October 2005

Environmental Technology Verification Report

CLARION SENSING SYSTEMS, INC. SENTINAL™ 500 SERIES CONTINUOUS MULTI-PARAMETER WATER QUALITY MONITOR

Prepared by
Battelle

Battelle
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Under a cooperative agreement with

EPA U.S. Environmental Protection Agency

ETV ETV ETV

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

Battelle
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ETV Joint Verification Statement

TECHNOLOGY TYPE:	**MULTI-PARAMETER WATER MONITORS FOR DISTRIBUTION SYSTEMS**
APPLICATION:	**MONITORING DRINKING WATER QUALITY**
TECHNOLOGY NAME:	**Sentinal™ 500 Series**
COMPANY:	**Clarion Sensing Systems, Inc.**
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The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies. Information and ETV documents are available at www.epa.gov/etv.

ETV works in partnership with recognized standards and testing organizations, with stakeholder groups (consisting of buyers, vendor organizations, and permitters), and with individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The Advanced Monitoring Systems (AMS) Center, one of six technology areas under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center evaluated the performance of the Clarion Sensing Systems, Inc., Sentinal™ 500 Series in continuously measuring free chlorine, temperature, conductivity, pH, and oxidation-reduction potential (ORP) in drinking water. This verification statement provides a summary of the test results.

VERIFICATION TEST DESCRIPTION

The performance of the Sentinal™ 500 was assessed in terms of its accuracy, response to injected contaminants, inter-unit reproducibility, ease of use, and data acquisition. The verification test was conducted between August 9 and October 28, 2004, and consisted of three stages, each designed to evaluate a particular performance characteristic of the Sentinal™ 500. All three stages of the test were conducted using a recirculating pipe loop at the U.S. EPA's Test and Evaluation (T&E) Facility in Cincinnati, Ohio.

In the first stage of this verification test, the accuracy of the measurements made by the Sentinal™ 500 units was evaluated during nine, 4-hour periods of stable water quality conditions by comparing each Sentinal™ 500 unit measurement to a grab sample result generated each hour using a standard laboratory reference method and then calculating the percent difference (%D). The second stage of the verification test involved evaluating the response of the Sentinal™ 500 units to changes in water quality parameters by injecting contaminants (nicotine, arsenic trioxide, and aldicarb) into the pipe loop. Two injections of three contaminants were made into the recirculating pipe loop containing finished Cincinnati drinking water. The response of each water quality parameter, whether it was an increase, decrease, or no change, was documented and is reported here. In the first phase of Stage 3 of the verification test, the performance of the Sentinal™ 500 units was evaluated during 52 days of continuous operation, throughout which references samples were collected once daily. The final phase of Stage 3 (which immediately followed the first phase of Stage 3 and lasted approximately one week) consisted of a two-step evaluation of the Sentinal™ 500 performance to determine whether this length of operation would negatively impact the results from the Sentinal™ 500. First, as during Stage 1, a reference grab sample was collected every hour during a 4-hour analysis period and analyzed using the standard reference methods. Again, this was done to define a formal time period of stable water quality conditions over which the accuracy of the Sentinal™ 500 could be evaluated. Second, to evaluate the response of the Sentinal™ 500 to contaminant injection after the extended deployment, the duplicate injection of aldicarb, which was also included in the Stage 2 testing, was repeated. In addition, a pure *E. coli* culture, including the *E. coli* and the growth medium, was included as a second injected contaminant during Stage 3. Inter-unit reproducibility was assessed by comparing the results of two identical units operating simultaneously. Ease of use was documented by technicians who operated and maintained the units, as well as the Battelle Verification Test Coordinator.

QA oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a technical systems audit, a performance evaluation audit, and a data quality audit of 10% of the test data.

This verification statement, the full report on which it is based, and the test/QA plan for this verification test are all available at www.epa.gov/etv/centers/center1.html.

TECHNOLOGY DESCRIPTION

The following description of the Sentinal™ 500 unit was provided by the vendor and does not represent verified information.

The Sentinal™ 500 is designed to remotely monitor and report drinking water quality. The Sentinal™ 500 uses a sensor array to acquire information about drinking water quality on site in near-real time by analyzing the water quality and comparing it to its normal baseline values and notifies utility/security personnel if water quality changes significantly from its baseline. The Sentinal™ 500 used in this verification test measured free chlorine, temperature, conductivity, pH, and ORP in drinking water. The sensors measured these parameters by potentiometric, amperometric, and conductance methods.

The Sentinal™ 500 consists of sensors and their respective meters with digital displays; a data acquisition, analysis, and management microprocessor; a communications link such as radio, cellular networks, satellite networks, wireless Ethernet or LANs (as configured during this test), and a receiving station where the data are presented and alarms are distributed. The systems can serve up their own Web pages to the network, and other monitoring sites can be accessed through each site. The system could be configured to actuate valves and pumps to shut off or divert water for on-site treatment.

For this verification test, the continuous data were stored on the on-board computer and downloaded daily by plugging an Ethernet cable into a laptop and entering an IP address into Microsoft Explorer. A Web page was called up, and the data could be easily downloaded as an Excel spreadsheet. System software (the Sentinal™ Data Acquisition and Management Device) could be configured to average all of the data over time to determine site-specific normal baselines. The software also can be programmed to recognize when deviations (threshold set by the user) from the baseline occur and either triggers “alerts” or “alarms,” depending on the degree of deviation. All aspects of the data acquisition could be configured for remote observation and data collection.

The Sentinal™ 500 is 30 inches by 36 inches and weighs about 30 pounds. Prices for Sentinal™ systems range from $12,600 to $24,500. The cost of the system as configured for the verification test is $17,000. Other costs include $800 annually for replacement chlorine sensor gel caps and electrolyte gel and a one-time purchase of a calibration kit for $540.

VERIFICATION OF PERFORMANCE

Evaluation Parameter			Free Chlorine	Temperature	Conductivity	pH	ORP
Stage 1—Accuracy	Units 1 and 2, range of %D (median)		3.4 to 117.1 (26.2)	-18.4 to 2.7 (-3.7)	-26.8 to -22.4 (-24.6)	-6.1 to 0.5 (-1.9)	[a]
Stage 2—Response to Injected Contaminants	Nicotine	Reference	−	NC	NC	NC	−
		Sentinal™ 500	−	NC	NC	NC	−
	Arsenic trioxide	Reference	−	NC	+	+	−
		Sentinal™ 500	−	NC	+	+	−
	Aldicarb	Reference	−	NC	NC	NC	−
		Sentinal™ 500	−	NC	NC	NC	−
Stage 3—Accuracy During Extended Deployment	Units 1 and 2, range of %D (median)		-54.8 to 50.0 (-21.5)	-7.8 to 2.7 (-2.7)	-0.8 to 5.5 (2.1)	-7.2 to 1.6 (0.3)	[a]
Stage 3—Accuracy After Extended Deployment	Unit 1, %D		-10.9	-0.5	2.5	0.0	[a]
	Unit 2, %D		-18.5	-3.1	0.3	1.2	[a]
Stage 3—Response to Injected Contaminants	*E. coli*	Reference	−	NC	+	−	−
		Sentinal™ 500	−	NC	+	−	−
	Aldicarb	Reference	−	NC	NC	−	−
		Sentinal™ 500	−	NC	NC	−	−
Injection Summary	For a reason that is not clear, aldicarb altered the pH, as measured by the reference method, during the Stage 3 injections, but not during the Stage 2 injections.						
Inter-unit Reproducibility (Unit 2 vs. Unit 1)	Slope (intercept)		0.86 (0.10)	0.98 (-0.04)	1.01 (-4.13)	1.05 (-0.3)	0.89 (72)
	r^2		0.87	1.00	0.98	0.95	0.98
	p-value		0.92	0.23	0.74	0.17	0.87
	All sensors generated results that were similar according to the results of the t-test. However, the slopes of the ORP and free chlorine sensor data plotted against one another suggest that the results from each unit were somewhat different from one another.						
Ease of Use and Data Acquisition	Based on the performance of the free chlorine sensors, they may have to be adjusted periodically to maintain the accuracy of the measurements. The memory module in Unit 1 had to be replaced and, twice, each unit had to be rebooted before data could be downloaded.						

[a] ORP was not included in the accuracy evaluation because of the lack of an appropriate reference method.
+/− = Parameter measurement increased/decreased upon injection.
NC = No obvious change was noted through a visual inspection of the data.

Original signed by Gregory A. Mack 10/17/05
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NOTICE: ETV verifications are based on an evaluation of technology performance under specific, predetermined criteria and the appropriate quality assurance procedures. EPA and Battelle make no expressed or implied warranties as to the performance of the technology and do not certify that a technology will always operate as verified. The end user is solely responsible for complying with any and all applicable federal, state, and local requirements. Mention of commercial product names does not imply endorsement.

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ETV Advanced Monitoring Systems Center

CLARION SENSING SYSTEMS, INC. SENTINAL™ 500 SERIES CONTINUOUS MULTI-PARAMETER WATER QUALITY MONITOR

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Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, has financially supported and collaborated in the extramural program described here. This document has been peer reviewed by the Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation by the EPA for use.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six verification centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

Acknowledgments

The authors wish to acknowledge the support of all those who helped plan and conduct the verification test, analyze the data, and prepare this report. We would like to thank Roy Haught and John Hall of the U.S. Environmental Protection Agency's (EPA's) Test and Evaluation (T&E) Facility (operated by Shaw Environmental, Inc. [Shaw]) in Cincinnati, Ohio, for hosting the verification test. The U.S. EPA primary contract to Shaw provided significant support in interfacing the continuous monitors with the pipe loop, as well as facilitating the experimental plan. The T&E Facility's contribution included providing the reference analyses and operating the pipe loop, as well as reviewing the test/quality assurance (QA) plan and the reports. In addition, we would like to thank Steve Allgeier of EPA's Office of Water, Gary Norris and Alan Vette of the EPA National Exposure Research Laboratory, Lisa Olsen of the U.S. Geological Survey, Matthew Steele of the City of Columbus Water Quality Assurance Laboratory, and Ron Hunsinger of East Bay Municipal Utility District, who also reviewed the test/QA plan and/or the reports.

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List of Abbreviations

AMS	Advanced Monitoring Systems
°C	degree centigrade
DI	deionized
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
L	liter
µS/cm	microSiemens per centimeter
mg/L	milligram per liter
mV	millivolt
NIST	National Institute of Standards and Technology
ORP	oxidation reduction potential
%D	percent difference
PE	performance evaluation
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
QMP	quality management plan
SD	standard deviation
T&E	Test and Evaluation
TSA	technical systems audit

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center evaluated the performance of the Clarion Sensing Systems, Inc., Sentinal™ 500 Series water quality monitor in continuously measuring free chlorine, temperature, conductivity, pH, and oxidation-reduction potential (ORP) in drinking water. Continuous multi-parameter water monitors for distribution systems were identified as a priority technology verification category through the AMS Center stakeholder process.

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the Sentinal™ 500 Series water quality monitor. Following is a description of the Sentinal™, based on information provided by the vendor. The information provided below was not verified in this test.

The Sentinal™ 500 (Figure 2-1) is designed to remotely monitor and report drinking water quality. The Sentinal™ 500 uses a sensor array to acquire information about drinking water quality on site in near-real time by analyzing the water quality and comparing it to its normal baseline values and notifies utility/security personnel if water quality changes significantly from its baseline. The Sentinal™ 500 used in this verification test measured pH, temperature, free chlorine, conductivity, and the ORP of drinking water. The sensors measured these parameters by potentiometric, ampero-metric, and conductance methods.

Figure 2-1. Clarion Sensing System's Sentinal™ 500

The Sentinal™ 500 consists of sensors and their respective meters with digital displays; a data acquisition, analysis, and manage-ment microprocessor; a communications link such as radio, cellular networks, satellite networks, wireless Ethernet or LANs (as configured during this test), and a receiving station where the data are presented and alarms are distributed. The systems can serve up their own Web pages to the network, and other monitoring sites can be accessed through each site. The system could be configured to actuate valves and pumps to shut off or divert water for on-site treatment. No reagents were required.

For this verification test, the data were stored on the on-board computer and downloaded daily by plugging an Ethernet cable into a laptop and entering an IP address into Microsoft Explorer. An Internet Web page was called up, and the data could be easily downloaded as an Excel spreadsheet. System software (the Sentinal™ Data Acquisition and Management Device) could be configured to average all of the data over time to determine site-specific normal baselines. The software also can be programmed to recognize when deviations (threshold set by the user) from the baseline occur and either triggers "alerts" or "alarms," depending on the degree of deviation. All aspects of the data acquisition could be configured for remote observation and data collection.

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Chapter 3
Test Design

3.1 Introduction

The multi-parameter water monitors tested consisted of instrument packages that connect to or are inserted in distribution system pipes for continuous monitoring. Also included in this technology category were technologies that can be programmed to automatically sample and analyze distribution system water at regular intervals. The minimum requirement for participation in this verification test was that the water monitors were able to measure residual chlorine, as well as at least one other water quality parameter. Residual chlorine is a particularly important water quality parameter because changes in its concentration can indicate the presence of contamination within a distribution system, and chlorination is a very common form of water treatment used by water utilities in the United States.

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Multi-Parameter Water Monitors for Distribution Systems*(1) and assessed the performance of the Sentinal™ 500 units in continuously monitoring pH, conductivity, free chlorine, ORP, and temperature in terms of the following:

- Accuracy
- Response to injected contaminant
- Inter-unit reproducibility
- Ease of use and data acquisition.

Accuracy was quantitatively evaluated by comparing the results generated by two Sentinal™ 500 units to grab sample results generated by a standard laboratory reference method. Response to injected contaminants was evaluated qualitatively by observing whether the measured water quality parameters were affected by the injection of several contaminants. Inter-unit reproducibility was assessed by comparing the results of two identical units operating simultaneously. Ease of use was documented by technicians who operated and maintained the units, as well as the Battelle Verification Test Coordinator.

3.2 Test Stages

This verification test was conducted between August 9 and October 28, 2004, and consisted of three stages, each designed to evaluate a particular performance characteristic of the Sentinal™ 500. All three stages of the test were conducted using a recirculating pipe loop at the U.S. EPA's Test and Evaluation (T&E) Facility in Cincinnati, Ohio. The recirculating pipe loop consisted of ductile iron pipe, 6 inches in diameter and 100 feet long, which contained approximately 240 gallons of Cincinnati drinking water with a flow rate of approximately 1 foot/second. The water within the pipe loop had a residence time of approximately 24 hours. Water from the pipe loop was plumbed to two Sentinal™ 500 units by a section of 2-inch polyvinyl chloride (PVC) pipe in series with a shut-off valve with a ribbed nozzle that was connected to the Sentinal™ 500 units with a 1/2-inch PVC hose and a hose clamp. Reference samples of approximately 1 liter (L) (enough volume to perform all the required analyses) to be analyzed by each standard laboratory reference method were collected from the reference sample collection valve located approximately 11 feet from the Sentinal™ 500 units on the PVC pipe.

3.2.1 Stage 1, Accuracy

During the first stage of this verification test, the accuracy of the measurements made by both Sentinal™ 500 units was evaluated by comparing the results from each unit to the result generated by a standard laboratory reference method. Stage 1 testing simulated the characteristics of a variety of water quality conditions by changing two variables: pH and temperature. Using nine sets of pH and temperature conditions, this evaluation consisted of separate four-hour testing periods of continuous analysis, with reference method sampling and analysis every hour. Four sets of conditions involved varying only the pH by injecting the pipe loop with a steady stream of sodium bisulfate. Those sets consisted of pHs of approximately 7, 8, and 9 pH units (ambient pH at the T&E Facility was between 8 and 9) and a temperature between 21 and 23 degrees centigrade (°C) (T&E Facility ambient during the time of testing). Two other sets included changing the water temperature to between 13 and 14°C and testing at pHs of approximately 7 and 8; and two sets at approximately these pHs, but at a temperature of approximately 27°C. One set (Set 2) was repeated as Set 3. The pipe loop ambient conditions were analyzed at the start and end of this stage. Prior to each testing period with unique conditions, the water in the pipe loop was allowed to equilibrate until the pH and temperature were at the desired level, as determined by the standard reference methods. This equilibration step took approximately 12 hours from the time the sodium bisulfate was added (to decrease pH) or the temperature was adjusted.

3.2.2 Stage 2, Response to Injected Contaminants

The second stage of the verification test involved testing the response of the Sentinal™ 500 units to changes in water quality parameters by injecting contaminants into the pipe loop. Two separate injections of three contaminants were made into the recirculating pipe loop containing finished Cincinnati drinking water. Each injection was made over a period of approximately 15 seconds by connecting the injection tank to the pipe loop's recirculating pump. The three contaminants were nicotine, arsenic trioxide (adjusted to pH 12 to get it into solution), and aldicarb. With the exception of the first nicotine injection, each of these contaminants was dissolved in approximately 5 gallons of pipe loop water that had been dechlorinated using granular carbon filtration to prevent degradation of the contaminant prior to injection. Upon injection, concentrations of these contaminants within the pipe loop were approximately 10 milligrams per liter (mg/L). For the first nicotine injection, however, not enough nicotine to attain this concentration was available so the available nicotine was dissolved into 2 gallons of the dechlorinated pipe loop water and injected. The resulting nicotine concentration in the pipe loop was approximately 6 mg/L. Because the qualitative change in water quality parameters was similar for both nicotine injections despite the concentration difference, it was not necessary to repeat the 10 mg/L injection of nicotine. For all three sets of injections, a reference sample was collected prior to the injection and again at 3, 15, and 60 minutes after the injection. The difference between reference method results occurring before and then again after injection indicated the directional change in water quality caused by the injected contaminant. For each injected contaminant, the results from the Sentinal™ 500 units were evaluated based on how well their directional change matched that of the reference method result. After each injection, the pipe loop was allowed to re-equilibrate for approximately 12 hours so that each Sentinal™ 500 unit returned to a steady baseline. Injected contaminants were obtained from Sigma-Aldrich (St. Louis, Missouri) or ChemService (West Chester, Pennsylvania) and were accompanied by a certificate of analysis provided by the supplier. Battelle QA staff audited the gravimetric preparation of these solutions.

3.2.3 Stage 3, Extended Deployment

In the first phase of Stage 3 of the verification test, the performance of the Sentinal™ 500 units was evaluated during 52 days of continuous operation. The Sentinal™ 500 required no regularly scheduled maintenance during this deployment. To track the performance of the Sentinal™ 500 with respect to the reference results, reference samples were collected and analyzed for the selected parameters at least once per day (excluding weekends and holidays) for the duration of Stage 3. All continuously measured data were graphed, along with the results from the reference measurements, to provide a qualitative evaluation of the data. Throughout the duration of the deployment, the average percent difference (%D), as defined in Section 5.1, between the results from the Sentinal™ 500 units and those from the reference methods was evaluated.

The final phase of Stage 3 (which immediately followed the first phase of Stage 3 and lasted approximately one week) consisted of a two-step evaluation of the Sentinal™ 500 performance after the 52-day extended deployment to determine whether this length of operation would negatively affect the results from the Sentinal™ 500. First, while the Sentinal™ 500s were continuously operating, a reference sample was collected every hour during a 4-hour analysis period and analyzed using the standard reference methods. This was done to define a formal time period of stable water quality conditions for the accuracy of the Sentinal™ 500 to be evaluated. Second, to evaluate the response of the Sentinal™ 500 to contaminant injection after the extended deployment, the duplicate injection of aldicarb, which was also included in the Stage 2 testing, was repeated. In addition, a pure *E. coli* culture, including the *E. coli* and the growth medium, was included as a second injected contaminant during Stage 3. *E. coli* was intended as an injected contaminant during Stage 2, but was not available until later in the test. During this contaminant injection component of Stage 3, reference samples were collected as they were during Stage 2.

3.3 Laboratory Reference and Quality Control Samples

The Sentinal™ 500 units were evaluated by comparing their results with laboratory reference measurements. The following sections provide an overview of the applicable procedures, analyses, and methods.

3.3.1 Reference Methods

To eliminate the possibility of using stagnant water residing in the reference sample collection valve (dead volume) as the reference samples, the first step in the reference sample collection procedure included collecting and discarding approximately 1 L of water, which was estimated to be approximately 10 times the dead volume of the reference sample collection valve. Then, from the same valve, approximately 1 L of water was collected in a glass beaker and carried directly to a technician, who immediately began the reference analyses. All the analyses were performed within minutes of sample collection. The standard laboratory methods used for the reference analyses are shown in Table 3-1. Also included in the table are method detection limits and quality control (QC) measurement differences. Battelle technical staff collected the reference samples, and technical staff at the T&E Facility performed the analyses. The T&E Facility provided calibrated instrumentation, performed all method QA/QC, and provided calibration records for all instrumentation. The T&E Facility provided reference sample results upon the analysis of the reference samples (within one day). Because previous work at the T&E facility[2] showed that the laboratory reference method for ORP using a grab sample is not directly comparable to a continuous measurement in a flowing pipe, accuracy results were not included for ORP. ORP reference and continuous measurement results were, however, included for the purpose of a qualitative accuracy evaluation in figures showing the continuous data and reference method results. Although the ORP reference value may not be equivalent to the continuous measurement, changes in the continuous measurements were evaluated with the reference results to determine whether the sensor was identifying increases and decreases correctly and whether both units were producing similar results.

Table 3-1. Reference Methods

Parameter	Method	Reference Instruments	Method Detection Limit	Acceptable Differences for QC Measurements
pH	EPA 150.1[3]	Corning 320 pH meter	NA	±0.3 pH units
Conductivity	SM 2510[4]	YSI 556 multi-parameter water monitor	2 microSiemens/ centimeter (µS/cm)	±25%D
Free chlorine	SM 4500-G[5]	Hach 2400 portable spectrophotometer	0.01 mg/L as Cl_2	±25%D
ORP[a]	SM 2580-B[6]	YSI 556 multi-parameter water monitor	NA	±25%D
Temperature	EPA 170.1[7]	YSI 556 multi-parameter water monitor	NA	±1°C

[a] The reference method for measuring ORP is not directly comparable because of the difference in potential in a flowing pipe compared to that measured in a grab sample.
NA = not applicable.

3.3.2 Reference Method Quality Control Samples

As shown in Table 3-2, duplicate reference samples were collected and analyzed once daily during Stages 1 and 2 and weekly during Stage 3. Also, laboratory blanks consisting of American Society for Testing and Materials Type II deionized (DI) water were analyzed with the same frequency. These blank samples were most important for chlorine because it was the only parameter that needed confirmation of the lack of contamination. For the other parameters, the performance evaluation (PE) audit confirmed the accuracy of the method and the absence of contamination. Duplicate measurements had to be within the acceptable differences provided in Table 3-1.

Table 3-2. Reference Analyses and Quality Control Samples

Stage	Sampling Periods (length)	Reference Sample Frequency	Reference Samples per Period	QC Samples per Period	Total QC Samples
1: Accuracy	9 (4 hours)	One at start, one every hour thereafter	5	One duplicate and one DI water blank daily	18
2: Response to injected contaminants	6 (one injection)	One pre-injection; one at 3, 15, and 60 minutes post-injection	4	One duplicate and one DI water blank daily	12
3: Extended deployment	1 (52 days)	Once each weekday	37	One duplicate and one DI water blank each week	16
3: Post-extended deployment accuracy	1 (4 hours)	Same as Stage 1	5	Same as Stage 1	2
3: Response to injected contaminants	4 (one injection)	Same as Stage 2	4	Same as Stage 2	8

Chapter 4
Quality Assurance/Quality Control

QA/QC procedures were performed in accordance with the quality management plan (QMP) for the AMS Center[8] and the test/QA plan [1] for this verification test.

4.1 Audits

4.1.1 Performance Evaluation Audit

A PE audit was conducted to assess the quality of the reference measurements made in this verification test. With the exception of temperature, each type of reference measurement was compared with a National Institute of Standards and Technology (NIST)-traceable standard reference water sample. The standard reference water samples had certified values of each water quality parameter that were unknown to the analyst. These samples were analyzed in the same manner as the rest of the reference analyses to independently confirm the accuracy of the reference measurements. The temperature PE audit was performed by comparing two independent thermometer results. As Table 4-1 shows, all PE audit results were within the acceptable differences provided in Table 3-1. The %D was calculated using the following equation:

$$\%D = \frac{C_R - C_N}{C_N} \times 100\%$$

where C_R is the reference method result and C_N is the NIST value for each respective water quality parameter (or, for temperature, data from the second thermometer). Other QC data collected during this verification test were reference method duplicate analysis results, which are also shown in Table 4-1. All parameters were always within the differences defined in Table 3-1. Because pH units are measured on a logarithmic, rather than linear, scale, and the measurement of temperature is extremely precise; the quality control metrics for those two parameters were the absolute units rather than percent difference.

4.1.2 Technical Systems Audit

The Battelle Quality Manager performed a technical systems audit (TSA) to ensure that the verification test was performed in accordance with the AMS Center QMP,[8] the test/QA plan,[1] published reference methods, and any standard operating procedures used by the T&E Facility. The TSA noted no adverse findings. A TSA report was prepared, and a copy was distributed to the EPA AMS Center Quality Manager.

Table 4-1. Performance Evaluation Audit and Reference Method Duplicate Analysis Results

Parameter	PE Audit			Duplicate Analysis	
	NIST Standard Value	Reference Method Result	Difference	Average of Absolute Values of Difference	Range of Difference
pH	9.26	9.18	-0.08 pH units	0.04 pH units	0.0 to 0.13 pH units
Conductivity (µS/cm)	1,920	1,706	-11.15%	0.25%	-1.9 to 0.7%
Free chlorine (mg/L)	4.19	3.62	-13.6%	2.62%	-7.3 to 2.1%
Temperature (°C)	23.0[a]	23.80	0.00°C	0.02 °C	-0.18 to 0.29°C

[a] Since a standard for temperature does not exist, the PE audit for temperature was performed by comparing the results with those from a second thermometer.

ORP was not included in the accuracy evaluation because of the lack of an appropriate reference method.

4.1.3 Audit of Data Quality

At least 10% of the data acquired during the verification test was audited. Battelle's Quality Manager traced the data from the initial acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit also were checked.

4.2 Quality Assurance/Quality Control Reporting

Each assessment and audit was documented in accordance with Sections 3.3.4 of the QMP for the ETV AMS Center.[8] Once the assessment report was prepared, the Battelle Verification Test Coordinator ensured that a response was provided for each adverse finding or potential problem and implemented any necessary follow-up corrective action. The Battelle Quality Manager ensured that follow-up corrective action was taken. The results of the TSA were sent to the EPA.

4.3 Data Review

Records generated in the verification test were reviewed before these records were used to calculate, evaluate, or report verification results. Table 4-2 summarizes the types of data recorded. The review was performed by a technical staff member involved in the verification test, but not the staff member who originally generated the record.

Table 4-2. Summary of Data Recording Process

Data to Be Recorded	Where Recorded	How Often Recorded	By Whom	Disposition of Data
Dates, times, and details of test events	ETV data sheets and testing notebook	Start/end of test and at each change of a test parameter	Battelle and T&E Facility	Used to organize/check test results; manually incorporated in data spreadsheets as necessary
Calibration information (Sentinal™ 500 units and reference methods)	ETV data sheets and testing notebook	Upon each calibration	Battelle and T&E Facility	Manually incorporated in data spreadsheets as necessary
Sentinal™ 500 units results	Recorded electronically by each monitor and then downloaded to computer daily	Recorded continuously	Battelle	Excel files
Reference method procedures	ETV laboratory record books or data recording forms	Throughout sample analysis process	T&E Facility	Transferred to spreadsheets or laboratory record book

Chapter 5
Statistical Methods

The statistical methods presented in this chapter were used to verify the Sentinal™ 500 units' accuracy, response to injected contaminants, and inter-unit reproducibility.

5.1 Accuracy

Throughout this verification test, results from the Sentinal™ 500 units were compared to the results obtained from analysis of a grab sample by the reference methods. During Stage 1, the percent difference (%D) between these two results was calculated using the following equation:

$$\%D = \frac{C_m - C_R}{C_R} \times 100\%$$

where C_R is the result determined by the reference method and C_m is the result from a Sentinal™ 500 unit; the Sentinal™ 500 unit results were recorded every 30 seconds, whereas collecting the reference samples took only a few seconds. Therefore, C_m was the measurement recorded closest to the time the reference sample was collected. Water quality stability, as well as the stability of each sensor, was evaluated during the four-hour time period when reference samples were analyzed every hour for each of the parameters. Ideally, if the result from a Sentinal™ 500 unit and a reference method measurements were the same, there would be a percent difference of zero. During Stages 2 and 3, the continuous data, graphed with the reference method results, were visually examined to evaluate the response of the Sentinal™ 500 units to the injection of contaminants and their stability over an extended deployment. During the accuracy and contaminant injection components of Stage 3, the data were evaluated as they were for Stages 1 and 2, respectively.

5.2 Response to Injected Contaminants

To evaluate the response (i.e., the increase or decrease of water quality parameter measured by the of the Sentinal™ 500 units) to contaminant injections, the pre- and post-injection reference samples were graphed as individual data points, along with the continuous measurements. The reference results showed the effect of each injection on the chemistry of the water in the pipe loop, and the continuous results from the Sentinal™ 500 unit highlighted its response to such changes.

5.3 Inter-unit Reproducibility

The results obtained from two identical Sentinal™ 500 units were compared to assess inter-unit reproducibility. Each time a reference sample was collected and analyzed (approximately 127 times throughout this verification test), the results from each Sentinal™ 500 unit were compared to evaluate whether the two units were generating similar results. This was done in two ways. First, the results from one unit were graphed against the results of the other unit. In this evaluation, a slope of unity and a coefficient of determination (r^2) of 1.0 would indicate ideal inter-unit reproducibility. Slopes above 1.0 may indicate a high bias from Unit 2 (graphed on the y-axis) or a low bias for Unit 1 with respect to each other. Similarly, slopes below 1.0 may indicate a low bias for Unit 2 or a high bias for Unit 1, again with respect to each other. Second, the data from each unit were included in a paired t-test, with the assumption that the data from each unit had equal variances. The t-test calculated the probability of obtaining the subject results from the two units if there was no significant difference between their results. Therefore, probability values (p-values) of less than 0.05 (i.e., less than a 5% probability that this data set would be generated if there actually was no difference between the two units) indicated a significant difference between the two units. In addition, the results from both units were graphed together for the Stages 2 and 3 results, allowing a visual comparison.

Chapter 6
Test Results

As mentioned previously, this verification test was conducted in three stages that focused on three different aspects of multi-parameter water monitors for distribution systems. The three stages are summarized in Table 6-1. The first stage consisted of an evaluation (with varied pHs and temperatures) of the accuracy of each sensor: free chlorine, temperature, conductivity, and pH. ORP also was measured; but, because a laboratory reference measurement equivalent to the on-line continuous measurement was not available, ORP was not included in the accuracy evaluation. The second stage of the verification test consisted of an evaluation of the response of the Sentinal™ 500 units to the injection of several contaminants into the pipe loop. The third stage consisted of deploying the Sentinal™ 500 units for 52 consecutive days with minimal intervention for maintenance. In addition, contaminant injections were performed at the close of Stage 3 to confirm that the Sentinal™ 500 units were still responsive to contaminant injection after the extended deployment. Two Sentinal™ 500 units were tested to evaluate inter-unit reproducibility. In addition, required maintenance and operational characteristics were documented throughout the verification test. This chapter provides the results of the three testing stages, the inter-unit reproducibility data, and ease of use information.

Table 6-1. Summary of Test Stages and Type of Data Presentation

Stage	Summary	Data Presentation
1	Accuracy when pH and temperature were varied	Table of percent differences between Sentinal™ 500 units and reference measurements
2	Response to contaminant injection	Graphs of Sentinal™ 500 unit measurements and reference measurements, table showing the effect of injections on both reference and Sentinal™ 500 measurements
3	Extended deployment with minimal maintenance along with post-extended deployment accuracy and response to contaminant injections	Graphs of Sentinal™ 500 unit measurements with reference measurements, table showing average percent differences throughout extended deployment, table showing the effect of injections on both reference and Sentinal™ 500 measurements

6.1 Accuracy

Tables 6-2a–d list the data from the accuracy evaluation performed during the first stage of the verification test. During four-hour periods, the water quality conditions were held stable, and reference samples were collected and analyzed five times, once at the start of the designated test period and four times at one-hour increments thereafter. Because reference sample collection took just a few seconds and the results from the Sentinal™ 500 units were recorded every 30 seconds, the water quality parameter measurement at the time closest to reference sample collection was compared to the reference sample. For each unit, this approach resulted in five paired Sentinal™ 500 and reference results for each of nine sets of water conditions used to simulate pH and temperature variations at a water utility. The average and standard deviations of these five results are shown in the tables below, as well as the percent differences between the average results from both Sentinal™ 500 units and the average of the reference results.

Table 6-2a. Accuracy Evaluation Under Various Conditions—Free Chlorine

Set	Conditions	Reference Average (SD) [mg/L]	Unit 1 Average (SD) [mg/L]	Unit 1 % D	Unit 2 Average (SD) [mg/L]	Unit 2 % D
1	ambient pH, ambient temperature	0.91 (0.08)	1.00 (0.00)	9.9	0.97 (0.00)	6.6
2	decreased pH, ambient temperature	0.78 (0.02)	0.86 (0.05)	10.3	1.05 (0.08)	34.6
3	decreased pH, ambient temperature	0.65 (0.01)	0.82 (0.00)	26.2	0.82 (0.00)	26.2
4	decreased pH, ambient temperature	0.29 (0.02)	0.34 (0.01)	17.2	0.34 (0.01)	17.2
5	ambient pH, decreased temperature	0.41 (0.08)	0.83 (0.05)	102.4	0.89 (0.05)	117.1
6	decreased pH, decreased temperature	1.47 (0.06)	1.86 (0.07)	26.5	1.52 (0.02)	3.4
7	ambient pH, increased temperature	0.60 (0.04)	0.96 (0.03)	60.0	1.05 (0.02)	75.0
8	decreased pH, increased temperature	0.54 (0.05)	0.72 (0.07)	33.3	0.67 (0.05)	24.1
9	ambient pH, ambient temperature	0.91 (0.03)	1.20 (0.02)	31.9	1.08 (0.02)	18.7

Table 6-2b. Accuracy Evaluation Under Various Conditions—Temperature

Set	Conditions	Reference Average (SD) [°C]	Unit 1 Average (SD) [°C]	Unit 1 % D	Unit 2 Average (SD) [°C]	Unit 2 % D
1	ambient pH, ambient temperature	22.66 (0.33)	21.80 (0.11)	-3.8	21.40 (0.14)	-5.6
2	decreased pH, ambient temperature	22.73 (0.23)	21.89 (0.07)	-3.7	21.46 (0.12)	-5.6
3	decreased pH, ambient temperature	21.61 (0.16)	21.05 (0.07)	-2.6	21.05 (0.07)	-2.6
4	decreased pH, ambient temperature	21.93 (0.15)	21.72 (0.04)	-1.0	21.11 (0.05)	-3.7
5	ambient pH, decreased temperature	13.82 (0.44)	11.98 (0.19)	-13.3	11.64 (0.22)	-15.8
6	decreased pH, decreased temperature	12.63 (0.26)	10.52 (0.25)	-16.7	10.31 (0.21)	-18.4
7	ambient pH, increased temperature	26.60 (0.27)	27.31 (0.05)	2.7	26.82 (0.02)	0.8
8	decreased pH, increased temperature	26.69 (0.23)	27.34 (0.07)	2.4	26.76 (0.06)	0.3
9	ambient pH, ambient temperature	22.79 (0.21)	22.41 (0.29)	-1.7	21.86 (0.31)	-4.1

Table 6-2c. Accuracy Evaluation Under Various Conditions—Conductivity

Set	Conditions	Reference Average (SD) [µS/cm]	Unit 1		Unit 2	
			Average (SD) [µS/cm]	% D	Average (SD) [µS/cm]	% D
1	ambient pH, ambient temperature	451 (1)	334 (2)	-25.9	341 (1)	-24.4
2	decreased pH, ambient temperature	484 (10)	360 (8)	-25.6	365 (8)	-24.6
3	decreased pH, ambient temperature	503 (6)	380 (4)	-24.5	380 (4)	-24.5
4	decreased pH, ambient temperature	694 (12)	515 (8)	-25.8	517 (8)	-25.5
5	ambient pH, decreased temperature	412 (1)	318 (1)	-22.8	319 (1)	-22.6
6	decreased pH, decreased temperature	501 (10)	380 (10)	-24.2	389 (9)	-22.4
7	ambient pH, increased temperature	447 (1)	327 (2)	-26.8	337 (1)	-24.6
8	decreased pH, increased temperature	529 (2)	391 (4)	-26.1	397 (2)	-25.0
9	ambient pH, ambient temperature	442 (1)	329(1)	-25.6	336 (0)	-24.0

Table 6-2d. Accuracy Evaluation Under Various Conditions—pH

Set	Conditions	Reference Average (SD) [pH unit]	Unit 1 Average (SD) [pH unit]	Unit 1 % D	Unit 2 Average (SD) [pH unit]	Unit 2 % D
1	ambient pH, ambient temperature	8.76 (0.02)	8.62 (0.00)	-1.6	8.80 (0.00)	0.5
2	decreased pH, ambient temperature	7.89 (0.09)	7.72 (0.14)	-2.2	7.77 (0.16)	-1.5
3	decreased pH, ambient temperature	7.52 (0.04)	7.32 (0.04)	-2.7	7.32 (0.04)	-2.7
4	decreased pH, ambient temperature	6.73 (0.12)	6.38 (0.07)	-5.2	6.32 (0.06)	-6.1
5	ambient pH, decreased temperature	8.48 (0.02)	8.52 (0.02)	0.5	8.51 (0.01)	0.4
6	decreased pH, decreased temperature	7.31 (0.08)	7.06 (0.09)	-3.4	7.09 (0.10)	-3.0
7	ambient pH, increased temperature	8.37 (0.05)	8.30 (0.04)	-0.8	8.34 (0.03)	-0.4
8	decreased pH, increased temperature	7.60 (0.06)	7.32 (0.02)	-3.7	7.27 (0.01)	-4.3
9	ambient pH, ambient temperature	8.74 (0.01)	8.65 (0.01)	-1.0	8.67 (0.02)	-0.8

Of the parameters that were evaluated for accuracy, the free chlorine sensor generated the largest range of percent differences compared to the reference method (with the median shown in parentheses): from 3.4 to 117.1 (26.2); for temperature, -18.4 to 2.7 (-3.7); for conductivity -26.8 to -22.4 (-24.6); and for pH, -6.1 to 0.5 (-1.9).[1] The chlorine sensor was calibrated by the vendor before the verification test, but was not recalibrated throughout Stage 1. The tendency evidenced by the range and median was for the sensor to drift high. As discussed in Section 6.2, calibration of the free chlorine sensor was required to maintain accurate free chlorine measurements. The temperature sensors generated very small percent differences (between -6% and 0%) with respect to the reference method at ambient temperatures, larger negative percent differences (between -13% and -18%) when the temperature of the water in the pipe loop was decreased, and small positive percent differences (between 0% and 3%) when the temperature of the pipe loop water was increased. This trend in percent differences is thought to be chiefly a result of the reference sample collection and analysis procedure. Reference samples were carried to a laboratory bench approximately 25 feet from the reference sample collection valve. Therefore, upon sample collection, the reference sample immediately began equilibrating with the ambient

[1] Throughout this report, median values are provided when a range of values is presented. The median of a set of positive and negative numbers provides a good indicator of the overall direction of the percent differences in the data set (i.e., whether most values were positive or negative). The disadvantage is that, unless the signs of all the data are the same, information about the magnitude of change is not available from the median. In summary, the medians in this report provide the direction, not magnitude, of difference information.

air, causing the trends in percent differences with respect to the reference method. The conductivity results generated a consistently negative percent difference throughout Stage 1, but one recalibration of the conductivity sensor to match the reference result corrected the negative percent difference. Stages 2 and 3 exhibited very small conductivity percent differences.

The standard deviations of the reference and continuous measurements collected during each test period were, with few exceptions, very small with respect to the average result. In only a few instances was the standard deviation greater than 5% of the average result. This shows both that the water conditions during these test periods were very stable and that there was very little variability in the sensors themselves.

6.2 Response to Injected Contaminants

Six injections of contaminants were performed during the second stage of this verification test; i.e., duplicate injections of nicotine, arsenic trioxide, and aldicarb. Table 6-3 shows the directional change of each reference and Sentinal™ 500 measurement in response to the contaminant injections. In general, free chlorine and ORP were the only parameters clearly affected (for both the reference and continuous measurements) by all six injections. Figures 6-1 through 6-4 show the responses of free chlorine, ORP, conductivity, and pH. The blue and yellow lines on the graphs represent the measurements made by each Sentinal™ 500 unit, and the magenta data points represent the results from the laboratory reference method. Because accuracy was the focus of the first stage of verification testing, percent differences between the Sentinal™ 500 units and the reference method results are not presented here; however, the reference method results are included in these figures to confirm that the fluctuations in the continuous results are due to changes in water chemistry as the result of the injected contaminants. The figures are divided with vertical lines that define the approximate time period for each injection. Each injection time period defined on the figures is approximately 24 hours, but the times vary somewhat depending on when chlorine was added to restore the system to pre-injection conditions. The contaminant that was injected and whether it was the first or second replicate are shown at the top of each section of the figures. For each injection, at least four reference sample results were collected and are included in these figures. The first occurred within approximately one hour prior to contaminant injection during a period of stable water quality conditions. The next three reference data points were from samples collected 3, 15, and 60 minutes after contaminant injection. For some of the injections, another reference sample was collected the following day to show that the pipe loop system had recovered or was in the process of recovering after the injection. This final reference data point also served as the first reference sample collected for some of the injections, representing the stable baseline just prior to injection.

Table 6-3. Effect of Contaminant Injections Prior to Extended Deployment

Parameter	Nicotine		Arsenic Trioxide		Aldicarb	
	Reference	Sentinal™ 500	Reference	Sentinal™ 500	Reference	Sentinal™ 500
Free chlorine	–	–	–	–	–	–
Temperature	NC	NC	NC	NC	NC	NC
Conductivity	NC	NC	+	+	NC	NC
pH	NC	NC	+	+	NC	NC
ORP	–	–	–	–	–	–

+/− = Parameter measurement increased/decreased upon injection.
NC = No change in response to the contaminant injection.

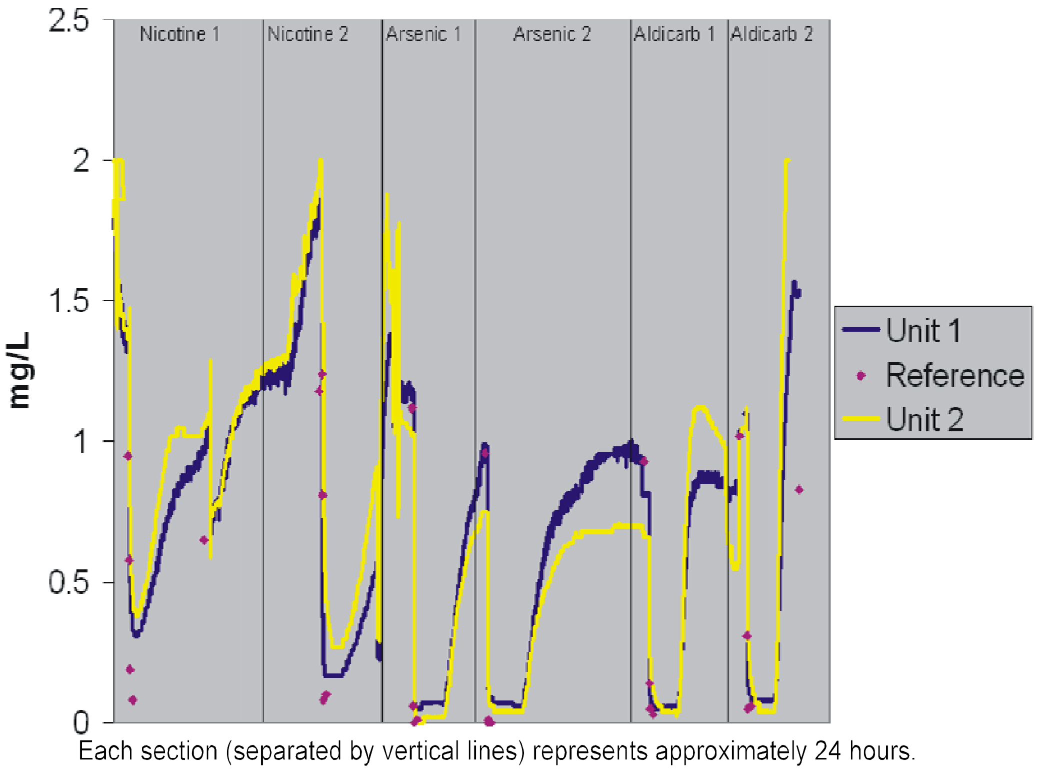

Figure 6-1. Stage Contaminant Injection Results for Free Chlorine

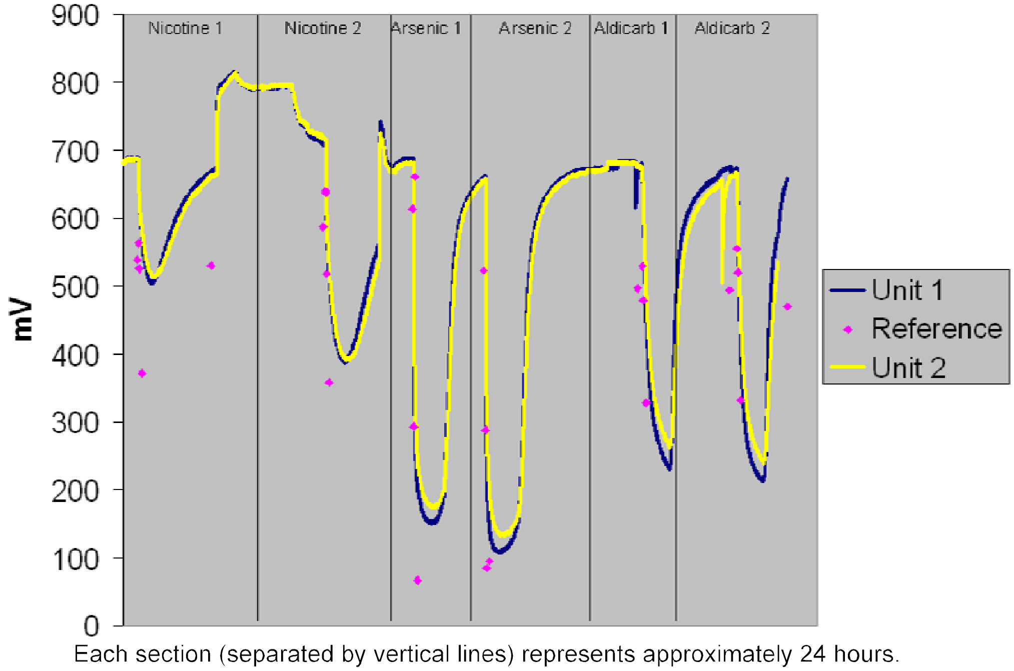

Figure 6-2. Stage 2 Contaminant Injection Results for ORP

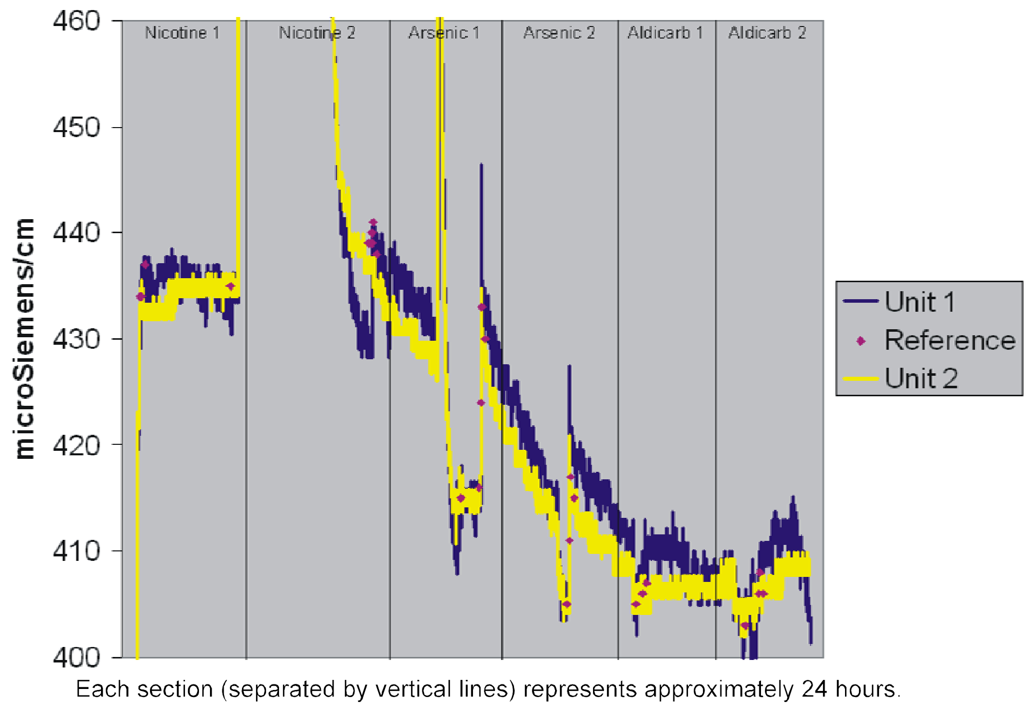

Figure 6-3. Stage 2 Contaminant Injection Results for Conductivity

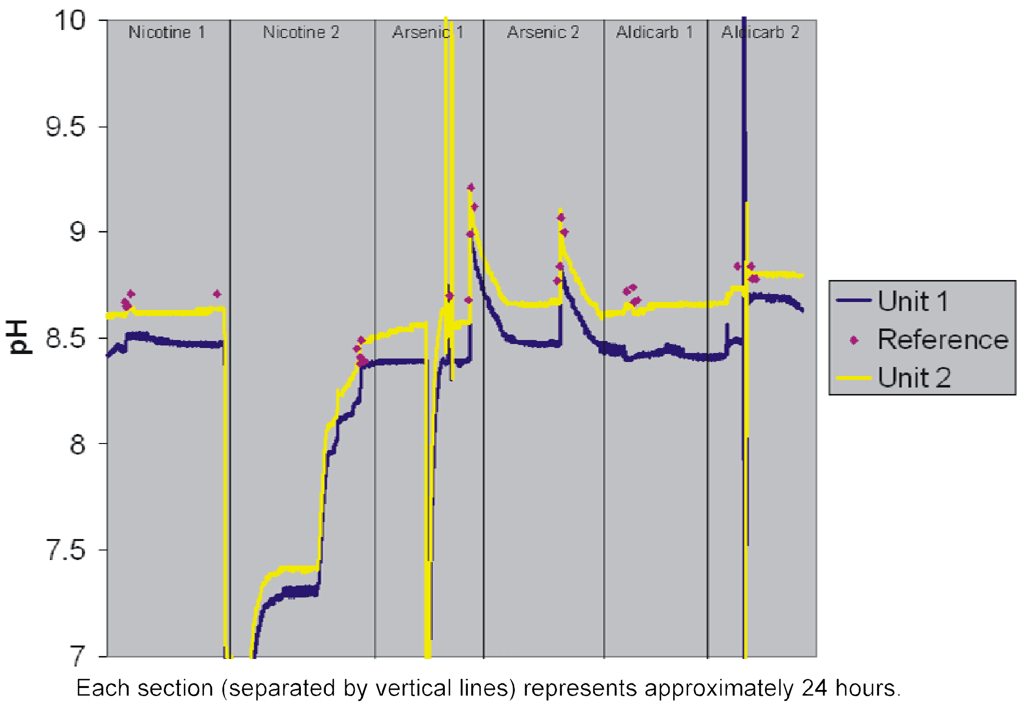

Figure 6-4. Stage 2 Contaminant Injection Results for pH

Figure 6-1 shows how the measurement of free chlorine was affected by the contaminant injections. Prior to the injections, the free chlorine level was maintained at approximately 1 mg/L. At the start of Stage 2, the Sentinal™ 500 unit's measurements had drifted significantly higher than the reference measurement, a trend that had been observed during Stage 1. Nonetheless, in each case, within one hour of contaminant injection, the free chlorine level, as measured by the laboratory reference method, dropped to its low point. As evidenced by the vertical drop in the line representing the free chlorine concentration, it was clear that the chlorine sensor on the Sentinal™ 500 units responded to the decrease in free chlorine levels as a result of the presence of the contaminant. In addition to the high measurements prior to the injections, the Sentinal™ 500 units recovered from both nicotine injections to levels higher than for the reference method. Note that just prior to the first arsenic injection, the chlorine measurements dropped to match the reference measurement much more closely. At this time, the chlorine sensors were calibrated to match the reference method measurements. Thereafter, the sensors seemed less prone to recovering to a result biased high, but Unit 2 appeared to have drifted low after the arsenic injection. Also, after the first aldicarb injection, Unit 2 recovered to a high measurement and Unit 1 drifted low. Both sensors were calibrated prior to the final aldicarb injection, which is evidenced by the convergence of their respective lines. Also, after the second aldicarb injection, both chlorine sensors recovered to very high measurements, requiring calibration prior to the next stage of the verification test. For each injection, the drop in free chlorine levels was followed by the restoration of the pipe loop system to approximately pre-injection conditions through the addition of sodium hypochlorite. This is shown in Figure 6-1 by the rapidly increasing free chlorine concentration after the sensor reaches a low point in free chlorine concentration.

The ORP in water is dependent on the occurrence of oxidation-reduction chemical reactions within the water. Therefore, when free chlorine is reacting with injected contaminants, it can be expected that the ORP would be affected. Figure 6-2 shows that ORP tracked the concentration of free chlorine upon injection of the contaminants. The free chlorine reacted with the contaminants, and the concentration dropped, as did the ORP. It is difficult to determine if the change in ORP is in response to the drop in free chlorine or to the presence of the contaminant itself. Conductivity and pH were affected (as measured by both the reference and continuous measurement) by the injection of arsenic trioxide only. However, this may have been due to the pH adjustment required to get it into solution.

6.3 Extended Deployment

Figures 6-5 through 6-9 show the continuous measurements from both Sentinal™ 500 units during the 52-day extended deployment stage of the verification test. Those measurements are represented by the blue and yellow lines, while the results of the reference samples, collected once daily throughout this deployment, are represented by the magenta symbols. The x-axis on each figure represents the period of time between September 1, 2004, and October 22, 2004, and the y-axis gives the results of each water quality measurement. Data points were recorded every 30 seconds during the verification test; but, for the extended deployment figures, only data points collected approximately every 2 minutes were depicted. This was done so that a standard spreadsheet could be used to generate these figures. This approach was inconsequential to interpreting the figures.

The objective of this stage of the verification test was to evaluate the performance of the Sentinal™ 500 unit over an extended period of time with minimal intervention to simulate a situation in which the units may be deployed at a remote location. The continuous trace was visually evaluated to see whether any aspects of the data were noteworthy. A second, more quantitative, evaluation was then performed to get an indication of the accuracy of the extended deployment measurements. This evaluation, much like the accuracy evaluation conducted during the first stage of testing, included calculating the percent differences between the average continuous measurements and average reference sample results throughout the extended deployment, as well as the standard deviation of each of those measurements. The standard deviation of the results provided a means to evaluate the stability of the water conditions during Stage 3, as well as how the standard deviations of the continuous measurements differed from the standard deviations of the reference measurements. Similar relative standard deviations between the continuous and reference measurements indicate that variability was mostly dependent on the water conditions and not due to systematic variability in the Sentinal™ 500 unit results. (Note that the reference results were only generated during business hours, so any fluctuations occurring during off hours were not reflected in the standard deviation of the reference results. Because of this, free chlorine, a parameter that varied at times during weekends when the supply of chlorine ran low, might have been expected to have a larger variability than other more stable parameters.) Table 6-4 lists the percent differences, along with the average and standard deviations of the reference and continuous results during the extended deployment. The range and median (see the footnote in Section 6.1 for direction on interpreting the median) percent difference for each water quality parameter, as measured for each reference sample analyzed during the extended deployment, are also given.

For free chlorine, visual inspection of the data in Figure 6-5 revealed that, at the start of Stage 3, the Sentinal™ 500 units' measurements were dropping from the high reading to which they had

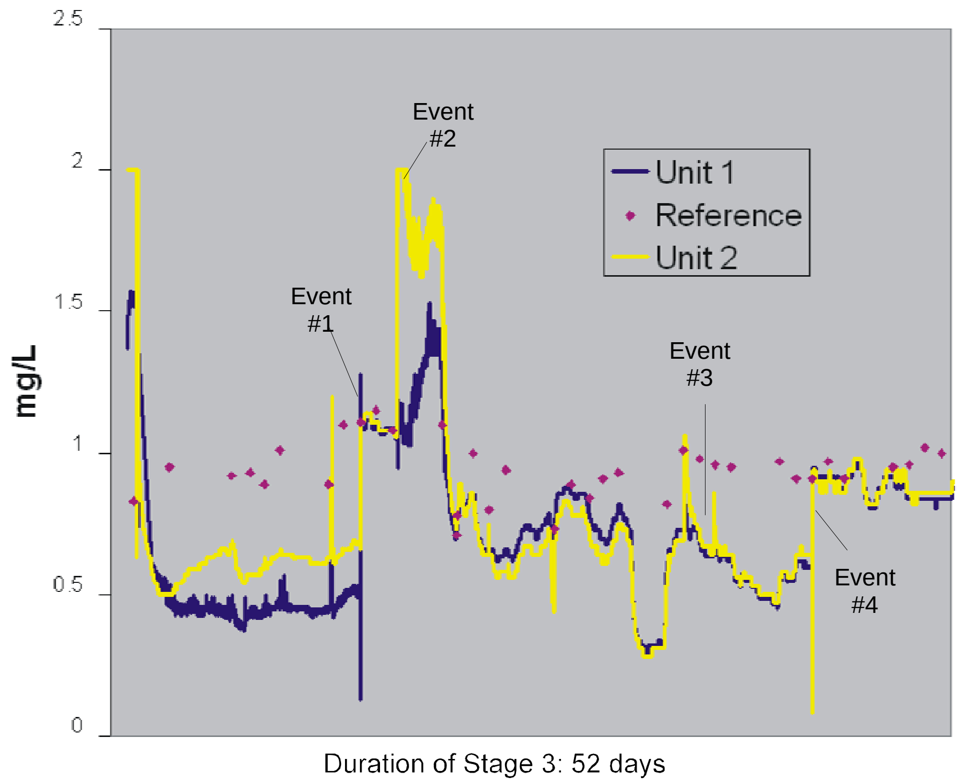

Figure 6-5. Extended Deployment Results for Free Chlorine

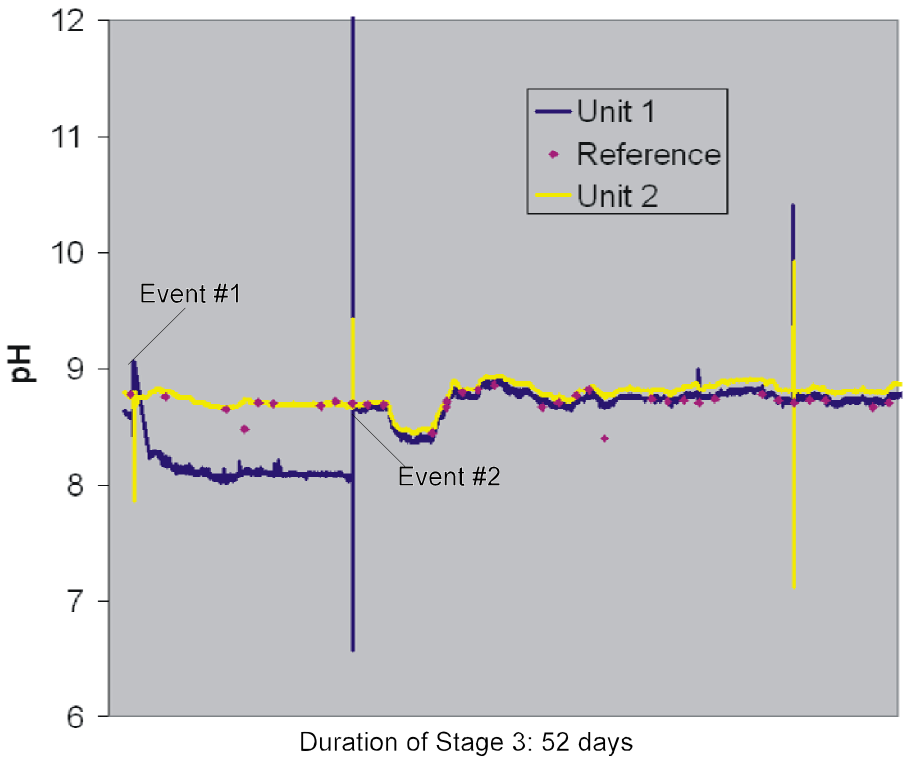

Figure 6-6. Extended Deployment Results for pH

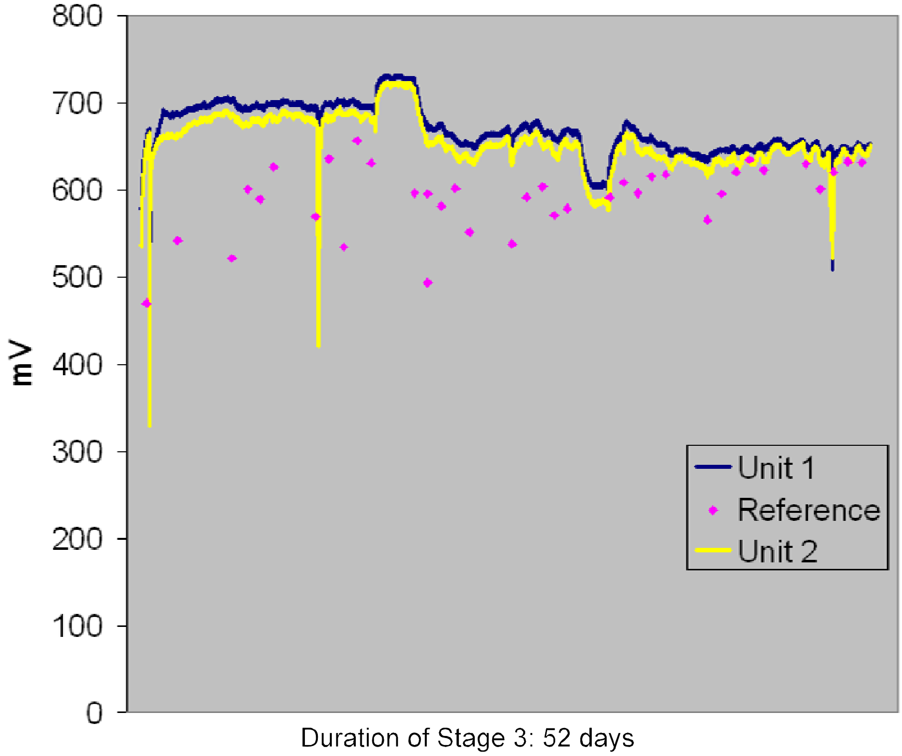

Figure 6-7. Extended Deployment Results for ORP

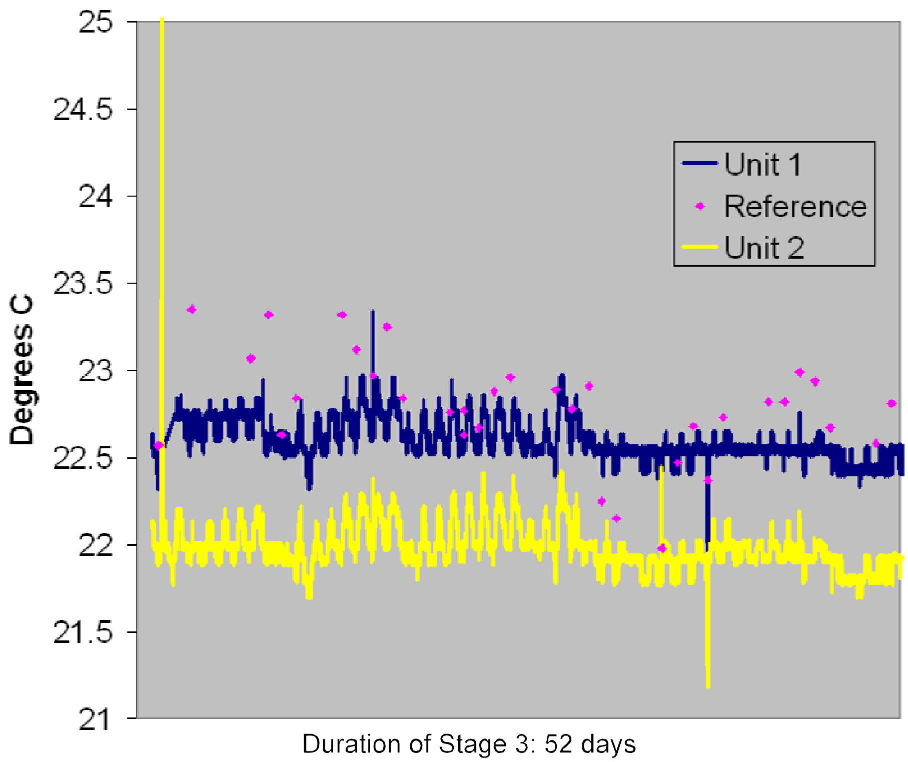

Figure 6-8. Extended Deployment Results for Temperature

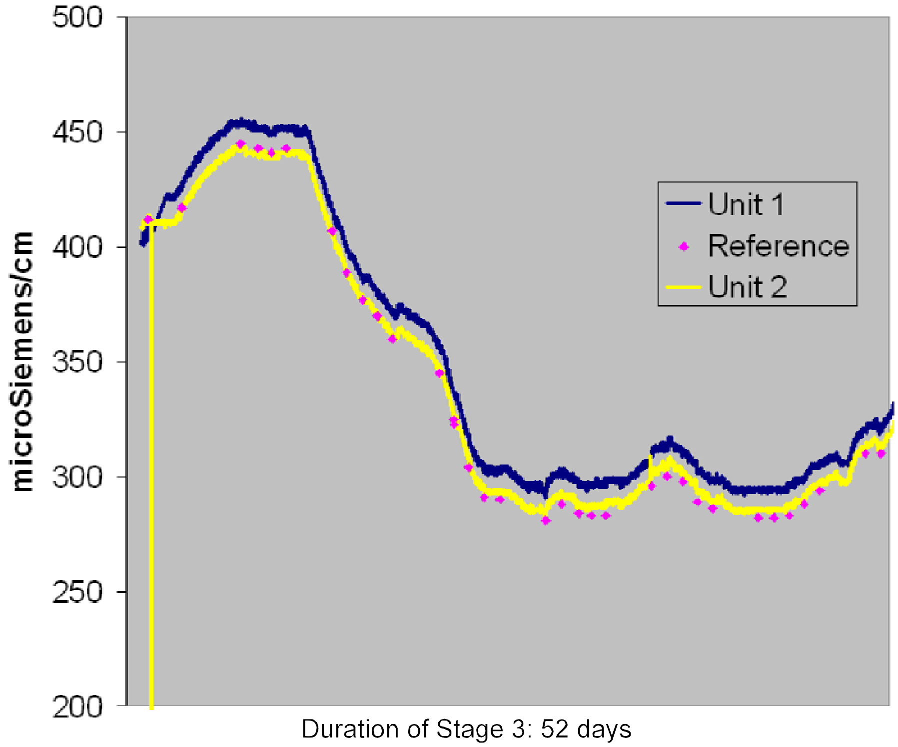

Figure 6-9. Extended Deployment Results for Conductivity

Table 6-4. Accuracy During Extended Deployment

Parameter	Reference average (SD)[(a)]	Unit 1		Unit 2		Both Units %D Range (median)
		Average (SD)[(a)]	%D	Average (SD)[(a)]	%D	
Free chlorine	0.95 (0.09)	0.74 (0.22)	-22.1	0.76 (0.22)	-20.0	-54.8 to 50.0 (-21.5)
Temperature	22.83 (0.36)	22.58 (0.08)	-1.1	21.95 (0.08)	-3.9	-7.8 to 2.7 (-2.7)
Conductivity	333 (57)	345 (55)	3.6	335 (54)	0.6	-0.8 to 5.5 (2.1)
pH	8.72 (0.07)	8.60 (0.27)	-1.4	8.78 (0.08)	0.7	-7.2 to 1.6 (0.3)

(a) Free chlorine, mg/L; temperature, °C; conductivity, µS/cm; pH, pH units.

recovered after Stage 2. This drop was caused by the calibration of the sensors to match the reference result. It is not clear why the sensors did not track the reference measurements better thereafter; but, for the first approximately one-third of the extended deployment, the free chlorine measurements were approximately 0.5 mg/L (with some variation) for both Sentinal™ 500 units, while the reference method measurement was approximately 1 mg/L. At that point, Clarion directed the verification staff to recalibrate the chlorine and pH sensors based on the reference method result (free chlorine Event #1 in Figure 6-5). When this was done, both Sentinal™ 500 units tracked the free chlorine reference measurements rather well for several days until the measured chlorine concentrations drifted high (to nearly 2 mg/L) for a three-day period (free chlorine Event #2). The sensors recovered without recalibration and, with a few exceptions, tracked the reference method results fairly well until the supply of sodium hypochlorite (used to maintain the chlorine concentrations in the pipe loop) ran low after a weekend and the chlorine level dropped to less than 0.5 mg/L. After this drop, both chlorine sensors recovered to a measurement somewhat lower than the reference method (free chlorine Event #3). This continued until near the end of the extended deployment when the results from the two Sentinal™ 500 units abruptly converged to a measurement very similar to that of the reference measurement. This marked the time that Clarion again directed the verification staff to calibrate the chlorine sensors to match the reference method result (free chlorine Event #4). During the extended deployment, the percent differences for both Sentinal™ 500 units ranged from -54.8 to 50.0, with a median of -21.5. The average free chlorine concentration, as measured by the reference method, was 0.95 ± 0.09 mg/L.

The pH results are presented in Figure 6-6. For the first approximately one-third of the extended deployment, Unit 2 and the reference method were measuring the pH as approximately 8.8, while Unit 1 was measuring it as approximately 8.0. The start of Stage 3 corresponded with a data logging memory problem in Unit 1. The Clarion representative removed the memory module, had it repaired, and replaced it a couple of days later. The large difference between Units 1 and 2 began the same day the memory module was reinstalled in Unit 1 (pH Event #1 in Figure 6-6). For a reason that is not known, the pH sensor was either improperly calibrated or not calibrated that day. Both pH sensors were calibrated several days later (at the direction of Clarion), which is shown by the convergence of pH measurements for both units with the reference measurements (pH Event #2). After that, both pH sensors maintained the accuracy of the results rather well. The average pH, as measured by the reference method, was 8.72 ± 0.07, and the average pH measurements for Units 1 and 2, respectively, were 8.60 ± 0.27 and 8.78 ± 0.08. Overall, during the extended deployment, the percent difference for the pH sensor ranged from -7.2 to 1.6, with a median of 0.3.

The other three water quality parameters were not affected by the pH adjustment. The ORP, temperature, and conductivity sensors were allowed to operate without intervention throughout the extended deployment. The measurements from these three sensors are shown in Figures 6-7 through 6-9. In Figure 6-7, the ORP results are shown along with a laboratory reference method result. The reference method is not an accurate representation of water in a flowing pipe, but it can be used to evaluate a trend in the decrease and increase in the ORP, as it was in the previous section for the contaminant injections.

The Unit 1 and 2 conductivity results tracked the reference method results throughout the extended deployment. The temperature results from both Units 1 and 2 had regular variability because the test was conducted in a facility where the water temperature was heavily affected by the outdoor temperature; therefore, the water temperature changed as a function of the high and low for the day. Also, Unit 2 temperature results appeared to be biased low with respect to Unit 1 and the reference method.

6.4 Accuracy and Response to Injected Contaminants After Extended Deployment

After the 52-day deployment of the Sentinal™ 500 units with minimal intervention, their performance was evaluated during a 4-hour period of ambient pH and temperature during which reference samples were collected hourly. The results of this evaluation are given in Table 6-5. The percent differences determined after the extended deployment for free chlorine, conductivity, and pH were considerably different from those determined during Stage 1. This is due to the fact that each of these sensors was calibrated (as previously discussed) at least once between Stage 2 and Stage 3. In all three cases, the percent differences were closer to zero in the post-extended deployment accuracy evaluation.

Table 6-5. Post-Extended Deployment Results

Parameter	Reference average (SD)[a]	Unit 1 average (SD)[a]	Unit 1 %D	Unit 2 average (SD)[a]	Unit 2 %D
Free chlorine	0.92 (0.02)	0.82 (0.05)	-10.9	0.75 (0.10)	-18.5
Temperature	22.66 (0.16)	22.55 (0.01)	-0.5	21.95 (0.05)	-3.1
Conductivity	356 (1)	365 (2)	2.5	357 (1)	0.3
pH	8.59 (0.01)	8.59 (0.00)	0.0	8.69 (0.01)	1.2

[a] Free chlorine, mg/L; temperature, °C; conductivity, µS/cm; pH, pH units.

A second evaluation of the response to injected contaminants after the extended deployment used four contaminants. Two were a repeat of the aldicarb injections performed during Stage 2 and two were injections of *E. coli*, which was not available for injection during the earlier stage of the test. Table 6-6 gives the directional change of each reference measurement and Sentinal™ 500 measurement in response to the contaminant injections. In general, free chlorine, ORP, and pH were the three parameters that were affected (for both the reference and continuous measurements) by all four injections. These parameters are shown in Figures 6-10 through 6-12. Conductivity is shown in Figure 6-13. The response of the chlorine sensor was consistent for all four injections. The recovery of the chlorine sensors was not as consistent. After the first injection, the recovery was difficult to evaluate because of a chlorine concentration increase resulting from occurrences in the Cincinnati water system that could not be controlled. After the second and third injections, the sensors both recovered to a concentration less than the reference method. Therefore, the sensors were recalibrated prior to the final injection. After the final injection, the chlorine sensors recovered fully. As during Stage 2, the ORP sensor tracked the chlorine response for each injection. Again, it is difficult to determine whether the ORP change is due to the reaction of chlorine or the presence of the contaminant itself. For pH, the reference results indicated a decrease in response to all of the contaminant injections; this result was unexpected. Aldicarb had not altered the pH during the Stage 2 injections. In addition, the conductivity increased (in both the reference and continuous measurements) very slightly upon injection of the *E. coli.*

Table 6-6. Effect of Contaminant Injections After Extended Deployment

	E. coli		Aldicarb	
Parameter	**Reference**	**Sentinal™ 500**	**Reference**	**Sentinal™ 500**
Free chlorine	–	–	–	–
Temperature	NC	NC	NC	NC
Conductivity	+	+	NC	NC
pH	–	–	–	–
ORP	–	–	–	–

+/− = Parameter measurement increased/decreased upon injection.
NC = No change in response to the contaminant injection.

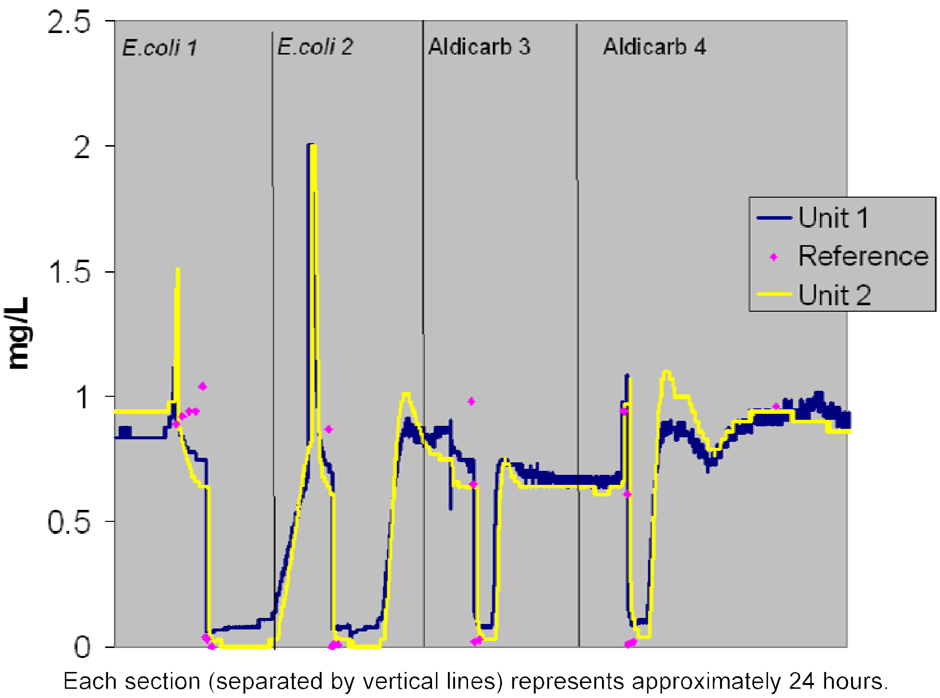

Figure 6-10. Stage 3 Contaminant Injection Results for Free Chlorine

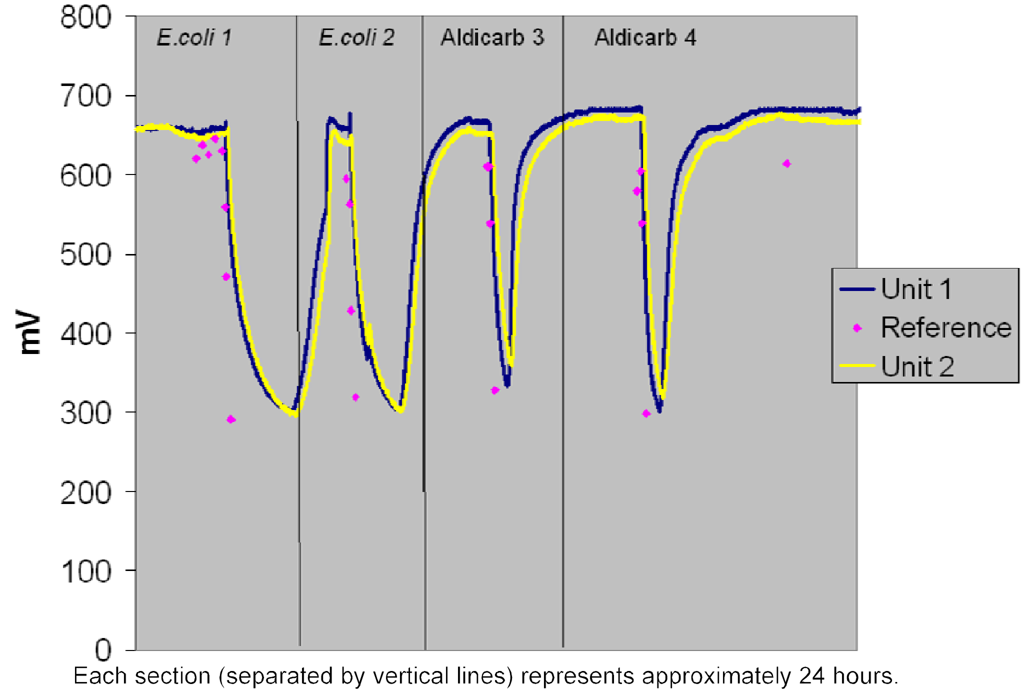

Figure 6-11. Stage 3 Contaminant Injection Results for ORP

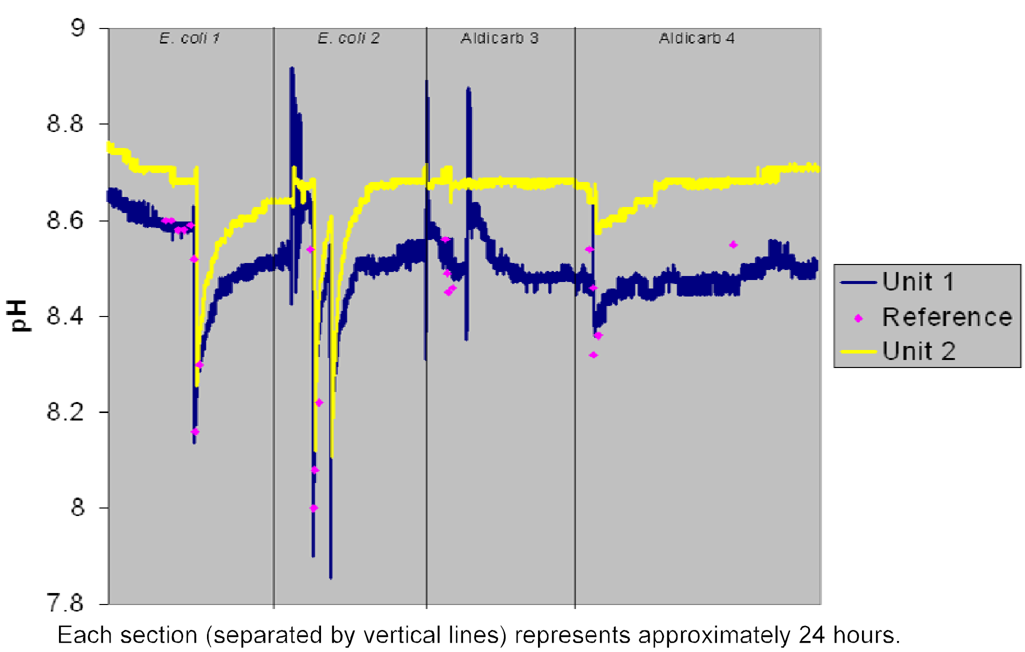

Figure 6-12. Stage 3 Contaminant Injection Results for pH

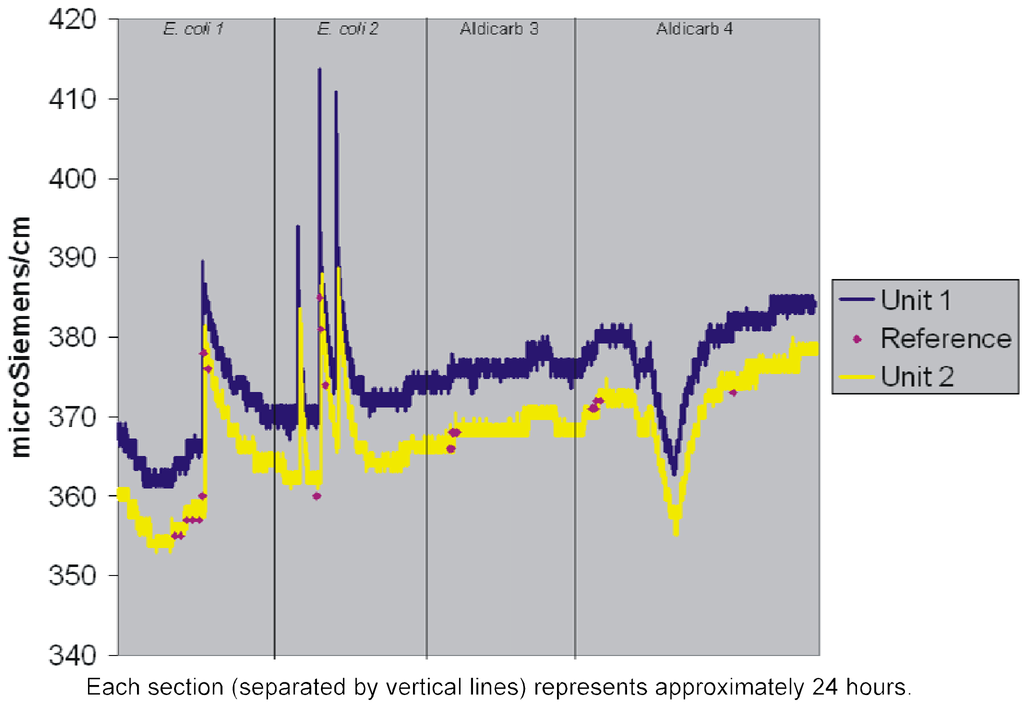

Figure 6-13. Stage 3 Contaminant Injection Results for Conductivity

6.5 Inter-unit Reproducibility

Two Sentinal™ 500 units were compared throughout the verification test to determine whether they generated results that were similar to one another. This was done using the Sentinal™ 500 data collected whenever a reference sample was collected throughout the verification test. Two evaluations were performed to make this comparison. First, the results from Unit 2 were graphed on the y-axis; those from Unit 1 were graphed on the x-axis; a line was fitted to the data; and the slope, intercept, and coefficient of determination (r^2) of this line were determined. Second, a t-test assuming equal variances was performed on those same data. For the linear regression analysis, if both Sentinal™ 500 units reported the identical result, the slope of such a regression would be unity (1), the intercept zero (0), and the coefficients of determination (r^2) 1.0. The slope can indicate whether the results are biased in one direction or the other, while the coefficients of determination provide a measure of the variability of the results. The t-test shows whether the sensors generated statistically similar data. Small p-values (<0.05 at a 5% confidence level) would suggest that the results from the two Sentinal™ 500 units are significantly different from one another. Table 6-7 gives the slope, intercept, and coefficients of determination for the inter-unit reproducibility evaluation and the p-value for the t-test performed for each sensor.

The temperature, conductivity, and pH sensors had coefficients of determination greater than 0.95 and slopes within 5% of unity, indicating that their results were very similar and repeatable. Confirming that evaluation, the t-test p-value for those sensors was 0.23, 0.74, and 0.17, respectively.

Table 6-7. Inter-unit Reproducibility Evaluation

Parameter	Slope	Intercept	r^2	t-test p-value
Free chlorine	0.86	0.10	0.87	0.92
Temperature	0.98	-0.04	1.00	0.23
Conductivity	1.01	-4.13	0.98	0.74
pH	1.05	-0.3	0.95	0.17
ORP	0.89	72	0.98	0.87

As can be seen from Table 6-7, the ORP sensors had a coefficient of determination of 0.98, indicating that they were highly correlated with one another; but the slopes were approximately 11% less than unity, indicating that Unit 2 measurements were lower than Unit 1. This evaluation was supported by the figures throughout Chapter 6, which show that Unit 2 measurements were slightly less than Unit 1. However, based on the t-test, this difference was not significant.

The free chlorine sensor had a lower coefficient of determination and a slope that deviated from unity by more than 10%. This lower correlation was observed in the figures for the extended deployment when the Sentinal™ 500 units drifted by varying degrees. In addition, calibrating the chlorine sensor several times during the verification test increased the degree of variability in the free chlorine results. Because of this, the t-test indicated that the results from the free chlorine sensors were statistically the same.

6.6 Ease of Use and Data Acquisition

Throughout the duration of the verification test, the verification staff was not required to perform any routine maintenance. However, on several occasions, Clarion or verification test staff (at the request of Clarion) adjusted the chlorine sensor reading to match the reference sample measurement. Therefore, the accuracy of the free chlorine measurement was directly affected by this adjustment. Based on the performance of the free chlorine sensors, they may have to be adjusted periodically to maintain the accuracy of measurements. This would require a means of measuring the chlorine content of the water, as well as a site visit, to make the adjustment. No other maintenance was necessary during the test.

Data were saved onto memory modules mounted onto the Sentinal™ 500 units. With a 30-second data collection frequency, the storage capacity of the modules was not reached during the three-month test. One of the modules had to be removed for repair during the verification test. Also, in two instances, the Sentinal™ 500 units failed to download properly. Both units were rebooted, and the problem was resolved. This system may need to be reset periodically if the units are deployed remotely.

Chapter 7
Performance Summary

Evaluation Parameter			Free Chlorine	Tem-perature	Conductivity	pH	ORP
Stage 1—Accuracy	Units 1 and 2, range of %D (median)		3.4 to 117.1 (26.2)	-18.4 to 2.7 (-3.7)	-26.8 to -22.4 (-24.6)	-6.1 to 0.5 (-1.9)	[a]
Stage 2— Response to Injected Contaminants	Nicotine	Reference	–	NC	NC	NC	–
		Sentinal™ 500	–	NC	NC	NC	–
	Arsenic trioxide	Reference	–	NC	+	+	–
		Sentinal™ 500	–	NC	+	+	–
	Aldicarb	Reference	–	NC	NC	NC	–
		Sentinal™ 500	–	NC	NC	NC	–
Stage 3—Accuracy During Extended Deployment	Units 1 and 2, range of %D (median)		-54.8 to 50.0 (-21.5)	-7.8 to 2.7 (-2.7)	-0.8 to 5.5 (2.1)	-7.2 to 1.6 (0.3)	[a]
Stage 3—Accuracy After Extended Deployment	Unit 1, %D		-10.9	-0.5	2.5	0.0	[a]
	Unit 2, %D		-18.5	-3.1	0.3	1.2	[a]
Stage 3—Response to Injected Contaminants	*E. coli*	Reference	–	NC	+	–	–
		Sentinal™ 500	–	NC	+	–	–
	Aldicarb	Reference	–	NC	NC	–	–
		Sentinal™ 500	–	NC	NC	–	–
Injection Summary	For a reason that is not clear, aldicarb altered the pH, as measured by the reference method, during the Stage 3 injections, but not during the Stage 2 injections.						
Inter-unit Reproducibility (Unit 2 vs. Unit 1)	Slope (intercept)		0.86 (0.10)	0.98 (-0.04)	1.01 (-4.13)	1.05 (-0.3)	0.89 (72)
	r^2		0.87	1.00	0.98	0.95	0.98
	p-value		0.92	0.23	0.74	0.17	0.87
	All sensors generated results that were similar according to the results of the t-test. However, the slopes of the ORP and free chlorine sensor data plotted against one another suggest that the results from each unit were somewhat different from one another.						
Ease of Use and Data Acquisition	Based on the performance of the free chlorine sensors, they may have to be adjusted periodically to maintain the accuracy of the measurements. The memory module in Unit 1 had to be replaced and, twice, each unit had to be rebooted before data could be downloaded.						

[a] ORP was not included in the accuracy evaluation because of the lack of an appropriate reference method.
+/– = Parameter measurement increased/decreased upon injection.
NC = No obvious change was noted through a visual inspection of the data.

Chapter 8
References

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