October 2005

Environmental Technology Verification Report

ROSEMOUNT ANALYTICAL MODEL WQS CONTINUOUS MULTI-PARAMETER WATER QUALITY MONITOR

Prepared by
Battelle

Under a cooperative agreement with

U.S. Environmental Protection Agency

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

ETV Joint Verification Statement

TECHNOLOGY TYPE: **MULTI-PARAMETER WATER MONITORS FOR DISTRIBUTION SYSTEMS**

APPLICATION: **MONITORING DRINKING WATER QUALITY**

TECHNOLOGY NAME: **Model WQS**

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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 Rosemount Analytical Multi-Parameter/Optical Water Quality System (Model WQS) 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 WQS unit 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 WQS unit. All three stages of the test were conducted using a recirculating pipe loop at the U.S. EPA's Test and Evaluation Facility in Cincinnati, Ohio.

In the first stage of this verification test, the accuracy of the measurements made by the WQS units was evaluated during nine, 4-hour periods of stable water quality conditions by comparing each WQS 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 WQS 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 WQS 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 WQS performance to determine whether this length of operation would negatively impact the results from the WQS. 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 WQS could be evaluated. Second, to evaluate the response of the WQS unit 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 WQS unit was provided by the vendor and does not represent verified information.

The WQS unit measures pH, ORP, conductivity, temperature, and free chlorine in drinking water. The system combines user-specified instruments and sensors to create a customized system for monitoring water quality. The WQS unit does not need added reagents and uses minimum process flows of less than 183 milliliters per minute. The WQS unit uses three basic electrochemical principles of operation: millivolt measurements for pH and ORP, conductance/resistance measurements for conductivity, and amperometric/polarographic measurements for chlorine residuals. The WQS unit continuously monitors each parameter to provide constant surveillance of water quality events to ensure that acceptable water quality conditions are maintained. The WQS unit includes a sensor, cables, and instruments to measure water quality parameters. The verified WQS unit was 26 inches high and 32 inches wide. The width varies by system from 26 inches to 50 inches wide. The data output from the system is available as 4/20 mA analog, highway addressable remote transducer (HART®) or Foundation fieldbus® (H1), RS-485, Ethernet, or Modbus RTU digital outputs. It uses 115/230-volt alternating current or 24-volt direct current.

During this verification test, a Fluke (Everette, Washington) data logger was configured to the WQS unit to record the data every 30 seconds. The data logger was connected to a laptop computer that stored the data onto its hard drive as a delimited text file that was easily imported into a spreadsheet. The costs of the units as configured for the verification test ranged from $12,000 to $15,000. In addition, calibration reagents cost approximately $200 annually.

VERIFICATION OF PERFORMANCE

Evaluation Parameter			**Free Chlorine**	**Temperature**	**Conductivity**	**pH**	**ORP**
Stage 1—Accuracy	Units 1 and 2, range of %D (median)		-11.1 to 96.7 (14.5)	-5.9 to 1.5 (-1.7)	2.9 to 5.3 (4.2)	-7.4 to -1.1 (-3.0)	(a)
Stage 2— Response to Injected Contaminants	Nicotine	Reference	–	NC	NC	NC	–
		WQS	–	NC	NC	NC	–
	Arsenic trioxide	Reference	–	NC	+	+	–
		WQS	(b)	NC	+	+	–
	Aldicarb	Reference	–	NC	NC	NC	–
		WQS	–	NC	NC	NC	–
Stage 3—Accuracy During Extended Deployment	Units 1 and 2, range of %D (median)		-36.2 to 68.3 (1.6)	-4.1 to 2.4 (-0.2)	3.4 to 6.7 (5.2)	-2.8 to 1.8 (-1.2)	(a)
Stage 3—Accuracy After Extended Deployment	Unit 1, %D		-1.1	0.6	5.1	-0.6	(a)
	Unit 2, %D		-2.2	0.2	5.3	-0.9	(a)
Stage 3— Response to Injected Contaminants	*E. coli*	Reference	–	NC	+	–	–
		WQS	–	NC	NC	–	–
	Aldicarb	Reference	–	NC	NC	–	–
		WQS	(b)	NC	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)		0.48 (0.45)	1.01 (-0.19)	1.00 (0.26)	0.97 (0.25)	0.97 (-4.38)
	r^2		0.271	0.999	1.00	0.958	0.950
	p-value		0.367	0.882	0.787	0.832	0.011(c)
	With the exception of ORP, the t-test indicated that the sensors on each unit were performing similarly. For ORP, the linear correlation between the two units was very high, but the extremely small variability in the signal caused the difference between the two units to be statistically significant. Although the free chlorine sensors were not highly correlated with one another, the large variability in their measurements prevented the t-test from determining a significant difference between the units.						
Ease of Use and Data Acquisition	Based on the performance of the free chlorine sensors, calibration and membrane replacement may have to occur periodically to maintain accurate measurements, especially those involving response to injected contaminants. Also, the regular variability in free chlorine and pH measurements may prevent observing small changes in those water quality parameters.						

(a) Because a laboratory reference measurement equivalent to the on-line continuous measurement was not available, ORP was not included in the accuracy evaluation.

(b) Results from duplicate injections did not agree.

(c) The difference between the results from the two sensors was statistically significant.

+/− = 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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Original signed by Andrew P. Avel 1/17/06
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ETV Advanced Monitoring Systems Center

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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 substantially 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 District, and Ron Hunsinger of East Bay Municipal Utility District, who also reviewed the test/QA plan and/or the reports.

Contents

Figures

Tables

List of Abbreviations

AMS	Advanced Monitoring Systems
°C	degree centigrade
Cl_2	free chlorine
DI	deionized
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
µS/cm	microSiemens per centimeter
mg/L	milligram per liter
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
WQS	Water Quality System

Chapter 1
Background

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.

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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 Rosemount Analytical Multi-Parameter/Optical Water Quality System (WQS) 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 WQS water quality monitor. Following is a description of the WQS unit, based on information provided by the vendor. The information provided below was not verified in this test.

The WQS unit (Figure 2-1) measures pH, oxidation-reduction potential (ORP), conductivity, temperature, and free chlorine (Cl_2) in drinking water. The system combines user-specified instruments and sensors to create a customized system for monitoring water quality. The WQS unit does not need added reagents and uses minimum process flows of less than 183 milliliters per minute. The WQS unit uses three basic electrochemical principles of operation: millivolt measurements for pH and ORP, conductance/resistance measurements for conductivity, and amperometric/polarographic measurements for chlorine residuals. The WQS unit continuously monitors each parameter to provide constant surveillance of water quality events to ensure that acceptable water quality conditions are maintained.

Figure 2-1. Rosemount Analytical WQS Unit

The WQS unit includes a sensor, cables, and instruments to measure water quality parameters. The verified WQS unit was 26 inches high and 32 inches wide. The width varies by system from 26 inches to 50 inches wide. The data output from the system is available as 4/20 mA analog, highway addressable remote transducer (HART®) or Foundation fieldbus® (H1), RS-485, Ethernet, or Modbus RTU digital outputs. It uses 115/230-volt alternating current or 24-volt direct current.

During this verification test, a Fluke (Everette, Washington) data logger was configured to the WQS unit to record the data every 30 seconds. The data logger was connected to a laptop computer that stored the data onto its hard drive as a delimited text file that was easily imported into a spreadsheet. The costs of the units as configured for the verification test ranged from $12,000 to $15,000. In addition, calibration reagents cost approximately $200 annually.

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 WQS units in continuously monitoring pH, conductivity, free chlorine, ORP, and temperature in terms of the following:

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

Accuracy was quantitatively evaluated by comparing the results generated by two WQS 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 WQS units operating simultaneously. Ease of use was documented by technicians who operated and maintained the WQSs, 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 WQS unit. 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 WQS 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 WQS units with a 1/2-inch PVC hose and a hose clamp. Reference samples of approximately 1 liter (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 15 feet from the WQS 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 the WQS 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. These 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 time of testing). Two other sets of conditions included water temperature between 12 and 14°C and 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 (using a chiller connected to the pipe loop) until testing occurred.

3.2.2 Stage 2, Response to Injected Contaminants

The second stage of the verification test involved testing the response of the WQS units to changes in water quality parameters by injecting contaminants into the pipe loop. Two 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 water 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 each injection indicated the directional change in water quality caused by the injected contaminant. For each injected contaminant, the results from the WQS 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 WQS 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 WQS units was evaluated during 52 days of continuous operation. The WQS unit required no regularly scheduled maintenance during this deployment. To track the performance of the WQS unit 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 WQS 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 WQS unit performance after the 52-day extended deployment to determine whether this length of operation would negatively affect the results from the WQS. First, while the WQS units 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 WQS to be evaluated. Second, to evaluate the response of the WQS unit 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 WQS 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 (from the reference sample collection valve) approximately 1 L of water, which was estimated to be approximately 10 times the dead volume of the reference sample collection value. 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 tolerances. 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 data evaluation in the figures showing 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.

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 (μ/Scm)	±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)	Hach 2100P turbidimeter	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. Reference analyses of these blank samples were most important for free 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 percent difference (%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 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. 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: NIST Standard Value	PE Audit: Reference Method Result	PE Audit: Difference	Duplicate Analysis: Average of Absolute Values of Difference	Duplicate Analysis: Range of Difference
pH	9.26	9.18	-0.08 pH unit	0.04 pH unit	0.0 to 0.13 pH unit
Conductivity (µS/cm)	1,920	1,706	-11.1%	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)	23.80[a]	23.80	0.00°C	0.02°C	-0.18 to 0.29°C

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

[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.

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 (WQS unit and reference methods)	ETV data sheets and testing notebook	Upon each calibration	Battelle and T&E Facility	Manually incorporated in data spreadsheets as necessary
WQS unit results	Recorded electronically by each WQS unit and then downloaded to computer daily	Recorded continuously	Battelle	Delimited text 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 WQS unit's accuracy, response to injected contaminants, and inter-unit reproducibility.

5.1 Accuracy

Throughout this verification test, results from the WQS unit 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 WQS unit; the WQS 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 WQS 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 WQS unit 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 WQS 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 WQS unit highlighted its response to such changes.

5.3 Inter-unit Reproducibility

The results obtained from two identical WQS 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 WQS unit were compared to evaluate whether the two WQS units were generating similar results. This was done in two ways. First, the results from one were graphed against the results of the other unit. In this evaluation, a slope of unity and 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 WQS unit 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. Note also that one of the WQS units was equipped with a monochloramine sensor; however, because Cincinnati is a chlorinated system, the monochloramine levels are very low. Therefore, monochloramine results were not included in this report. The second stage of the verification test consisted of an evaluation of the response of the WQS units to the injection of several contaminants into the pipe loop. The third stage consisted of deploying the WQS unit 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 WQS units were still responsive to contaminant injection after the extended deployment. Two WQS 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 WQS units and reference measurements
2	Response to contaminant injection	Graphs of WQS unit measurements and reference measurements, table showing the effect of injections on reference and WQS measurements
3	Extended deployment with minimal maintenance along with post-extended deployment accuracy and response to contaminant injections	Graphs of WQS unit measurements with reference measurements, table showing average percent differences throughout extended deployment, table showing the effect of injections on reference and WQS 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 WQS 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 WQS units and reference results for each of the 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 difference between the average results of both WQS 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)	1.05 (0.03)	15.4	1.32 (0.11)	45.1
2	decreased pH, ambient temperature	0.78 (0.02)	0.79 (0.04)	1.3	0.91 (0.06)	16.7
3	decreased pH, ambient temperature	0.65 (0.01)	0.63 (0.01)	-3.1	0.73 (0.02)	12.3
4	decreased pH, ambient temperature	0.29 (0.02)	0.26 (0.01)	-10.3	0.29 (0.01)	0.0
5	ambient pH, decreased temperature	0.41 (0.08)	0.57 (0.02)	39.0	0.70 (0.03)	70.7
6	decreased pH, decreased temperature	1.47 (0.06)	1.52 (0.06)	3.4	1.67 (0.06)	13.6
7	ambient pH, increased temperature	0.60 (0.04)	0.60 (0.03)	0.0	1.18 (0.02)	96.7
8	decreased pH, increased temperature	0.54 (0.05)	0.48 (0.05)	-11.1	0.85 (0.03)	57.4
9	ambient pH, ambient temperature	0.91 (0.03)	1.67 (0.11)	83.5	1.32 (0.04)	45.1

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

		Reference	Unit 1		Unit 2	
Set	**Conditions**	**Average (SD) [°C]**	**Average (SD) [°C]**	**% D**	**Average (SD) [°C]**	**% D**
1	ambient pH, ambient temperature	22.66 (0.33)	22.17 (0.25)	-2.2	22.09 (0.25)	-2.5
2	decreased pH, ambient temperature	22.73 (0.23)	22.26 (0.22)	-2.1	22.20 (0.21)	-2.3
3	decreased pH, ambient temperature	21.61 (0.16)	21.50 (0.11)	-0.5	21.42 (0.11)	-0.9
4	decreased pH, ambient temperature	21.93 (0.15)	21.65 (0.04)	-1.3	21.61 (0.06)	-1.5
5	ambient pH, decreased temperature	13.82 (0.44)	13.21 (0.16)	-4.4	13.12 (0.18)	-5.1
6	decreased pH, decreased temperature	12.63 (0.26)	12.06 (0.24)	-4.5	11.88 (0.26)	-5.9
7	ambient pH, increased temperature	26.60 (0.27)	27.01 (0.16)	1.5	26.97 (0.15)	1.4
8	decreased pH, increased temperature	26.69 (0.23)	26.96 (0.15)	1.0	26.90 (0.14)	0.8
9	ambient pH, ambient temperature	22.79 (0.21)	22.49 (0.33)	-1.3	22.37 (0.39)	-1.8

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

		Reference	Unit 1		Unit 2	
Set	Conditions	Average (SD) [µS/cm]	Average (SD) [µS/cm]	% D	Average (SD) [µS/cm]	% D
1	ambient pH, ambient temperature	451 (1)	465 (2)	3.1	468 (1)	3.8
2	decreased pH, ambient temperature	486 (10)	500 (11)	2.9	503 (11)	3.5
3	decreased pH, ambient temperature	503 (6)	526 (7)	4.6	528 (7)	5.0
4	decreased pH, ambient temperature	694 (12)	730 (12)	5.2	731 (12)	5.3
5	ambient pH, decreased temperature	412 (1)	426 (2)	3.4	431 (2)	4.6
6	decreased pH, decreased temperature	501 (10)	516 (11)	3.0	523 (11)	4.4
7	ambient pH, increased temperature	447 (1)	463 (3)	3.6	466 (2)	4.3
8	decreased pH, increased temperature	529 (2)	548 (3)	3.6	552 (3)	4.3
9	ambient pH, ambient temperature	442 (1)	460 (1)	4.1	462 (0)	4.5

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)	8.60 (0.07)	-1.8	8.70 (0.14)	-0.7
2	decreased pH, ambient temperature	7.89 (0.09)	7.53 (0.20)	-4.6	7.59 (0.20)	-3.8
3	decreased pH, ambient temperature	7.52 (0.04)	7.09 (0.04)	-5.7	7.27 (0.10)	-3.3
4	decreased pH, ambient temperature	6.73 (0.12)	6.24 (0.06)	-7.3	6.23 (0.07)	-7.4
5	ambient pH, decreased temperature	8.48 (0.02)	8.36 (0.12)	-1.4	8.39 (0.06)	-1.1
6	decreased pH, decreased temperature	7.31 (0.08)	7.14 (0.13)	-2.3	6.95 (0.09)	-4.9
7	ambient pH, increased temperature	8.37 (0.05)	8.19 (0.11)	-2.2	8.17 (0.06)	-2.4
8	decreased pH, increased temperature	7.60 (0.06)	7.12 (0.13)	-6.3	7.18 (0.06)	-5.5
9	ambient pH, ambient temperature	8.74 (0.01)	8.54 (0.13)	-2.3	8.51 (0.06)	-2.6

Of the parameters that were evaluated for accuracy, the free chlorine sensors generated the largest range of percent differences compared to the reference method. For free chlorine, the range of percent differences (with the median shown in parentheses) was from -11.1 to 96.7 (14.5); for temperature, -5.9 to 1.5 (-1.7); for conductivity 2.9 to 5.3 (4.2); and for pH, -7.4 to -1.1 (-3.0).[1] The chlorine sensor was calibrated by the vendor prior to the verification test, but was not recalibrated during Stage 1. There was no obvious trend in the performance of the chlorine sensors. For Set 1, Unit 1 had a %D of 15.4% and Unit 2 had a %D of 45.1%. For Sets 2 through 4, both sensors' results were less than 20% different from the reference results. For Set 5, both sensors were more than 40% different than the reference measurement. Thereafter, Unit 1's agreement with the reference measurement improved considerably for Sets 6 through 8, but the percent difference of Unit 1 was more than 80% for Set 9. The agreement of Unit 2 with the reference measurement only improved for Set 6, whereas for the remaining sets, the continuous and reference method were at least 45% different from each other. The standard deviations for the reference method demonstrate that the variability in both the reference and continuous measurements was generally less than 10%.

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[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.

The temperature sensors (Table 6-2b) generated very small percent differences with respect to the reference method at ambient temperatures (between -2.5% and -0.5%), slightly larger negative percent differences (-5.9% to -4.4%) resulted when the temperature of the water in the pipe loop was decreased, and small positive percent differences (0.8% to 1.5%) resulted when the temperature of the pipe loop water was increased. This trend in percent differences is likely due to 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 air, thus causing a slight increase in water temperature in the brief time period between reference sampling and analysis.

The conductivity and pH results (Tables 6-2c and 6-2d) produced very small percent differences from the reference method. Across all sets of conditions, the percent differences for the conductivity measurements were between 0 and 7%, indicating that the WQS units were always slightly higher than the reference method.

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 WQS 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. Both the reference and continuous measurement for both of these water quality parameters decreased upon injection of contaminants. There was one exception during the second arsenic trioxide injection; Unit 1's chlorine sensors didn't respond to the contaminant injection, while the Unit 2 chlorine sensor did respond. Figures 6-1 through 6-4 show the responses of free chlorine, ORP, pH, and conductivity. The blue and yellow lines on the graphs represent the measurements made by each WQS 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 WQS 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.

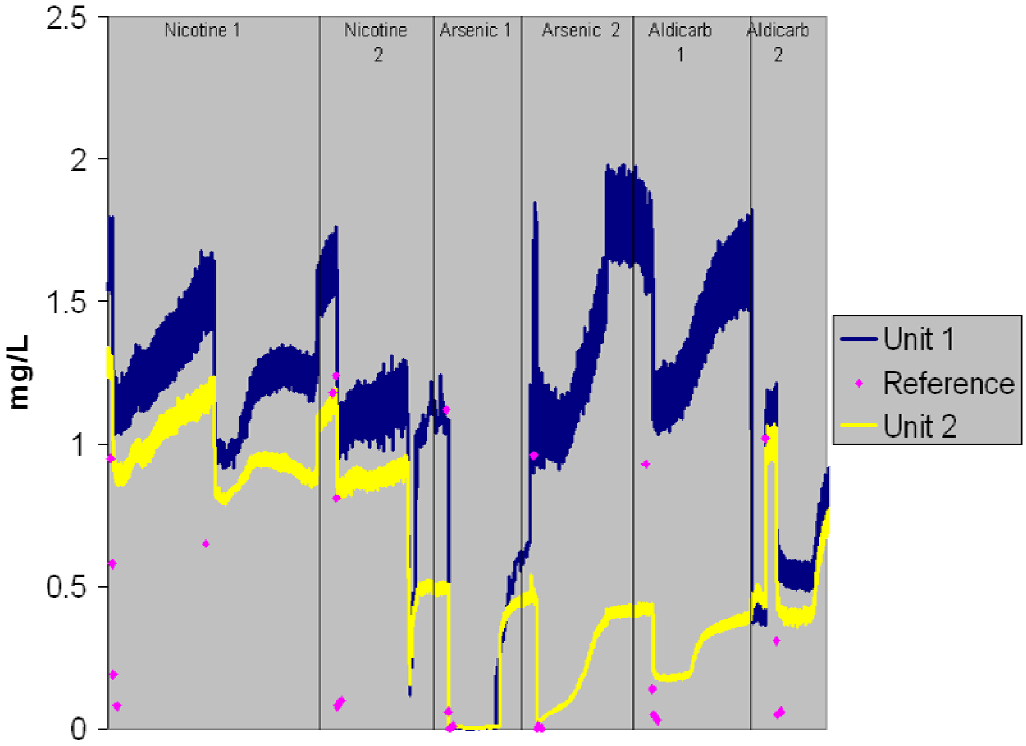
Table 6-3. Effect of Contaminant Injections Prior to Extended Deployment

Parameter	Nicotine Reference	Nicotine WQS	Arsenic Trioxide Reference	Arsenic Trioxide WQS	Aldicarb Reference	Aldicarb WQS
Free chlorine	–	–	–	– (a)	–	–
Temperature	NC	NC	NC	NC	NC	NC
Conductivity	NC	NC	+	+	NC	NC
pH	NC	NC	+	+	NC	NC
ORP	–	–	–	–	–	–

(a) Results from duplicate injections did not agree.

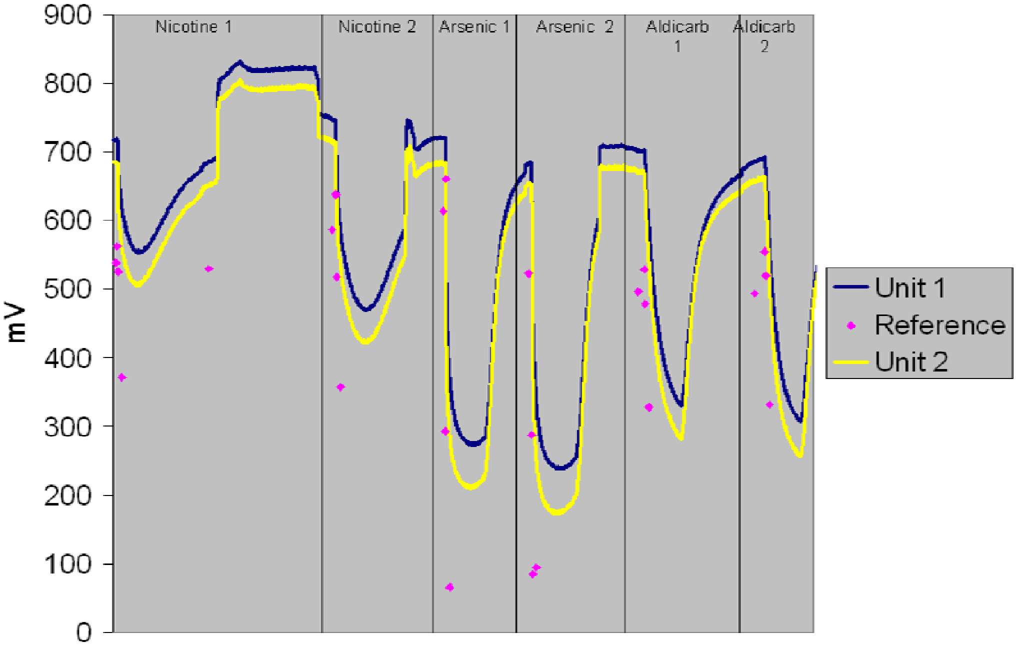
+/– = Parameter measurement increased/decreased upon injection.

NC = No change in response to the contaminant injection.



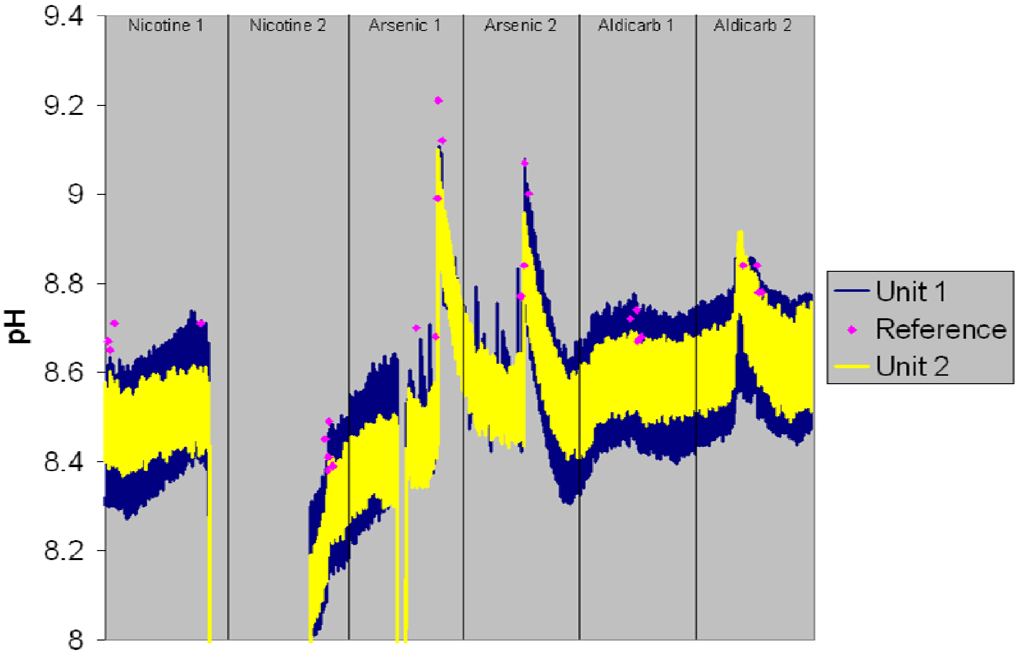
Each section (separated by vertical lines) represents approximately 24 hours.

Figure 6-1. Stage 2 Contaminant Injection Results for Free Chlorine



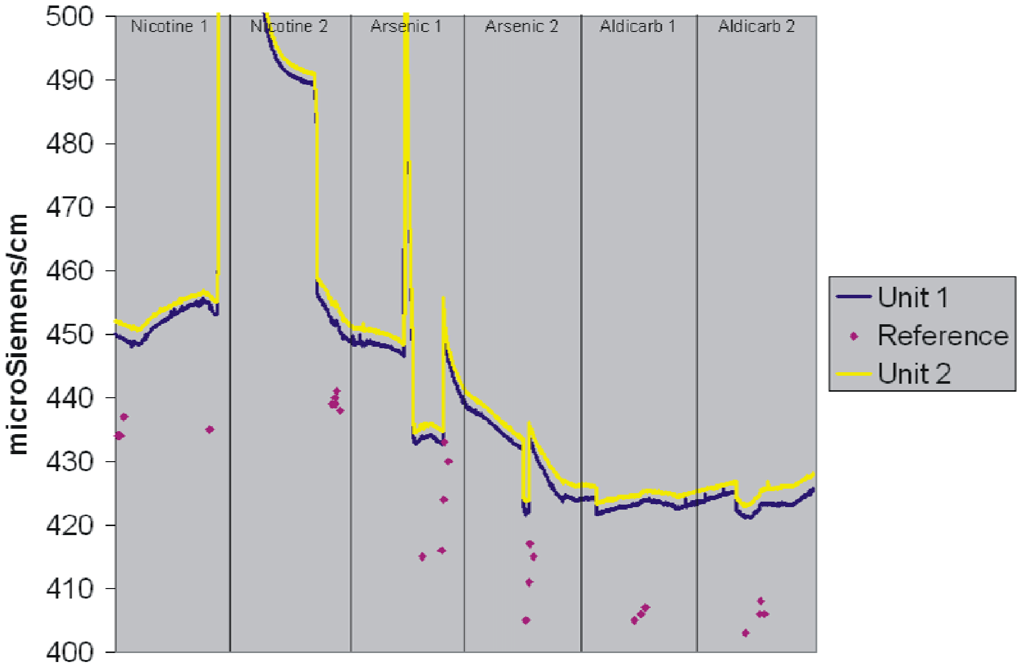
Each section (separated by vertical lines) represents approximately 24 hours.

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



Each section (separated by vertical lines) represents approximately 24 hours.

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



Each section (separated by vertical lines) represents approximately 24 hours.

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

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, as is evidenced by the reference method data point at the far left of the figure. However, the measurements of the WQS units at this time were between 1.5 and 2 mg/L for Unit 1 and approximately 1.25 mg/L for Unit 2, in both cases considerably higher than the reference method measurement. When nicotine was injected for the first time, the free chlorine sensors detected a drop in free chlorine of approximately 0.5 mg/L, while the reference measurement indicated that nicotine had reacted almost completely with the chlorine in the pipe loop water, taking the concentration to near zero. Following the drop in chlorine concentration corresponding to the first injection, the sensors recovered to readings similar to those before the first injection. The chlorine sensors responded to the second injection of nicotine as they did following the first injection. However, after that injection, the sensors did not return to their pre-injection readings, but remained steady at their respective post-injection concentration levels. In addition, Unit 2 drifted from approximately 1 mg/L to approximately 0.5 mg/L before the first arsenic trioxide injection. Unit 1 remained at a concentration of approximately 1 mg/L prior to the arsenic injection. The sharp drop in chlorine shown by both sensors between the second nicotine injection and the first arsenic injection was not due to a contaminant injection, but to a brief change in the pipe loop water chlorine level unrelated to the verification test. However, the Unit 2 chlorine sensor did not recover fully from that drop in chlorine. Figure 6-1 shows that both chlorine sensors have a consistent variability throughout this stage. In 3- to 4-minute intervals, the measurements oscillated by 5 to 20%. This variability is shown visually by the rather wide trace as opposed to the very thin trace shown for ORP. The response of each sensor is still clear, but small changes in chlorine concentration are obviously more difficult to detect.

The first injection of arsenic trioxide caused a decrease in free chlorine as measured by the WQS units as well as the reference method. After the free chlorine concentration reached its minimum point after injection, the pipe loop was restored to approximately pre-injection conditions by adding sodium hypochlorite. The WQS units recovered to approximately their pre-injection levels. Upon the second injection of arsenic trioxide, the reference method measurement again dropped almost completely to zero, as did the Unit 2 measurements. However, Unit 1 did not respond at all to the drop in free chlorine recognized by Unit 2 and the reference method. Both units responded to the addition of sodium hypochlorite to restore the pipe loop to pre-injection conditions. Unit 1 measured an increased concentration of approximately 1.75 mg/L, while Unit 2 recovered to a concentration measurement slightly lower than what it had been prior to the injection of arsenic (approximately 0.4 mg/L).

The free chlorine sensors on both units responded to the injection of aldicarb and then returned to approximately their pre-injection concentrations. After the first injection of aldicarb, Rosemount staff directed the verification staff to recalibrate the chlorine sensors. This is shown by the abrupt drop in Unit 1's measurement and the abrupt increase in Unit 2's measurement to match the first reference result of the final aldicarb injection. Both units responded similarly to this injection, but they did not drop to a chlorine concentration as low as was measured by the reference measurement.

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. Note the steep decline in reference free chlorine concentration upon each injection. Similarly, there is a steep decline in the ORP measurement.

Figures 6-3 and 6-4 show the injection results for pH and conductivity, the water quality parameters that were affected only by the injection of arsenic trioxide. This effect may have been due to the pH adjustment required to get this contaminant into solution.

6.3 Extended Deployment

Figures 6-5 through 6-9 show the continuous measurements from both WQS 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, while 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.

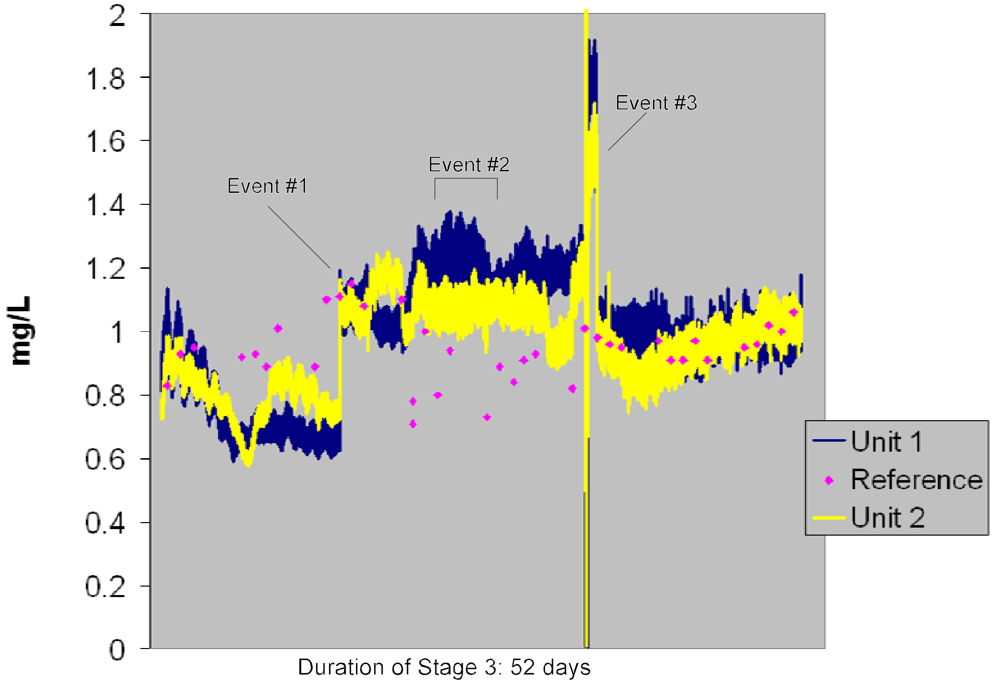


Figure 6-5. Extended Deployment Results for Free Chlorine

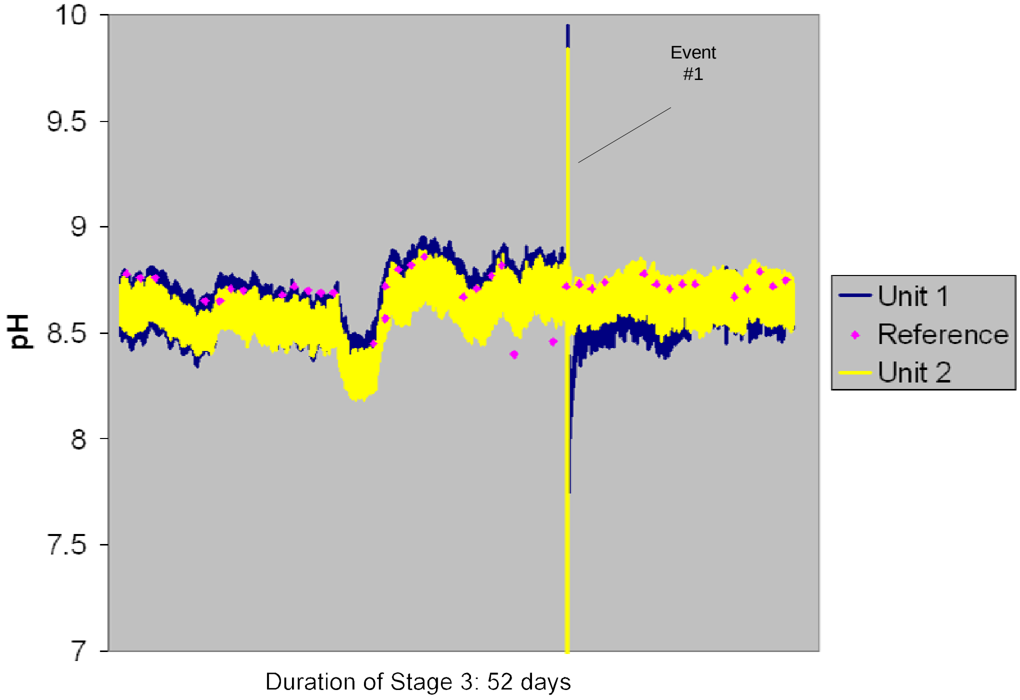


Figure 6-6. Extended Deployment Results for pH

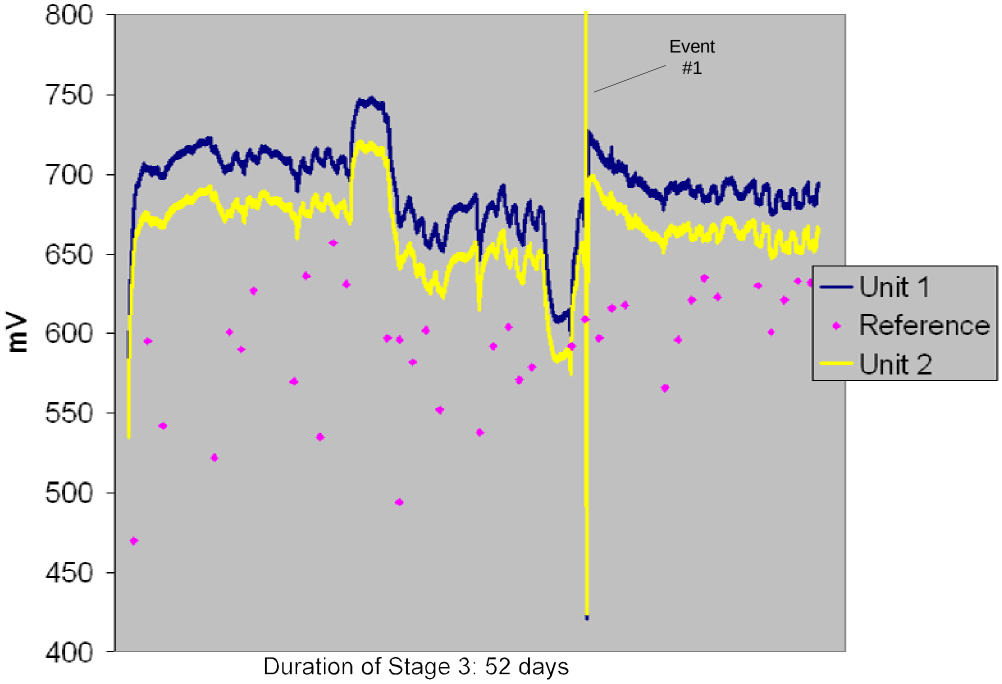


Figure 6-7. Extended Deployment Results for ORP

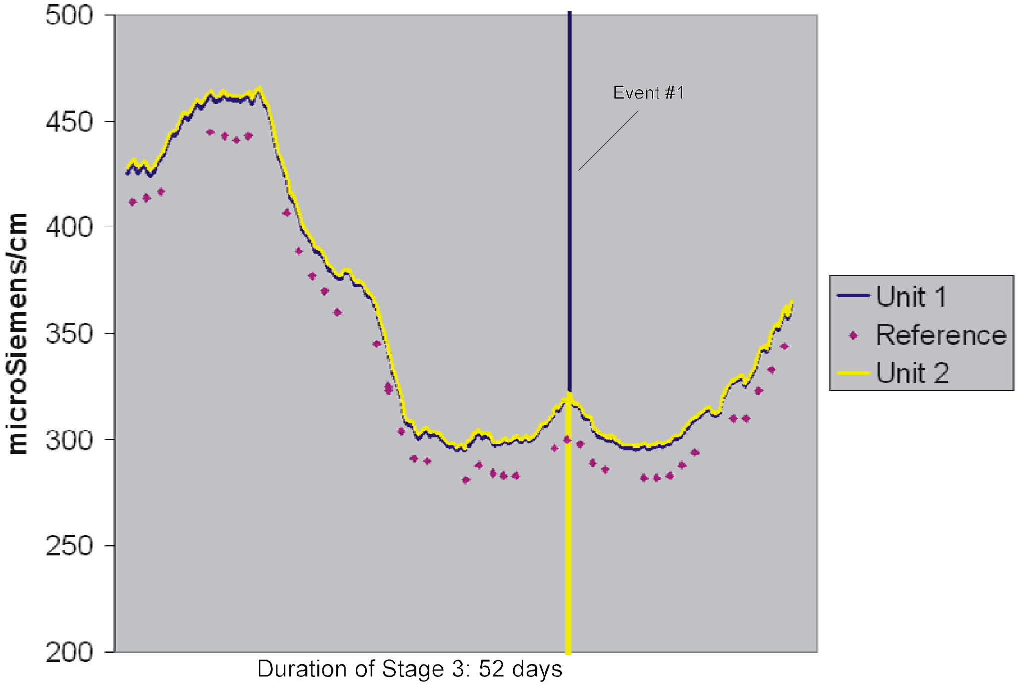


Figure 6-8. Extended Deployment Results for Conductivity

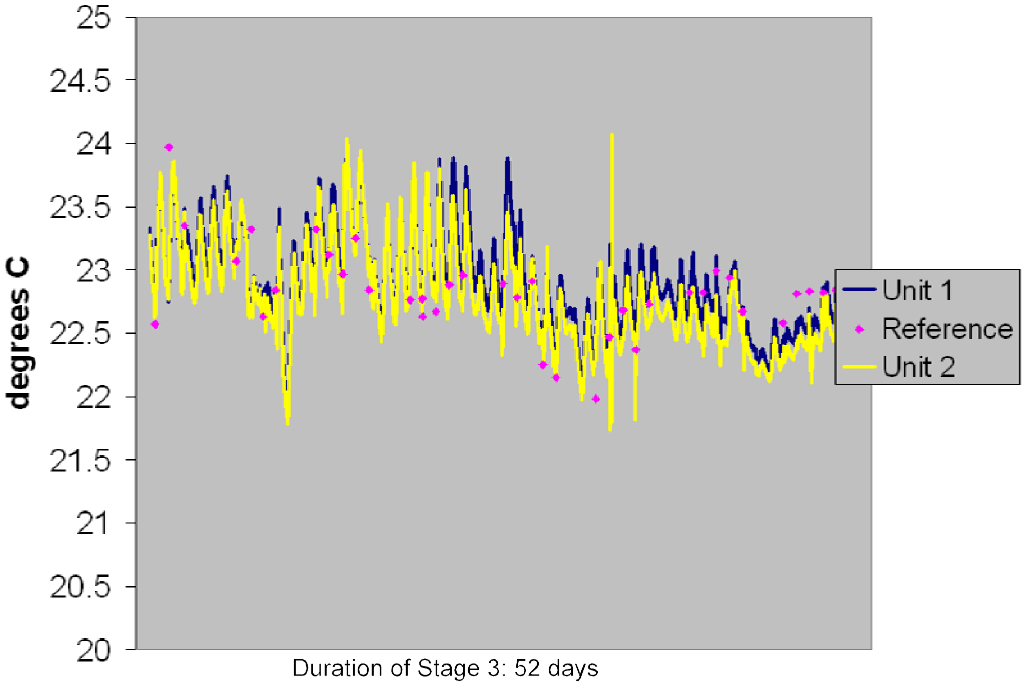


Figure 6-9. Extended Deployment Results for Temperature

The objective of this stage of the verification test was to evaluate the performance of the WQS 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 evaluated visually to see whether any aspects of the data were notable. 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 the variability was mostly dependent on the water conditions and not due to systematic variability in the WQS unit results. (Note that the reference results were only generated during business hours, so any fluctuations occurring during off hours are 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.

Table 6-4. Accuracy During Extended Deployment

Parameter	Reference Average (SD)[a]	Unit 1 Average (SD)[a]	Unit 1 %D	Unit 2 Average (SD)[a]	Unit 2 %D	Both WQS Units %D Range (median)
Free chlorine	0.95 (0.10)	1.00 (0.19)	5.3	0.97 (0.13)	2.1	-36.2 to 68.3 (1.6)
Temperature	22.83 (0.35)	22.81 (0.25)	-0.1	22.72 (0.28)	-0.5	-4.1 to 2.4 (-0.2)
Conductivity	333 (57)	349 (57)	4.8	351 (57)	5.4	3.4 to 6.7 (5.2)
pH	8.72 (0.07)	8.65 (0.13)	-0.8	8.63 (0.10)	-1.0	-2.8 to 1.8 (-1.2)

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

For free chlorine, visual inspection of the data in Figure 6-5 revealed that at the start of Stage 3, the WQS units' measurements were similar to the reference results, but drifted lower over the following several days (1 day = 1 magenta symbol). Thereafter, until approximately one-third of the way through the extended deployment, the free chlorine measurements were biased low with respect to the reference measurements. At that point (free chlorine Event #1 in Figure 6-5), the Rosemount representative directed the verification staff to recalibrate the free chlorine sensors based on the reference method result. For several days, both WQS units tracked the free chlorine reference measurements rather well until the measured chlorine concentrations drifted slightly high for approximately two weeks (free chlorine Event #2). After the Rosemount representative changed the membranes and calibrated both chlorine sensors (free chlorine Event #3), the WQS units consistently tracked the free chlorine reference measurements for the remainder of the extended deployment. During the entire extended deployment, the percent differences for both WQS units ranged from -36.2 to 68.3, with a median of 1.6. The average free chlorine concentration, as measured by the reference method, was 0.95 ± 0.10 mg/L.

The measurements from the pH, ORP, conductivity, and temperature sensors are shown in Figures 6-6 through 6-9. The pH sensor was recalibrated at the same time as the chlorine sensor (pH Event #1 in Figure 6-6) ; and, with the exception of the two reference measurements prior to recalibration, the accuracy after calibration was similar to that during the rest of the extended deployment, with percent differences ranging from -2.8 to 1.8 and a median of -1.2. The ORP and conductivity sensors were verified by Rosemount staff using standard solutions at the same time as the pH and chlorine sensors were calibrated (Event #1 in Figures 6-7 and 6-8). This intervention did not change the results from either of those sensors, but was done only to confirm the accurate measurement of the standard. The temperature sensor was allowed to operate without intervention throughout the extended deployment. In Figure 6-7, the ORP results are shown along with a laboratory reference method result. The ORP reference method does not provide a reliable result for water in a flowing pipe,(2) but it can be used to evaluate a trend in the decrease and increase in the ORP, as it was in Stage 2 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 varied regularly 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. However, Unit 2 temperature results appeared to be biased low with respect to Unit 1 and the reference method.

The regular variability in the free chlorine results that was discussed in Section 6.2 continued to be observed during this stage of the verification test. In fact, the degree of variability seemed to increase slightly from the start of this stage to the end. A similar variability was observed in the Stage 3 pH results. Again, the overall effect of this variability seemed small, but it may prevent small changes in free chlorine or pH from being noticed. With the exception of free chlorine, the standard deviations of the WQS measurements were similar in magnitude to those of the reference measurements, indicating that most of the variability in the measurements is due to the actual variability in the water quality parameters rather than substandard performance.

6.4 Accuracy and Response to Injected Contaminants After Extended Deployment

After the 52-day deployment of the WQS 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. With the exception of free chlorine, these results were comparable to those collected at the start of the verification test. The free chlorine results measured after extended deployment generated percent differences of approximately 2%. In contrast, the percent differences at the close of Stage 1 were greater than 45%. Between the end of Stage 1 and the start of the post-extended deployment accuracy evaluation, the chlorine sensors had been calibrated twice and the membranes had been replaced.

Table 6-5. Post-Extended Deployment Results

		Unit 1		Unit 2	
Parameter	**Reference Average (SD)(a)**	**Average (SD)(a)**	**%D**	**Average (SD)(a)**	**%D**
Free chlorine	0.92 (0.02)	0.91(0.03)	-1.1	0.90 (0.03)	-2.2
Temperature	22.66 (0.16)	22.79 (0.08)	0.6	22.71 (0.09)	0.2
Conductivity	356 (1)	374 (1)	5.1	375 (1)	5.3
pH	8.59 (0.01)	8.54 (0.05)	-0.6	8.51 (0.05)	-0.9

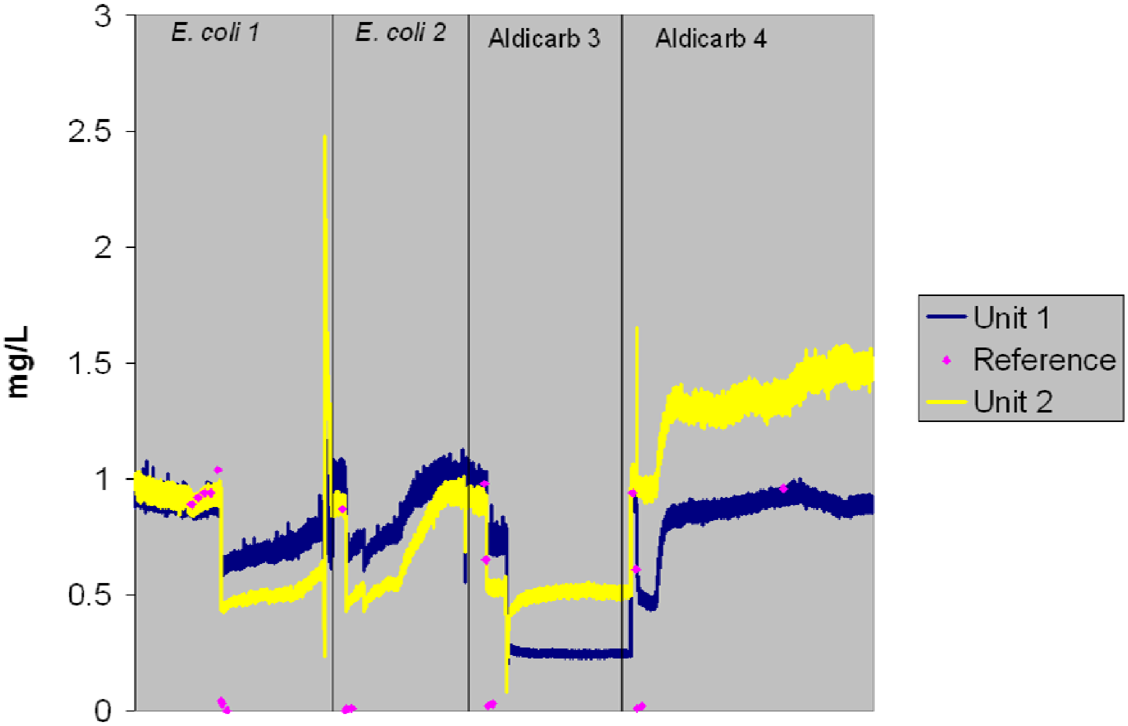
(a) Free chlorine, mg/L; temperature, °C; conductivity, µS/cm; pH, pH units.

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 and Figures 6-10 through 6-13 show the directional change of each reference and WQS measurement in response to the contaminant injections. In general, free chlorine, ORP, and pH were the parameters clearly affected (for the reference results and all but one of the continuous measurements) for all four injections.

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

	E. coli		Aldicarb	
Parameter	**Reference**	**WQS**	**Reference**	**WQS**
Free chlorine	–	–	–	–(a)
Temperature	NC	NC	NC	NC
Conductivity	+	NC	NC	NC
pH	–	–	–	NC
ORP	–	–	–	–

(a) Results from duplicate injections did not agree.
+/– = Parameter measurement increased/decreased upon injection.
NC = No change in response to the contaminant injection.



Each section (separated by vertical lines) represents approximately 24 hours.

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

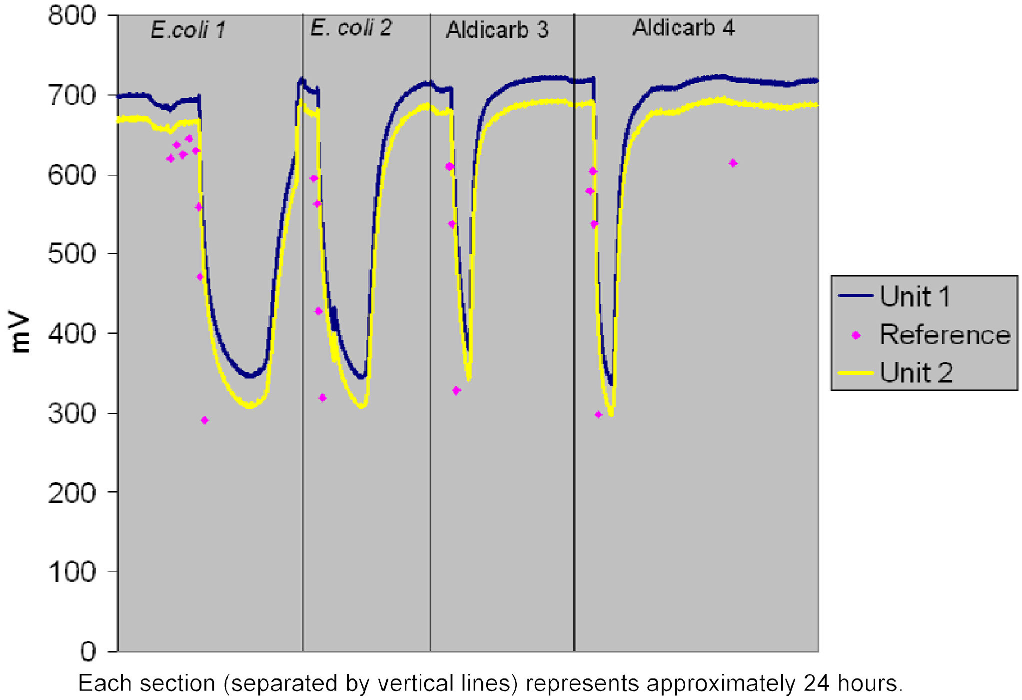


Figure 6-11. Stage 3 Contaminant Injection Results for ORP

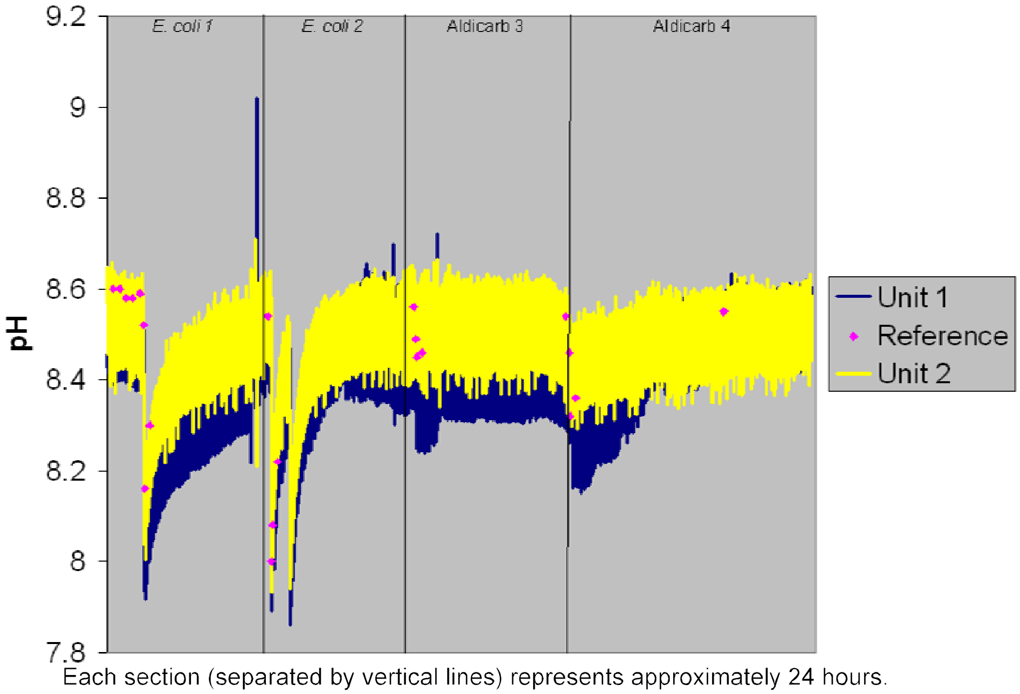


Figure 6-12. Stage 3 Contaminant Injection Results for pH

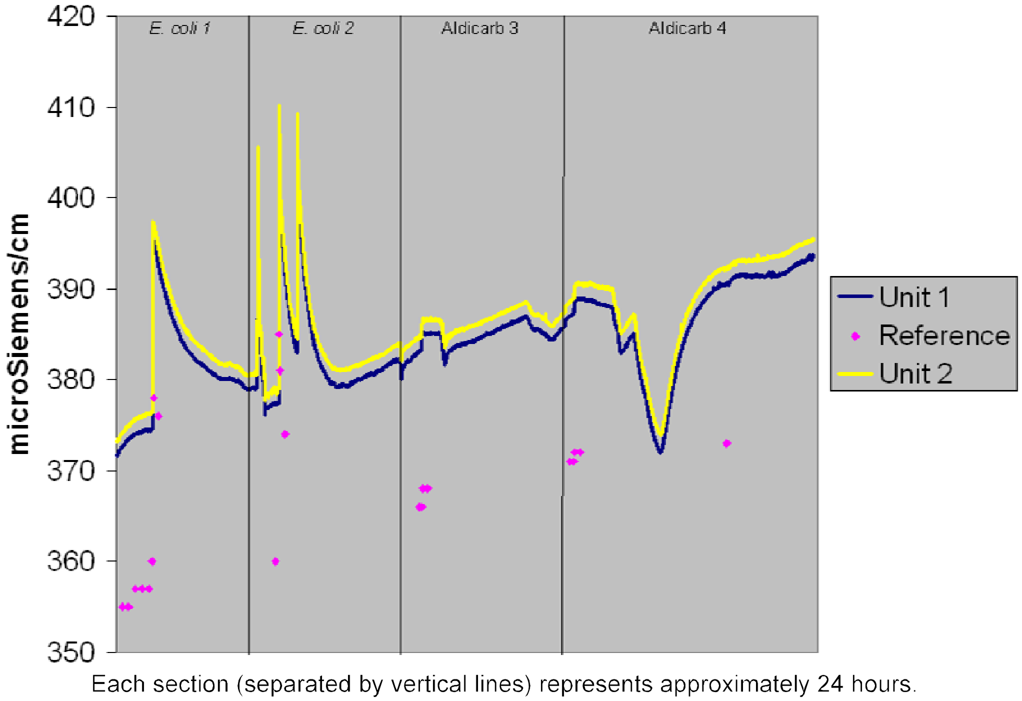


Figure 6-13. Stage 3 Contaminant Injection Results for Conductivity

For free chlorine, the reference concentration decreased from approximately 1 mg/L to near zero upon each of the four injections. The free chlorine sensors started out this portion of the test measuring concentrations similar to the reference results; however, upon injection, the WQS units' measurements did not drop lower than 0.5 mg/L. For the first three injections of this stage, the Unit 1 sensor responded to the contaminant injection in a similar way to the Unit 2 sensor. When the final injection of aldicarb was made, the Unit 2 sensor did not respond at all even though the reference method clearly indicated an immediate drop in the free chlorine concentration to nearly zero. The Unit 1 free chlorine concentration did decrease, but not to the level of the reference measurement. It also was notable that both free chlorine sensors recovered adequately to the pre-injection water conditions after the *E. coli* injections, but after the first aldicarb injection, recalibration was required to bring the sensor back to the pre-injection conditions. Because of Unit 2's lack of response to the final aldicarb injection, it seems that the membrane of the Unit 2 sensor may have become clogged or fouled during the contaminant injections. The ORP response was, as during Stage 2, consistent across all four injections. For the pH measured by the two WQS units and the reference method, a brief decrease was observed upon injecting the culture of *E. coli*, and the pipe loop quickly returned to the baseline pH. In addition, the pH measured by the reference method decreased very slightly during the aldicarb injections. This was an effect that had not been observed during the Stage 2 aldicarb injections, so it was unexpected. There was also an increase in the conductivity measurement upon injection of the *E. coli*. These slight changes in pH and conductivity due to the aldicarb and *E. coli* injections, respectively, were measured by the reference method, but were not indicated through visual observation by the WQS measurements.

6.5 Inter-unit Reproducibility

Two WQS units were compared throughout the verification test to determine whether they generated results that were similar to one another. This was done using the WQS 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, and a line was fitted to the data. Second, a t-test assuming equal variances was performed on those same data. For the linear regression analysis, if both WQS units reported the identical result, the slope of such a regression would be unity (1), the intercept zero (0), and the coefficient of determination (r^2) 1.0. The slope can indicate whether the results are biased in one direction or the other, while the coefficient of determination provides 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 units are significantly different from one another. Table 6-7 gives the slope, intercept, and coefficient of determination for the inter-unit reproducibility evaluation and the p-value for the t-test performed for each sensor.

Table 6-7. Inter-unit Reproducibility Evaluation

Parameter	Slope	Intercept	r^2	t-test p-value
Free chlorine	0.48	0.45	0.271	0.367
Temperature	1.01	-0.19	0.999	0.882
Conductivity	1.00	0.26	1.00	0.787
pH	0.97	0.25	0.958	0.832
ORP	0.97	-4.38	0.950	▨ 0.011

Shading indicates that the difference between the results of the two sensors was statistically significant.

As seen in Table 6-7, all of the sensors, except free chlorine, had coefficients of determination greater than 0.95 and slopes greater than 0.97, indicating that their results were very similar and repeatable. When a t-test was performed on this data, the p-values were much larger than 0.05 for pH, conductivity, free chlorine, and temperature, suggesting that the two sensors of each type were not significantly different from one another. However, for ORP, even though the regression data suggested that the results from each sensor were highly correlated with one another, the extremely small amount of variability in the ORP measurements caused the t-test result to suggest that there was, in fact, a significant difference between the results of the sensors. Even though this difference in performance was statistically significant, the magnitude in difference between the two sensors was small. In addition to the inter-unit statistical evaluation, the results for all four sensors were confirmed through a visual evaluation of the figures throughout Chapter 6. For temperature, conductivity, and pH, the results from the two WQS units are graphed nearly on top of one another; while for ORP, a small, but consistent, difference was evident.

The free chlorine sensor had a lower coefficient of determination and a slope that deviated from unity by greater than 50%. This lower correlation was observed in the figures when Unit 2 drifted to chlorine concentrations different from Unit 1, or when the two sensors responded differently to contaminant injections. However, even though the sensors were not as highly correlated with one another as the other sensors, the overall larger variability in the sensor measurements kept the t-test from determining the results as significantly different from one another. This result was also observed in the figures through frequent overlap of each sensor's line due to the variability in the signal.

6.6 Ease of Use and Data Acquisition

Throughout the verification test, the verification staff was not required to perform any routine maintenance. However, on three occasions, the chlorine sensors were recalibrated by Rosemount or by verification staff (at the direction of Rosemount) to match the reference sample measurement. The chlorine sensor membranes were replaced once during the verification test and debris deposited into the flow cells was cleaned out at that time. Based on the performance of the WQS free chlorine sensors, these maintenance activities may have to be performed periodically to maintain accurate measurements, especially those involving response to injected contaminants. This would require a means of measuring the chlorine concentration of the water, as well as a site visit to perform this maintenance. No other maintenance was necessary during the test.

A Fluke data logger was configured with a laptop PC to download the data to the PC's hard drive in real time. The files were saved as delimited text files for subsequent import into a spreadsheet. The data logger and laptop are not a standard feature of the Rosemount WQS.

Chapter 7
Performance Summary

Evaluation Parameter			Free Chlorine	Tem-perature	Conductivity	pH	ORP
Stage 1—Accuracy	Units 1 and 2, range of %D (median)		-11.1 to 96.7 (14.5)	-5.9 to 1.5 (-1.7)	2.9 to 5.3 (4.2)	-7.4 to -1.1 (-3.0)	(a)
Stage 2— Response to Injected Contaminants	Nicotine	Reference	–	NC	NC	NC	–
		WQS	–	NC	NC	NC	–
	Arsenic trioxide	Reference	–	NC	+	+	–
		WQS	(b)	NC	+	+	–
	Aldicarb	Reference	–	NC	NC	NC	–
		WQS	–	NC	NC	NC	–
Stage 3—Accuracy During Extended Deployment	Units 1 and 2, range of %D (median)		-36.2 to 68.3 (1.6)	-4.1 to 2.4 (-0.2)	3.4 to 6.7 (5.2)	-2.8 to 1.8 (-1.2)	(a)
Stage 3—Accuracy After Extended Deployment	Unit 1, %D		-1.1	0.6	5.1	-0.6	(a)
	Unit 2, %D		-2.2	0.2	5.3	-0.9	(a)
Stage 3— Response to Injected Contaminants	*E. coli*	Reference	–	NC	+	–	–
		WQS	–	NC	NC	–	–
	Aldicarb	Reference	–	NC	NC	–	–
		WQS	(b)	NC	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)		0.48 (0.45)	1.01 (-0.19)	1.00 (0.26)	0.97 (0.25)	0.97 (-4.38)
	r^2		0.271	0.999	1.00	0.958	0.950
	p-value		0.367	0.882	0.787	0.832	0.011(c)
	With the exception of ORP, the t-test indicated that the sensors on each unit were performing similarly. For ORP, the linear correlation between the two units was very high, but the extremely small variability in the signal caused the difference between the two units to be statistically significant. Although the free chlorine sensors were not highly correlated with one another, the large variability in their measurements prevented the t-test from determining a significant difference between the units.						
Ease of Use and Data Acquisition	Based on the performance of the free chlorine sensors, calibration and membrane replacement may have to occur periodically to maintain accurate measurements, especially those involving response to injected contaminants. Also, the regular variability in free chlorine and pH measurements may prevent observing small changes in those water quality parameters.						

(a) Because a laboratory reference measurement equivalent to the on-line continuous measurement was not available, ORP was not included in the accuracy evaluation.

(b) Results from duplicate injections did not agree.

(c) The difference between the results of the two sensors was statistically significant.

+/– = Parameter measurement increased/decreased upon injection.

NC = No obvious change was noted through a visual inspection of the data.

Chapter 8
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