unlike the other sensor from the same batch used at the ground water station and discussed above (Fig. 13). As a matter of fact, the amperometric sensor tested on finished water displayed excellent stability of the readings without additional calibration or cleaning for the entire duration of the test (Fig. 19). This has once again confirmed the suitability of the finished water applications for the amperometric systems.

Very similar results with discussed above were received from the tests conducted on final water produced by San Patricio WTP in Portland, TX as well as in several distribution systems (Ingleside, TX, and Pasco County, Florida). According to the side-by-side comparative testing, the finished water should be considered the most suitable application for amperometric sensors.

As illustrated through testing in dynamic applications (Semper, Northwest, Wemlinger WTP's and the Aurora Ground Water Station), any significant instability in sample parameters, such as flow, temperature, pH and chlorine concentration, must be considered interference requiring special attention and more frequent calibrations of the amperometric sensors against a reference method/analyzer. This may also require more maintenance for the sensors.

Conclusion

Prior to choosing an on-line chlorine analyzer, the application should be evaluated to define what technology will be most suitable – DPD or amperometric. Utilization of amperometric technology requires much better understanding of the nature of the sample to be tested and the application realities, making it difficult to perform consistently without significant initial evaluation.

The online amperometric sensing technology is more suitable for process control and less for analytical applications, because it always requires calibration against a reference analytical method. It has been demonstrated that online amperometric sensors may work well in static applications where chlorine concentration, sample flow, pressure, temperature and pH are stable, i.e. final discharge, or certain distribution systems. However, given the intrinsic uncertainties in the sensor design, materials and manufacturing processes, such instrumentation must undergo a rigorous evaluation prior to their use for regulatory reporting.

Due to the non-specific nature of the amperometric technology and limited ability of the membrane to provide selectivity toward chlorine species, the amperometric sensors will not efficiently distinguish between free and total chlorine. To avoid errors in the analysis it is necessary to always verify the type of chlorine in the water sample with an alternative reference method.

Presence of a particulate matter in the sample causing excessive sensor fouling affects accuracy of the analysis and will require extensive maintenance in terms of sensor cleaning, calibration and electrolyte replacement. The electrolyte must be replaced every time the amperometric system is left idle without sample and/or electrical power for longer than a few days.

The conducted study has demonstrated usefulness of the amperometric technology in process control applications as well as using it as a redundant or backup instrumentation. Additionally, the study has shown a necessity of ongoing verification of the amperometric instruments against a reference analysis, even if the sensors are used for process control.

The on-line reference analysis may be conducted in real time with use of DPD-based colorimetric analyzers which provided more accurate results in all of the tested applications. It was shown that the negative perception of this type of equipment based on the produced waste stream is highly exaggerated.

Acknowlegement

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