October 2005

Environmental Technology Verification Report

MAN-TECH ASSOCIATES INC.
TITRASIP™ SA SYSTEM
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: **TitraSip™ SA**

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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 Man-Tech Associates Inc. TitraSip™ SA (Stand-Alone) System in continuously measuring total chlorine, temperature, conductivity, pH, total alkalinity, and turbidity in drinking water. This verification statement provides a summary of the test results.

VERIFICATION TEST DESCRIPTION

The performance of the TitraSip™ 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 TitraSip™. 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 TitraSip™ units was evaluated during nine, 4-hour periods of stable water quality conditions by comparing each TitraSip™ 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 TitraSip™ 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 TitraSip™ 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 TitraSip™ performance to determine whether this length of operation would negatively impact the results from the TitraSip™. 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 TitraSip™ could be evaluated. Second, to evaluate the response of the TitraSip™ 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 TitraSip™ was provided by the vendor and does not represent verified information.

The TitraSip™ is designed for multi-parameter water quality testing. The system used for this verification test analyzed pH (following EPA Method 150.1, including calibration buffers with pHs of 4, 7, and 10), conductivity (following Standard Method [SM] 2510, which used a 1,413 microSiemens per centimeter standard for calibration), total alkalinity (following SM 2320B), total chlorine (following SM 4500-Cl B, with a potentiometric rather than a color, endpoint), temperature (following EPA Method 170.1), and turbidity (following SM 2130B, including calibration solutions of 0, 10, and 100 nephelometric turbidity unit polymer standards). Additional water quality parameters and modules (i.e., autosampler) may be added. TitraSip™ collects a sample from a free-flowing source (e.g., overfill cup) into the TitraSip™ Analysis Vessel and automatically completes analysis cycles at set time intervals (in this case, once every 30 minutes) to complete the analysis for all six water quality parameters without user intervention. The system includes a personal computer, software, interface, burets, turbidity module, pump/valve system for adding calibrants and standards, electrodes, overfill sample cup, and TitraSip™ Analysis Vessel. The system used for this verification test was positioned on a table top equipped with shelving for the sampling and analysis equipment. The total system was 30 inches high and 36 inches wide, excluding the personal computer. Data are automatically collected at the conclusion of each cycle of sample analysis. The PC-Titrate software controls all aspects of TitraSip™ operation. Data may be viewed directly on the personal computer as they are acquired or they may be exported as a database or spreadsheet file. The cost of the TitraSip™ used for the verification test was approximately $30,000. In addition, the calibration reagents cost approximately $220 per month, preventive maintenance costs approximately $2,797 (parts only) per year, and electrode replacement costs approximately $1,220 per year, assuming that new electrodes are needed every six months.

VERIFICATION OF PERFORMANCE

Evaluation Parameter			**Total Chlorine**	**Temperature**	**Conductivity**	**pH**	**Total Alkalinity**	**Turbidity**
Stage 1—Accuracy	Units 1 and 2, range of %D (median)		-13.2 to 20.6 (7.5)	-9.1 to 52.5 (-0.04)	37.9 to 94.3 (57.5)(a)	-2.2 to 5.4 (0.6)	3.2 to 30.4 (11.5)	-65.2 to 0.6 (-45.2)
Stage 2—Response to Injected Contaminants	Nicotine	Reference	–	NC	NC	NC	NC	(b)
		TitraSip™	–	NC	NC	NC	NC	(b)
	Arsenic trioxide	Reference	–	NC	+	+	+	(b)
		TitraSip™	–	NC	+(c)	+	+	(b)
	Aldicarb	Reference	–	NC	NC	NC	NC	(b)
		TitraSip™	–	NC	NC	NC	NC	(b)
Stage 3—Accuracy During Extended Deployment	Units 1 and 2, range of %D (median)		-18.0 to 30.0 (2.7)	-15.7 to 3.7 (-3.1)	-2.8 to 5.2 (0.7)	-4.4 to 0.7 (-1.1)	-16.5 to 14.4 (5.7)	-96.7 to 155.3 (-37.3)
Stage 3—Accuracy After Extended Deployment	Unit 1, %D		1.0	-2.2	0.3	-1.0	-0.4	35.3
	Unit 2, %D		0.0	-1.9	1.1	-2.1	4.5	41.2
Stage 3—Response to Injected Contaminants	*E. coli*	Reference	–	NC	+	–	+	+
		TitraSip™	–	NC	+	–	+	(c)
	Aldicarb	Reference	–	NC	NC	–	–	+
		TitraSip™	–	NC	NC	–	–	(c)
Injection Summary	For a reason that is not clear, aldicarb and total alkalinity 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)		1.06 (0.03)	1.06 (-1.22)	1.16 (-38.1)	0.94 (0.545)	0.79 (18.1)	0.67 (0.104)
	r^2		0.958	0.942	0.896	0.981	0.873	0.683
	p-value		0.481	0.915	0.110	0.851	0.149	0.449
	All sensors generated results that were similar and repeatable between the units.							
Ease of Use and Data Acquisition	The TitraSip™ units required daily calibration, which involved operator intervention. Initially, the sample cell on Unit 1 did not drain completely between pH calibration solutions, but once the drain problem was resolved, both units functioned properly. Monitor results were recorded once every 30 minutes, which is the maxiumum data collection frequency.							

(a) Calibration procedure for the conductivity meter was changed after Stage 1, resulting in much lower percent differences throughout the remainder of the verification test.

(b) Relatively large uncertainties in the reference and continuous measurements made it difficult to determine a significant change.

(c) Duplicate injection results did not agree.

+/– = 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
Gregory A. Mack Date
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Original signed by Andrew P. Avel 1/17/06
Andrew P. Avel Date
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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

MAN-TECH ASSOCIATES INC.
TITRASIP™ SA SYSTEM
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 verification 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 this report. 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 report.

Contents

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List of Abbreviations

AMS	Advanced Monitoring Systems
cm	centimeter
°C	degree centigrade
DI	deionized
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
µS/cm	microSiemens per centimeter
mg/L	milligram per liter
mV	millivolt
NIST	National Institute of Standards and Technology
ntu	nephelometric turbidity unit
%D	percent difference
PE	performance evaluation
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
QMP	quality management plan
SD	standard deviation
SM	Standard Method
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 Man-Tech Associates Inc. TitraSip™ SA (Stand-Alone) System water quality monitor in continuously measuring total chlorine, temperature, conductivity, pH, total alkalinity, and turbidity 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 TitraSip™ water quality monitor. Following is a description of the TitraSip™, based on information provided by the vendor. The information provided below was not verified in this test.

Figure 2-1. Man-Tech Associates Inc. TitraSip™ SA

The TitraSip™ (Figure 2-1) is designed for multi-parameter water quality testing. The system used for this verification test analyzed pH (following EPA Method 150.1,(1) including calibration buffers with pHs of 4, 7, and 10), conductivity (following Standard Method [SM] 2510,(2) which used a 1,413 microSiemens per centimeter [µS/cm] standard for calibration), total alkalinity (following SM 2320B),(3) total chlorine (following SM 4500-Cl B,(4) with a potentiometric rather than a color, endpoint), temperature (following EPA Method 170.1),(5) and turbidity (following SM 2130B,(6) including calibration solutions of 0, 10, and 100 nephelometric turbidity unit [ntu] polymer standards). Additional water quality parameters and modules (i.e., autosampler) may be added.

The TitraSip™ collects a sample from a free-flowing source (e.g., overfill cup) into the TitraSip™ Analysis Vessel and automatically completes analysis cycles at set time intervals (in this case, once every 30 minutes to complete the analysis of all six water quality parameters). Once the analysis is initiated, no user intervention is required. The system includes a personal computer, software, interface, burets, turbidity module, pump/valve system for adding calibrants and standards, electrodes, overfill sample cup, and TitraSip™ Analysis Vessel. The system used for this verification test was positioned on a table top equipped with shelving for the sampling and analysis equipment. The total system was 30 inches high and 36 inches wide, excluding the personal computer. Data are automatically collected at the conclusion of each cycle of sample analysis. The PC-Titrate software controls all aspects of TitraSip™ operation. Data may be viewed directly on the personal computer as they are acquired or they may be exported as a database or spreadsheet file. The cost of the TitraSip™ used for the verification test was approximately $30,000. In addition, the calibration reagents cost approximately $220 per month, preventive maintenance costs approximately $2,797 (parts only) per year, and electrode replacement costs approximately $1,220 per year, assuming that new electrodes are needed every six months.

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*(7) and assessed the performance of the TitraSip™ units for monitoring pH, conductivity, total chlorine, total alkalinity, turbidity, 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 TitraSip™ units to 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 TitraSip™ 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 TitraSip™ units. 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 the two TitraSip™ 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 TitraSip™ overfill cup with a 36-foot [1/4-inch internal diameter] 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 on the PVC pipe leading to them. The reference sample collection valve was approximately 2 feet from the origin of the PVC valve leading to the TitraSip™.

3.2.1 Stage 1, Accuracy

During the first stage of this verification test, the accuracy of the measurements made by both TitraSip™ 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 time of testing). Two other sets of conditions included changing the water temperature to between 12 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 evaluating the response of the TitraSip™ 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 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 TitraSip™ 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 at least 12 hours so that each TitraSip™ 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 TitraSip™ units was evaluated during 52 days of continuous operation. In Section 6.6, the level of maintenance required for the TitraSip™ throughout the verification test is discussed. To track the performance of the TitraSip™ 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 extended deployment, the average percent difference (%D), as defined in Section 5.1, between the results from the TitraSip™ 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 TitraSip™ unit performance after the 52-day extended deployment to determine whether this length of operation would negatively affect the results from the TitraSip™. First, while the TitraSip™ units were continuously operating (i.e., completing an analysis cycle approximately once every 30 minutes), 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 TitraSip™ to be evaluated. Second, to evaluate the response of the TitraSip™ 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 TitraSip™ 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 a reference sample collector 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 immediately upon the analysis of the reference samples (within one day).

Table 3-1. Reference Methods

Parameter	Method	Reference Instruments	Method Detection Limit	Acceptable Differences for QC Measurements
pH	EPA 150.1(1)	Corning 320 pH meter	NA	±0.3 pH units
Conductivity	SM 2510(2)	YSI 556 multi-parameter water monitor	2 µS/cm	±25%D
Total alkalinity	EPA 310.1(8)	Corning 320 pH meter	20 mg/L	±25%D
Total chlorine	SM 4500-G(9)	Hach 2400 portable spectrophotometer	0.01 mg/L as Cl_2	±25%D
Temperature	EPA 170.1(5)	YSI 556 multi-parameter water monitor	NA	±1°C
Turbidity	SM 2130B(6)	Hach 2100P turbidimeter	0.067 ntu	±25%D

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 total 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 test/QA plan(7) for this verification test and quality management plan (QMP) for the AMS Center.(10)

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 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. With the exception of one duplicate measure of turbidity, all six parameters were always within the differences defined in Table 3-1. Because pH units are measured on a logarithmic, rather than a linear, scale, and the measurement of temperature is extremely precise, the quality control metrics for those two parameters were the absolute units rather than the percent difference. No corrective action was taken for the one turbidity measurement (55.2%) that was outside the acceptable difference. If this outlier is removed, the upper range of percent difference was 18.2%, and the average absolute value of differences was 5.4%.

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

Parameter	PE Audit NIST Standard Value	 Reference Method Result	 Difference	Duplicate Analysis Average of Absolute Values of Difference	 Range of Difference
pH (pH unit)	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%
Total 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
Total alkalinity (mg/L)	358	360	0.6%	0.02%	-5.6 to 2.9%
Turbidity (ntu)	20	22.3	11.5%	7.49%	-8.7 to 55.2%

(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.

4.1.2 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 test/QA plan,(7) AMS Center QMP,(8) 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.

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 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 (TitraSip™ 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
TitraSip™ units results	Recorded electronically by each unit	Recorded as measurement cycles were completed	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 TitraSip™ units' accuracy, response to injected contaminants, and inter-unit reproducibility.

5.1 Accuracy

Throughout this verification test, results from the TitraSip™ 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 TitraSip™ unit; the TitraSip™ unit results were recorded approximately every 30 minutes, whereas collecting the reference samples took only a few seconds. Therefore, C_R was the reference measurement recorded closest to the time the TitraSip™ 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 TitraSip™ unit and a reference method measurement were the same, there would be a percent difference of zero. It should be noted that the formula for percent difference is sensitive to reference results that are small in magnitude. For example, if the reference turbidity is 0.1 ntu, and the online instrument reads 0.2, the percent difference is 100%. Alternatively, if the reference turbidity is 1.0 ntu, and the online instrument reads 1.1, the percent difference is only 10%. During Stages 2 and 3, the TitraSip™ data, graphed with the reference method results, were visually examined to evaluate the response of the TitraSip™ 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 TitraSip™ 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 TitraSip™ unit highlighted its response to such changes.

5.3 Inter-unit Reproducibility

The results obtained from two identical TitraSip™ 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 TitraSip™ unit were compared to evaluate whether the two TitraSip™ 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 1.00 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 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 TitraSip™ unit sensor: total chlorine, temperature, conductivity, pH, total alkalinity, and turbidity. The second stage of the verification test consisted of an evaluation of the response of the TitraSip™ units to the injection of several contaminants into the pipe loop. The third stage consisted of deploying the TitraSip™ 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 TitraSip™ units were still responsive to contaminant injection after the extended deployment. Two TitraSip™ 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 TitraSip™ units and reference measurements
2	Response to contaminant injection	Graphs of TitraSip™ unit measurements and reference measurements, table showing the effect of injections on both reference and TitraSip™ measurements
3	Extended deployment with minimal maintenance along with post-extended deployment accuracy and response to contaminant injections	Graphs of TitraSip™ unit measurements with reference measurements, table showing average percent differences throughout extended deployment, table showing the effect of injections on both reference and TitraSip™ measurements

6.1 Accuracy

Tables 6-2a–f 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. In evaluating accuracy in each four-hour period, measurements from each reference sample were compared with the TitraSip™ measurement taken closest to the time of the reference sample collection and analysis. For each unit, this approach resulted in five paired TitraSip™ 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 from both TitraSip™ units and the average of the reference results.

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

			Unit 1		Unit 2	
Set	Conditions	Reference Average (SD) [mg/L]	Average (SD) [mg/L]	% D	Average (SD) [mg/L]	% D
1	ambient pH, ambient temperature	0.97 (0.07)	0.96 (0.03)	-1.0	1.17 (0.08)	20.6
2	decreased pH, ambient temperature	0.86 (0.02)	0.88 (0.04)	2.3	0.93 (0.13)	8.1
3	decreased pH, ambient temperature	0.73 (0.01)	0.82 (0.04)	12.3	0.81 (0.06)	11.0
4	decreased pH, ambient temperature	0.38 (0.03)	0.44 (0.03)	15.8	0.33 (0.06)	-13.2
5	ambient pH, decreased temperature	0.51 (0.08)	0.56 (0.04)	9.8	0.58 (0.02)	13.7
6	decreased pH, decreased temperature	1.56 (0.05)	1.59 (0.06)	1.9	1.78 (0.03)	14.1
7	ambient pH, increased temperature	0.69 (0.01)	0.69 (0.06)	0.0	0.74[a](0.03)	7.2
8	decreased pH, increased temperature	0.65 (0.07)	0.63 (0.02)	-3.1	0.70 (0.06)	7.7
9	ambient pH, ambient temperature	0.98 (0.02)	0.94 (0.02)	-4.1	1.05 (0.09)	7.1

[a] One result was 3.07 mg/L. This was clearly an outlier due to air bubbles in the buret, so it was removed from the calculation of the percent difference.

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

			Unit 1		Unit 2	
Set	**Conditions**	**Reference Average (SD) [°C]**	**Average (SD) [°C]**	**% D**	**Average (SD) [°C]**	**% D**
1	ambient pH, ambient temperature	22.66 (0.33)	23.85 (0.99)	5.3	23.62 (1.11)	4.2
2	decreased pH, ambient temperature	22.73 (0.23)	23.21 (0.77)	2.1	23.64 (0.45)	4.0
3	decreased pH, ambient temperature	21.66 (0.08)	20.12 (0.51)	-7.1	20.24 (0.61)	-6.6
4	decreased pH, ambient temperature	21.93 (0.15)	20.31 (0.30)	-7.4	20.37 (0.14)	-7.1
5	ambient pH, decreased temperature(a)	13.82 (0.44)	21.08 (0.33)	52.5	18.82 (0.26)	36.2
6	decreased pH, decreased temperature(a)	12.63 (0.26)	18.99 (0.90)	50.4	17.88 (1.02)	41.6
7	ambient pH, increased temperature	26.60 (0.27)	24.33 (0.59)	-8.5	24.90 (0.59)	-6.4
8	decreased pH, increased temperature	26.69 (0.23)	24.26 (0.99)	-9.1	24.82 (0.97)	-7.0
9	ambient pH, ambient temperature	22.79 (0.21)	22.85 (0.51)	0.3	22.71 (0.59)	-0.4

(a) Increased percent differences were likely due to equilibration with the ambient air temperature *en route* to the continuous monitor. Prior to analysis by the TitraSip™, the water had traveled through 36 feet of 1/4-inch diameter tubing. During the decreased temperature condition, this maximized heat transfer to the water from ambient air; and vice versa during the increased temperature condition.

Table 6-2c. Accuracy Evaluation Under Various Conditions—Conductivity[(a)]

Set	Conditions	Reference Average (SD) [µS/cm]	Unit 1 Average (SD) [µS/cm]	Unit 1 % D	Unit 2 Average (SD) [µS/cm]	Unit 2 % D
1	ambient pH, ambient temperature	451 (1)	622 (23)	37.9	702 (3)	55.7
2	decreased pH, ambient temperature	484 (10)	763 (40)	57.6	803 (22)	65.9
3	decreased pH, ambient temperature	503 (60)	825 (202)	64.0	791 (3)	57.3
4	decreased pH, ambient temperature	694 (12)	1,056 (35)	52.2	1,107 (15)	59.5
5	ambient pH, decreased temperature	412 (1)	593 (6)	43.9	729 (2)	76.9
6	decreased pH, decreased temperature	501 (10)	761 (16)	51.9	924 (22)	84.4
7	ambient pH, increased temperature	447 (1)	656 (10)	46.8	851 (5)	90.4
8	decreased pH, increased temperature	529 (2)	778 (14)	47.1	1,028 (5)	94.3
9	ambient pH, ambient temperature	442 (1)	644 (9)	45.7	793 (3)	79.4

(a) After this stage of the verification test, Man-Tech changed the calibration procedure for the conductivity meter, which resulted in much more accurate results throughout the remainder of the test.

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

		Reference	Unit 1		Unit 2	
Set	**Conditions**	**Average (SD) [pH unit]**	**Average (SD) [pH unit]**	**% D**	**Average (SD) [pH unit]**	**% D**
1	ambient pH, ambient temperature	8.76 (0.02)	8.66 (0.04)	-1.1	8.74 (0.02)	-0.2
2	decreased pH, ambient temperature	7.56 (0.41)	7.81 (0.10)	3.3	7.87 (0.10)	4.1
3	decreased pH, ambient temperature	7.17 (0.40)	7.53 (0.06)	5.0	7.56 (0.03)	5.4
4	decreased pH, ambient temperature	6.70 (0.22)	6.55 (0.06)	-2.2	6.65 (0.07)	-0.7
5	ambient pH, decreased temperature	8.18 (0.36)	8.40 (0.03)	2.7	8.40 (0.01)	2.7
6	decreased pH, decreased temperature	7.31 (0.08)	7.25 (0.08)	-0.8	7.34 (0.09)	0.4
7	ambient pH, increased temperature	8.12 (0.23)	8.25 (0.03)	1.6	8.29 (0.01)	2.1
8	decreased pH, increased temperature	7.49 (0.25)	7.38 (0.04)	-1.5	7.52 (0.02)	0.4
9	ambient pH, ambient temperature	8.56 (0.19)	8.61 (0.02)	0.6	8.61 (0.01)	0.6

Table 6-2e. Accuracy Evaluation Under Various Conditions—Total Alkalinity

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	82.73 (1.51)	107.88 (1.60)	30.4	92.11 (0.17)	11.3
2	decreased pH, ambient temperature	71.52 (1.18)	73.82 (0.62)	3.2	80.06 (0.81)	11.9
3	decreased pH, ambient temperature	64.56 (0.54)	66.86 (0.21)	3.6	73.38 (0.15)	13.7
4	decreased pH, ambient temperature	39.84 (2.31)	41.27 (2.00)	3.6	44.91 (1.92)	12.7
5	ambient pH, decreased temperature	72.72 (1.58)	78.74 (0.16)	8.3	81.26 (0.11)	11.7
6	decreased pH, decreased temperature	59.84 (2.62)	64.46 (2.15)	7.7	66.77 (2.06)	11.6
7	ambient pH, increased temperature	72.24 (0.36)	79.54 (4.09)	10.1	83.30 (0.25)	15.3
8	decreased pH, increased temperature	60.64 (0.61)	64.25 (0.59)	6.0	69.06 (0.39)	13.9
9	ambient pH, ambient temperature	81.52 (0.59)	86.71 (0.39)	6.4	92.74 (0.23)	13.8

Table 6-2f. Accuracy Evaluation Under Various Conditions—Turbidity

Set	Conditions	Reference Average (SD) [ntu]	Unit 1 Average (SD) [ntu]	Unit 1 % D	Unit 2 Average (SD) [ntu]	Unit 2 % D
1	ambient pH, ambient temperature	1.27 (0.95)	0.48 (0.20)	-62.2	0.53 (0.06)	-58.3
2	decreased pH, ambient temperature	1.14 (0.40)	0.55 (0.20)	-51.8	0.61 (0.15)	-46.5
3	decreased pH, ambient temperature	0.97 (0.33)	0.70[(a)] (0.09)	-27.8	0.54 (0.10)	-44.3
4	decreased pH, ambient temperature	1.54 (0.20)	1.55 (0.10)	0.6	1.18 (0.04)	-23.4
5	ambient pH, decreased temperature	0.89 (0.41)	0.52 (0.40)	-41.6	0.33 (0.05)	-62.9
6	decreased pH, decreased temperature	0.99 (0.21)	0.55 (0.05)	-44.4	0.60 (0.04)	-39.4
7	ambient pH, increased temperature	0.92 (0.16)	0.48 (0.08)	-47.8	0.57 (0.14)	-38.0
8	decreased pH, increased temperature	1.00 (0.35)	0.54 (0.09)	-46.0	0.56 (0.04)	-44.0
9	ambient pH, ambient temperature	0.46 (0.11)	0.16 (0.04)	-65.2	0.19 (0.06)	-58.7

(a) One result was 4.85 ntu. It was clearly an outlier due to air bubbles reaching the turbidity meter, so it was not included in this calculation of percent difference. The average, including the outlier, was 1.53 ± 1.86 ntu.

Of the parameters that were evaluated for accuracy, the conductivity and turbidity sensors generated the largest range of percent differences compared to the reference method (with the median shown in parentheses): for conductivity, the percent differences ranged from 37.9 to 94.3 (57.5); for turbidity, -65.2 to 0.6 (-45.2); for total chlorine (excluding an outlier caused by a bubble in the buret), -13.2 to 20.6 (7.5); for pH, -2.2 to 5.4 (0.6); for total alkalinity, 3.2 to 30.4 (11.5); and for temperature, -9.1 to 52.5 (-0.04).[1] The conductivity measurements were consistently biased high with respect to the reference method. After this initial stage of the verification test, Man-Tech altered the calibration routine for the conductivity sensor; and, thereafter, as shown in the following sections, the accuracy of the conductivity measurements improved greatly. The turbidity measurements were consistently low with respect to the reference measurement. This persisted throughout the verification test, and it should be noted that the relatively low turbidity in the Cincinnati water caused small differences between the reference samples and the TitraSip™ unit's measurements increased the value of the percent differences between the two numbers. Also contributing to the higher percent differences is that

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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.

both the TitraSip™ and the reference method used calibration solutions ranging from less than 1 ntu to 100 ntu. Because of the low turbidity in the tested water, calibration solutions more focused on low turbidity may have improved agreement between the two measurements. In addition, the turbidity and total chlorine had one result that was clearly outlying and, therefore, was removed as noted on the appropriate table. After removing one outlier, the total chlorine percent differences were all less than 21%. For total alkalinity, there was one percent difference of 30.4%, but the rest of the sets resulted in percent differences of 15% or less. The range of percent differences for temperature also was always less than 10%, except during decreased temperature conditions. Because the TitraSip™ units were titrated on a 4-foot by 6-foot table, they had to be located one floor below the reference sample collection valve. The water sample traveled to the TitraSip™ in a tube that was approximately 36 feet from the PVC pipe connected to the pipe loop and that had an internal diameter of 1/4 inch. Because the water was in contact with the large surface area of the tubing, heat transfer from the ambient air was maximized, thus increasing the temperature of the water and most likely contributing to the positive percent differences. The temperature percent differences from the other test conditions were not as large, probably because the difference between the ambient air and increased water temperatures was not as great as the difference between the ambient air and decreased water temperatures.

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. The only exception to this was for turbidity, which was not controlled as part of the verification test, but was dependent on events occurring within the Cincinnati water utility. Also, small changes corresponded to rather large relative changes because of the low turbidity of the Cincinnati water. This shows that the water conditions during the test periods were very stable and that there was very little variability in the sensors themselves. The results were not remarkably different among the various sets; therefore, the TitraSip™ unit performance did not seem to be dependent on the water conditions.

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. As Table 6-3 shows, only the total chlorine measurement was visibly affected by all three contaminants. In the table, the directional change of each reference and TitraSip™ measurement is given.

Figures 6-1 through 6-5 show the response of total chlorine, pH, alkalinity, conductivity, and turbidity. The blue and yellow lines on the figure represent the measurements made by each TitraSip™ 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 TitraSip™ units and the reference method results are not presented here; however, the reference method results are included in these graphs to confirm that the fluctuations in the continuous results are due to changes in water chemistry as the result of the injected contaminants. The figure is divided with vertical lines that define the approximate time period for each injection. Each injection time period defined on the figure is approximately 24 hours, but the times vary depending on when chlorine was added to restore the system to

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

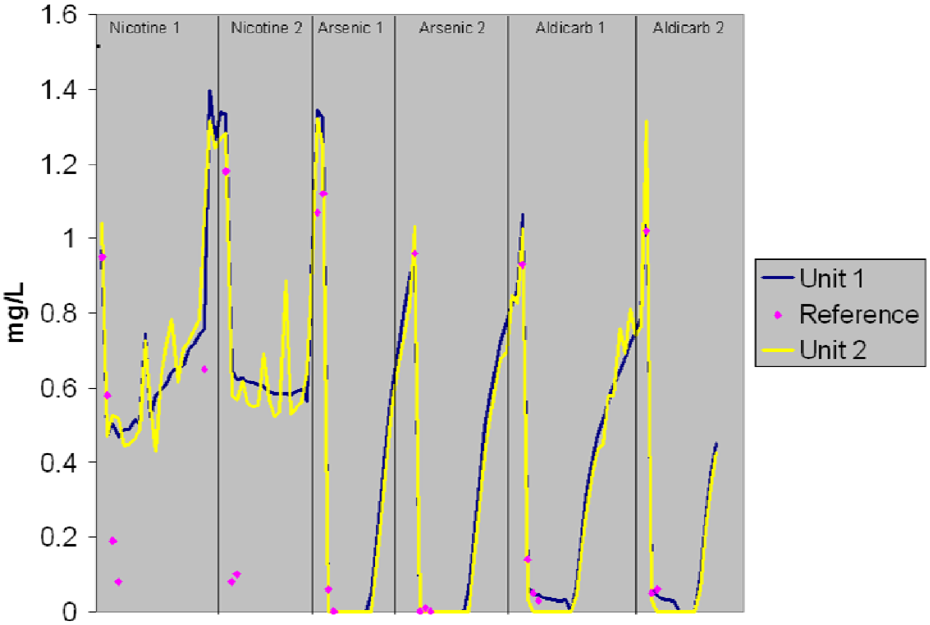
	Nicotine		Arsenic Trioxide		Aldicarb	
Parameter	**Reference**	**TitraSip™**	**Reference**	**TitraSip™**	**Reference**	**TitraSip™**
Total chlorine	–	–	–	–	–	–
Temperature	NC	NC	NC	NC	NC	CN
Conductivity	NC	NC	+	+[(a)]	NC	NC
pH	NC	NC	+	+	NC	NC
Total alkalinity	NC	NC	+	+	NC	NC
Turbidity	(b)	(b)	(b)	(b)	(b)	(b)

[(a)] During the second arsenic injection, the measurement made by Unit 1 did not increase as did the reference method and Unit 2 measurements. During the first injection, the reference method and both units indicated an increase.

[(b)] Relatively large uncertainties in the reference and continuous measurements made it difficult to determine a significant change.

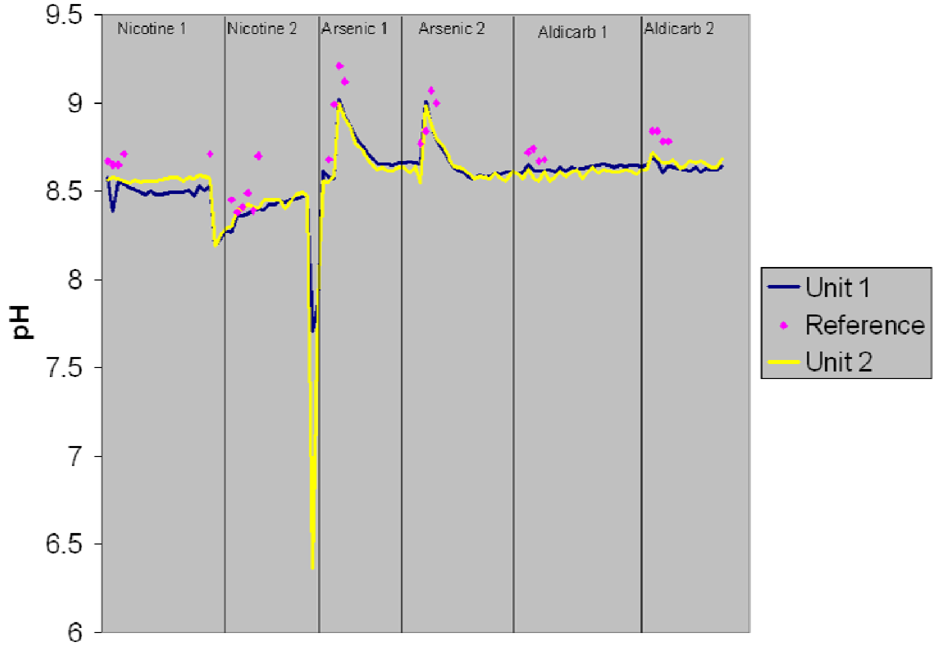
+/− = Parameter measurement increased/decreased upon injection.

NC = No change in response to the contaminant injection.



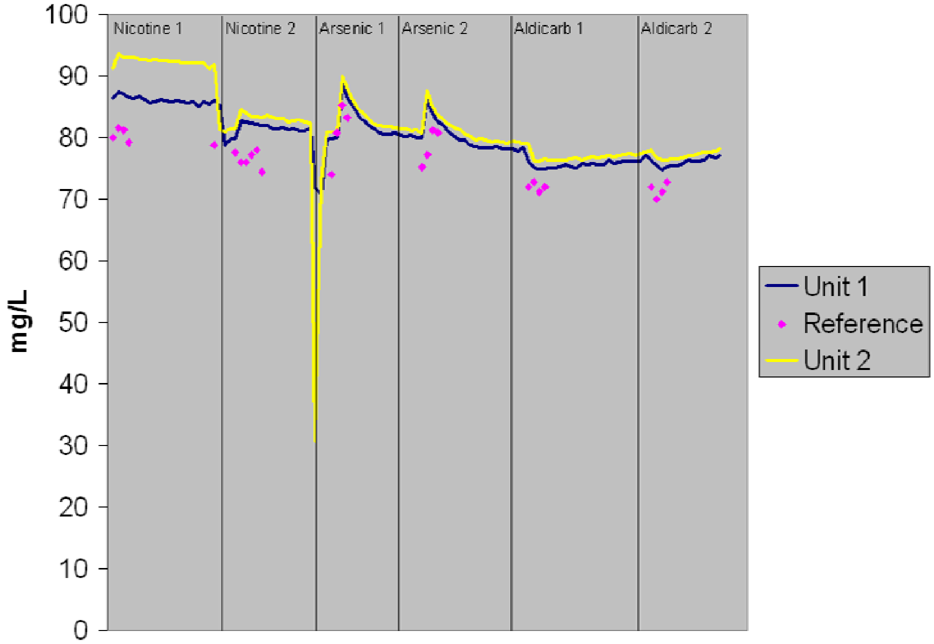
Each section of this figure represents the time between contaminant injection and the sensor's return to a baseline measurement (approximately 24 hours).

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



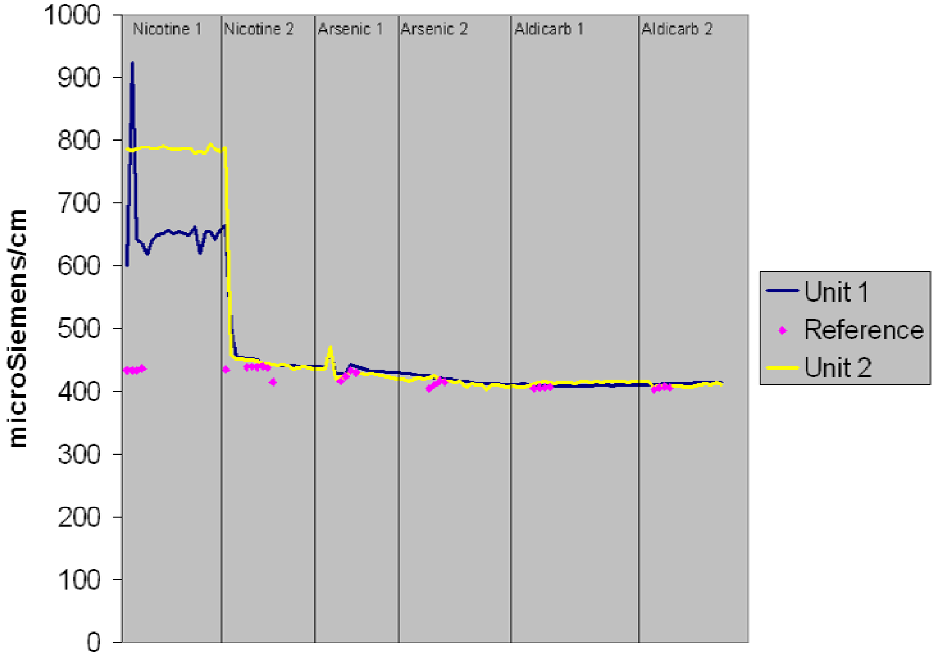
Each section of this figure represents the time between contaminant injection and the sensor's return to a baseline measurement (approximately 24 hours).

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



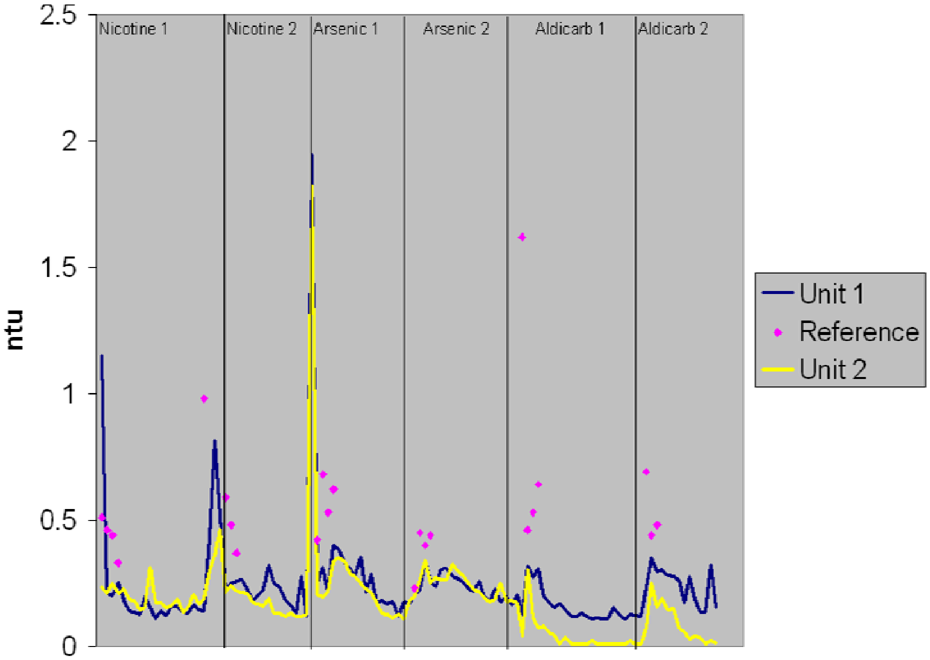
Each section of this figure represents the time between contaminant injection and the sensor's return to a baseline measurement (approximately 24 hours).

Figure 6-3. Stage 2 Contaminant Injection Results for Total Alkalinity



Each section of this figure represents the time between contaminant injection and the sensor's return to a baseline measurement (approximately 24 hours).

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



Each section of this figure represents the time between contaminant injection and the sensor's return to a baseline measurement (approximately 24 hours).

Figure 6-5. Stage 2 Contaminant Injection Results for Turbidity

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 figure. For each injection, at least four reference sample results were collected and are included in this figure. 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. Each of the reference measurement results are shown; but, because the TitraSip™ only collected data every 30 minutes, they are not aligned perfectly with the times of their analyses. They are aligned with the closest TitraSip™ analysis time.

Prior to the injections, the total chlorine level was between 0.9 and 1.3 mg/L and within 10% to 20% of the reference measurement. After injection, the total chlorine level, as measured by the reference method, dropped to between 0.5 and 0.2 mg/L for nicotine and to nearly 0 mg/L for arsenic and aldicarb. Upon the injection of nicotine, the chlorine level decreased to approximately 0.5 mg/L. For the other four injections, the TitraSip™ units immediately dropped to a concentration of nearly 0 mg/L, as had the laboratory reference method. After each injection, the total chlorine level in the pipe loop system was restored to approximately pre-injection conditions by adding sodium hypochlorite. This is shown in Figure 6-1 by the rapidly increasing total chlorine measurements after the low point was reached.

The pH and total alkalinity were affected by the arsenic trioxide injection. The conductivity reference measurement increased slightly upon injection of arsenic trioxide. That increase was measured by both TitraSip™ units during the first injection, but only by Unit 2 during the second injection. In addition, the effect of the injections on turbidity was not clear for the reference method or for the TitraSip™. For all the injections except the second arsenic injection, the level of turbidity measured by the reference method decreased from the time the pre-injection reference sample was collected until the subsequent reference samples were collected and analyzed. This suggests that 1) the contaminant injections did not increase the turbidity in the flowing water or, 2) that the uncertainty in the reference measurements was too large to determine whether turbidity was significantly affected. In any case, any change in turbidity due to the injections was not clear from the TitraSip™ measurements because of this overall uncertainty in the background turbidity measurements.

6.3 Extended Deployment

Figures 6-6 through 6-11 show the continuous measurements from both TitraSip™ 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 minutes during the verification test; and, for the extended deployment figures, all data points were depicted.

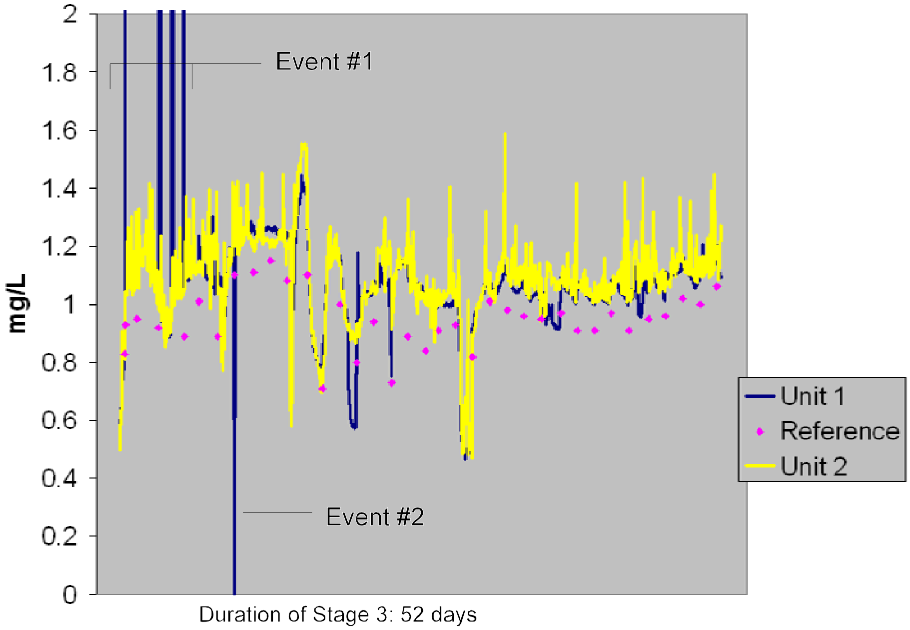


Figure 6-6. Extended Deployment Results for Total Chlorine

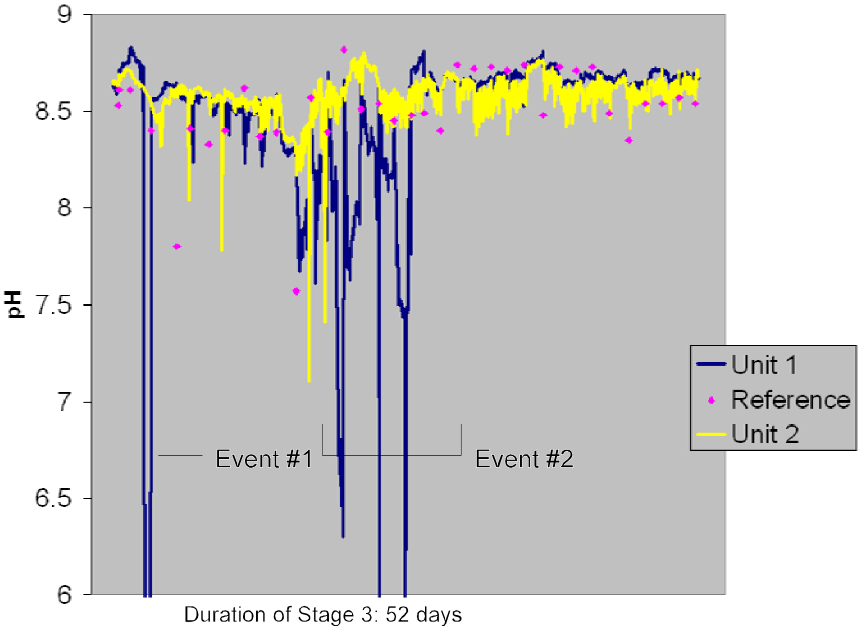


Figure 6-7. Extended Deployment Results for pH

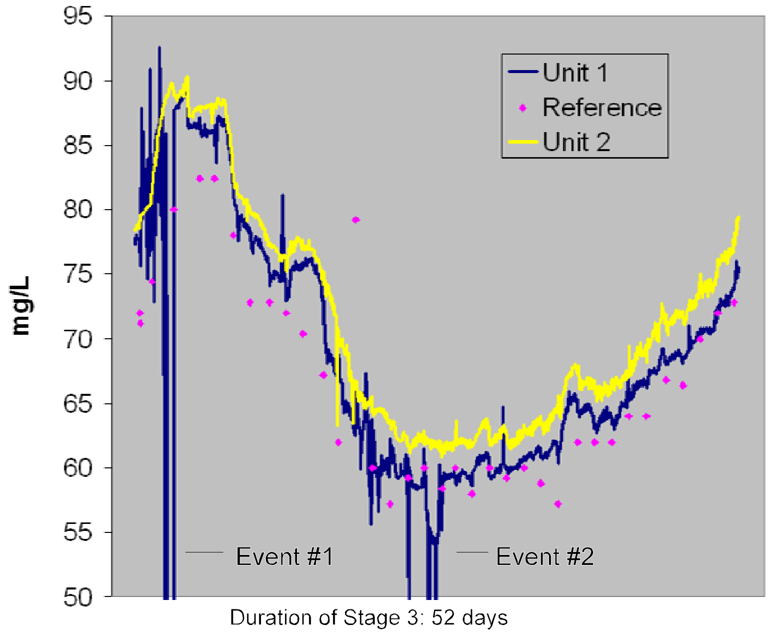


Figure 6-8. Extended Deployment Results for Total Alkalinity

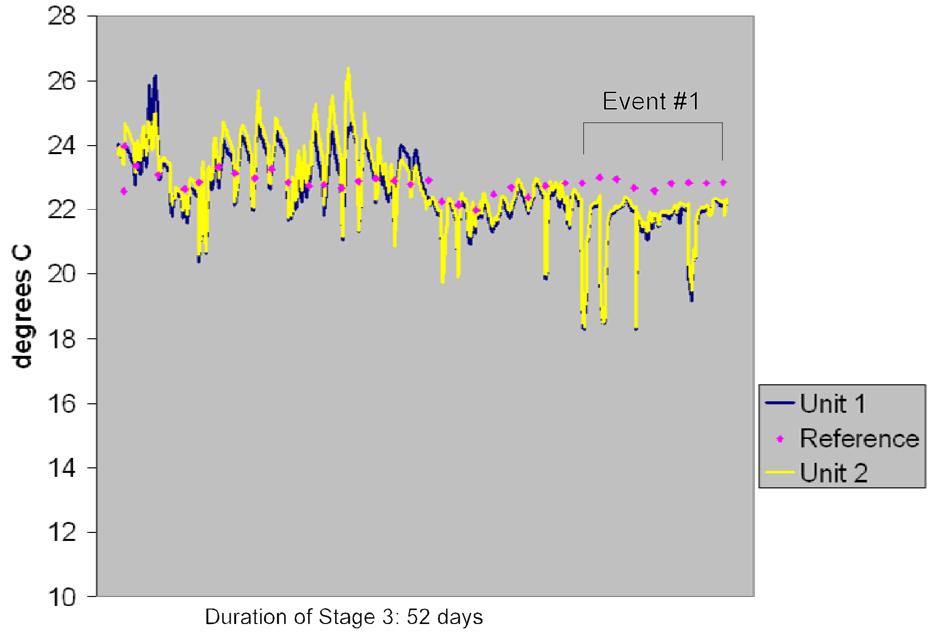


Figure 6-9. Extended Deployment Results for Temperature

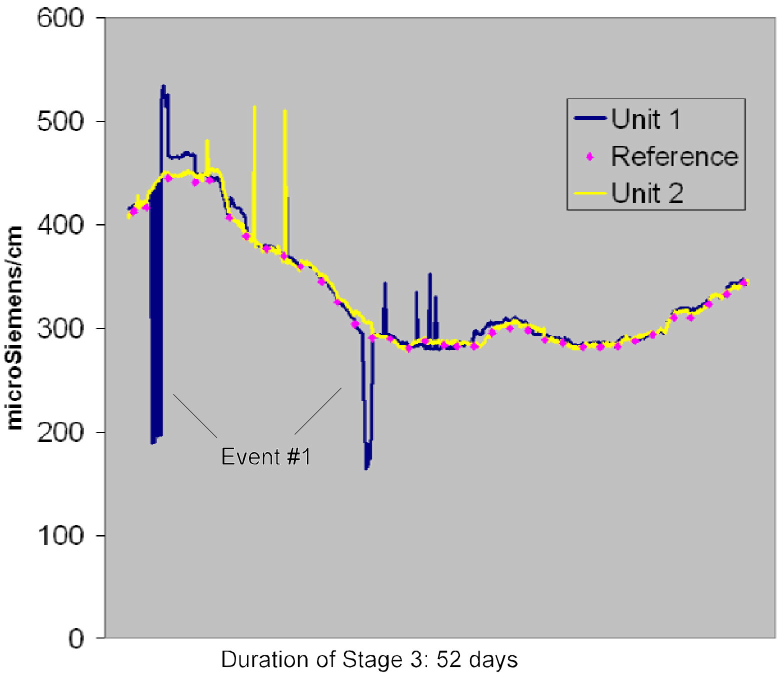


Figure 6-10. Extended Deployment Results for Conductivity

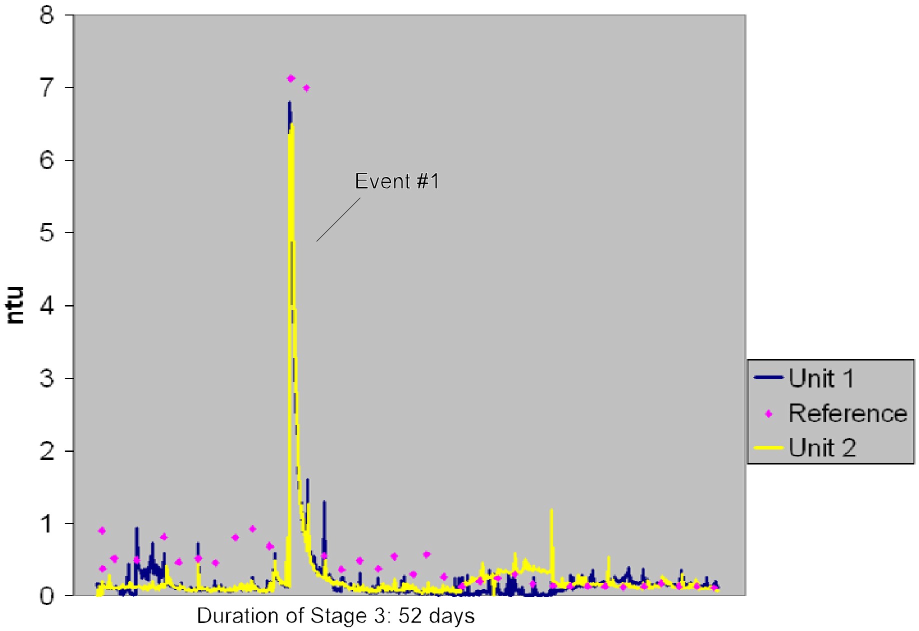


Figure 6-11. Extended Deployment Results for Turbidity

The objective of this stage of the verification test was to evaluate the performance of the TitraSip™ 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 indicate 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 TitraSip™ 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, total 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 intepreting 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

	Reference	Unit 1		Unit 2		Both Units %D
Parameter	**Average (SD)(a)**	**Average (SD)(a)**	**%D**	**Average (SD)(a)**	**%D**	**Range (median)**
Total chlorine(b)	1.05 (0.10)	1.08 (0.12)	2.9	1.08 (0.12)	2.9	-18.0 to 30.0 (2.7)
Temperature	22.81 (0.35)	21.88 (1.07)	-4.1	22.01 (1.12)	-3.5	-15.7 to 3.7 (-3.1)
Conductivity	352 (55)	336 (58)	1.2	335 (56)	0.9	-2.8 to 5.2 (0.7)
pH	8.73 (0.07)	8.60 (0.12)	-1.5	8.62 (0.10)	-1.3	-4.4 to 0.7 (-1.1)
Total alkalinity	66.86 (7.71)	68.99 (8.46)	3.2	71.61 (8.32)	7.1	-16.5 to 14.4 (5.7)
Turbidity	0.74 (1.57)	0.42 (1.09)	-43.2	0.35 (1.04)	-52.7	-96.7 to 155.3 (-37.3)

(a) Free chlorine, mg/L; temperature, °C; conductivity, µS/cm; total alkalinity, mg/L; pH, pH units.
(b) Four data points were omitted as outliers because of air bubbles in the titration buret.

For total chlorine, visual inspection of the data in Figure 6-6 revealed that, overall, the TitraSip™ measurements were consistently slightly higher than the laboratory reference measurements. During the early part of Stage 3, Unit 1 had four very high positive total chlorine spikes (total chlorine Event #1 in Figure 6-6) and one negative spike (total chlorine Event #2). Man-Tech determined that air bubbles in the buret that was used to titrate water with sodium thiosulfate were causing the problem. Periodically purging the buret manually eliminated any air bubbles, which is evidenced by the lack of large spikes in the total chlorine data throughout the remainder of Stage 3. With the exception of the aforementioned spikes, the percent difference for both TitraSip™ units ranged from -18.0 to 30.0, with a median of 2.7. The average total chlorine concentration, as measured by the reference method, was 1.05 ± 0.10 mg/L, while both TitraSip™ units measured an average of 1.08 mg/L ± 0.12.

The extended deployment pH results are shown in Figure 6-7. With the exception of one negative spike (pH Event #1 in Figure 6-7), the pH measurements from both units tracked each other and the reference measurements fairly well early in Stage 3. Unit 2 continued tracking the reference measurements rather well, while the Unit 1 pH measurements became extremely variable over the next several days (pH Event #2). Man-Tech determined that, during the calibration routine, the TitraSip™ Analysis Vessel on Unit 1 was not draining properly, preventing calibration reagent from emptying completely from the TitraSip™ Analysis Vessel prior to adding the next calibration reagent, thus invalidating the calibration and causing the variable results. During a service visit, Man-Tech determined that broken glass from the temperature probe was obstructing the drain. The temperature probe apparently broke when the system was installed. The temperature results was not affected; but when the glass was removed, the performance of the pH electrode became steadier; and both units tracked one another and the reference method well. The average pH, as measured by the reference method, was 8.73 ± 0.07, and the averages for Units 1 and 2, respectively, were 8.60 ± 0.12 and 8.62 ± 0.10. Overall, during the extended deployment, the percent difference for the pH sensor ranged from -4.4 to 0.7, with a median of -1.1.

As shown in Figure 6-8, the total alkalinity results for both units tracked one another and the reference results. However, there was a brief period of high variability in Unit 1 near the start and middle of the stage (total alkalinity Events #1 and #2 in Figure 6-8), which subsided quickly Because pH is the critical measurement in determining alkalinity, this variability probably corresponded with the aforementioned pH electrode calibration problem. One other aspect of the alkalinity data to note is that the Unit 2 results were consistently biased slightly high with respect to Unit 1.

The temperature results for 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 temperatures for the day. As shown in Figure 6-9, as Stage 3 progressed, the temperature results from both units became slightly lower with respect to the reference results (temperature Event #1 in Figure 6-9) probably because the Man-Tech units were located near an outside door that was often opened, while the reference measurement was performed on the second floor of the T&E Facility, where the ambient air temperature was not affected as much by the outdoor temperature.

As shown in Figure 6-10, the TitraSip™ units had a few low conductivity spikes (conductivity Event #1 in Figure 6-10), but the conductivity measurements from both units tracked the reference measurements very well. Figure 6-11 shows that, in the early part of Stage 3, the turbidity measurements were generally lower than the reference method measurement; however, this improved during the second half of the stage. The reason for this improvement was not apparent. One other item of note on Figure 6-11 is the high turbidity event about one-third of the way through the stage (turbidity Event #1 in Figure 6-11). The event was caused by an unknown occurrence in the Cincinnati water system. The reference result matched the TitraSip™ result rather well during that event.

6.4 Accuracy and Response to Injected Contaminants After Extended Deployment

After the 52-day deployment of the TitraSip™ units, 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 the conductivity measurement, the percent differences determined after the extended deployment for total chlorine, total alkalinity, turbidity, temperature, and pH were not considerably different from those determined during Stage 1. Because the TitraSip™ units were routinely calibrated, it was not expected that the extended deployment would negatively affect their results. However, as discussed in Section 6.1, Man-Tech introduced a new calibration procedure for the conductivity meter after the Stage 1 testing. Prior to using the new procedure, the difference between the TitraSip™ and the reference method was at least 40%; afterwards, it improved to less than 5%.

Table 6-5. Post-Extended Deployment Results

	Reference	Unit 1		Unit 2	
Parameter	**Average (SD)(a)**	**Average (SD)(a)**	**%D**	**Average (SD)(a)**	**%D**
Total chlorine	1.03 (0.03)	1.04 (0.01)	1.0	1.03 (0.03)	0.0
Temperature	22.66 (0.16)	22.16 (0.09)	-2.2	22.23 (0.06)	-1.9
Conductivity	356 (1)	357 (2)	0.3	360 (2)	1.1
pH	8.59 (0.01)	8.50 (0.01)	-1.0	8.41 (0.09)	-2.1
Total alkalinity	77 (0.83)	76.73 (0.12)	-0.4	80.49 (0.66)	4.5
Turbidity	0.17 (0.02)	0.23 (0.11)	35.3	0.24 (0.06)	41.2

(a) Total chlorine, mg/L; temperature, °C; conductivity, pH, pH units; µS/cm; total alkalinity, mg/L; turbidity, ntu.

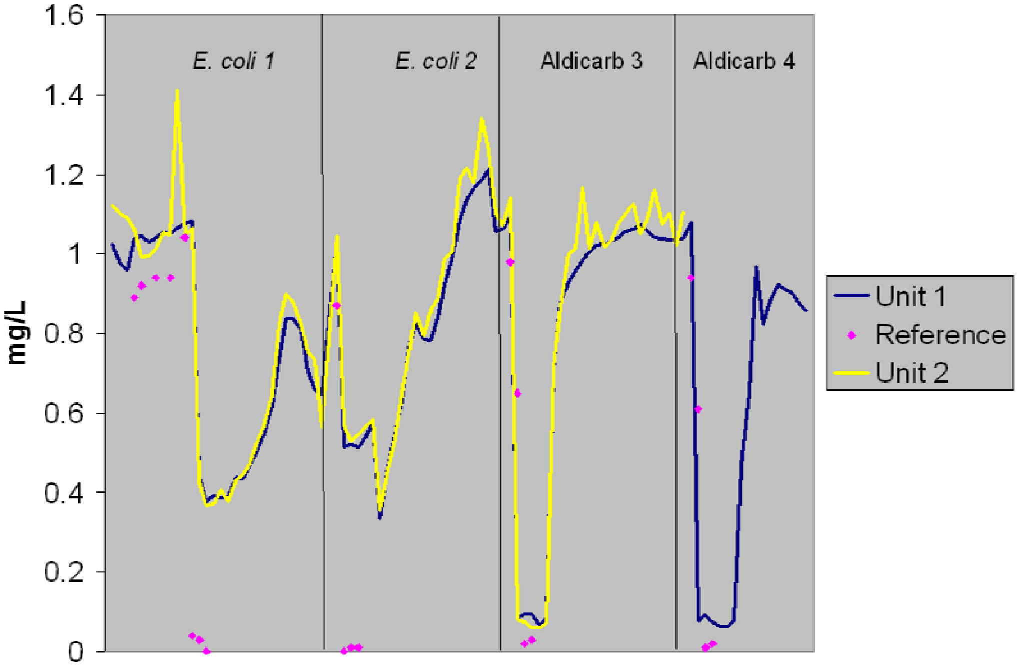
A second evaluation of the response to injected contaminants after the extended deployment used four contaminants. Two were a repeat of the aldicarb injections performed during Stage 2 and two were injections of *E. coli*, which was not available for injection during the earlier stage of the test. Table 6-6 shows the directional change of each reference and TitraSip™ measurement in response to the contaminant injections. In general, total chlorine was visibly affected (through visual observation of both the reference and continuous data) by all four injections. As shown in Figure 6-12, the reference result in each case was a drop to nearly 0 mg/L of chlorine almost immediately upon injection, but the TitraSip™ measurements did not drop as low as the reference result during the *E. coli* injection. Both units only reached approximately 0.4 or 0.5 mg/L. However, for the first aldicarb injection, both units responded in the same direction as the reference method. For the last aldicarb injection, Unit 1 responded as it had for the first injection, but the Unit 2 data were lost because of an operator error during the downloading process.

As Figure 6-13 shows, turbidity visually appeared to be affected by the first and last injection, but the results were not as clear for the middle two injections. The reference response to both *E. coli* injections and the final aldicarb injection indicated increases in turbidity between the pre-injection reference sample and the subsequent reference samples, specifically, the *E. coli* and

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

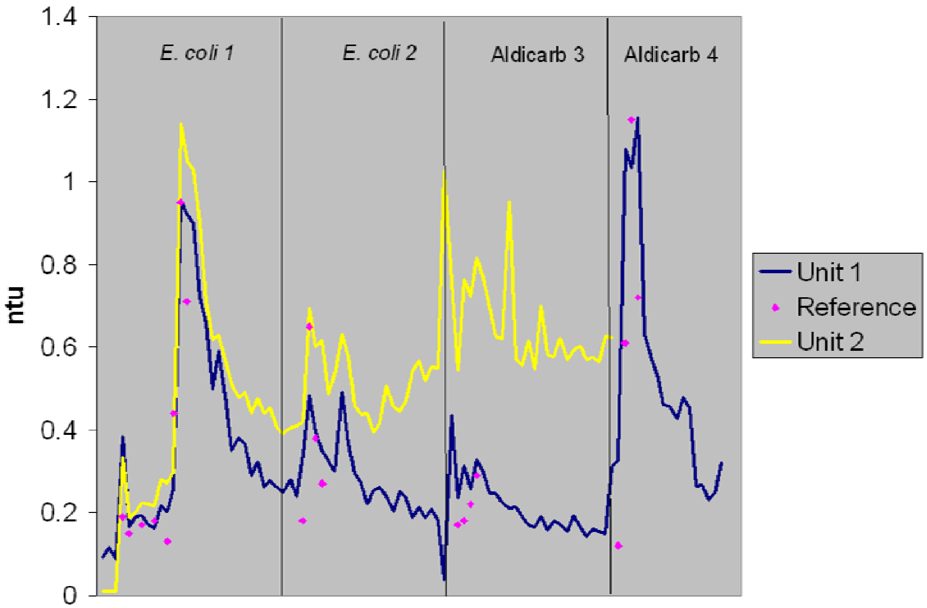
	E. coli		Aldicarb	
Parameter	**Reference**	**TitraSip™**	**Reference**	**TitraSip™**
Total chlorine	–	–	–	–
Temperature	NC	NC	NC	NC
Conductivity	+	+	NC	NC
pH	–	–	–	–
Total alkalinity	+	+	–	–
Turbidity	+	(a)	+	(a)

(a) One duplicate injection produced an obvious increase in turbidity; the other did not.
+/– = Parameter measurement increased/decreased upon injection.
NC = No change in response to the contaminant injection.



Each section of this figure represents the time between contaminant injection and the sensor's return to a baseline measurement (approximately 24 hours).

Figure 6-12. Stage 3 Contaminant Injection Results for Total Chlorine

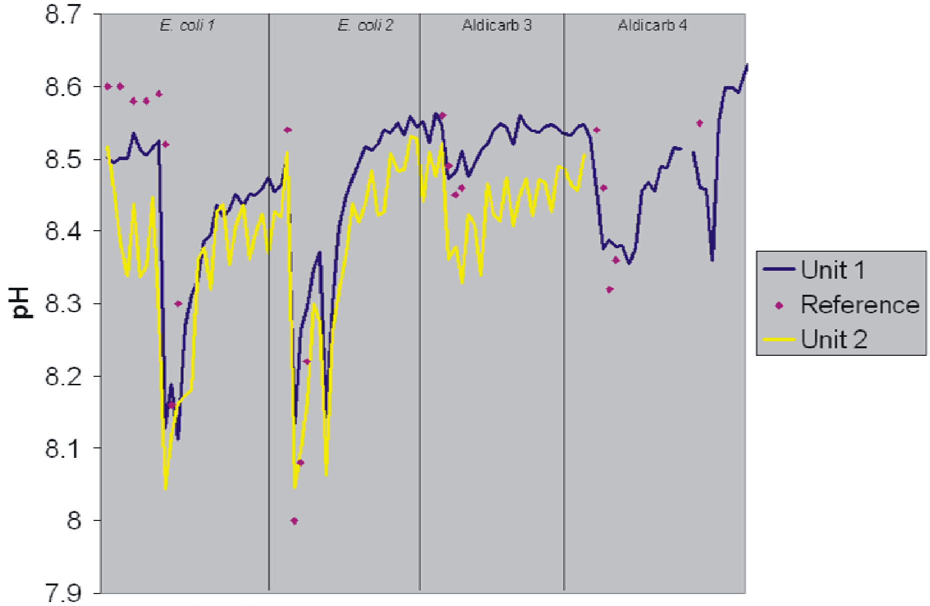


Each section of this figure represents the time between contaminant injection and the sensor's return to a baseline measurement (approximately 24 hours).

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

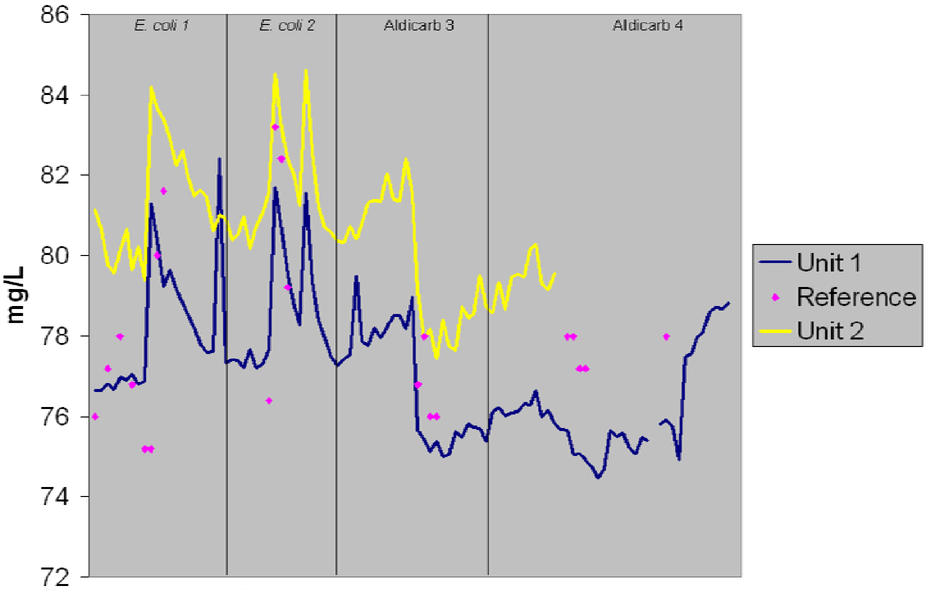
aldicarb injections produced changes of 0.82, 0.12, 0.43, and 1.03 ntu, respectively. Because of the inherent turbidity of an *E. coli* culture, it was expected that turbidity would be consistently responsive to that contaminant. Also, because aldicarb was completely dissolved, it was not expected to increase the turbidity of the water upon injection. However, the conditions surrounding the injection of both contaminants, such as the potential co-injection of air bubbles, may have affected the turbidity as much as or more than the contaminant itself. Regardless of what caused the variations in turbidity, the continuous monitor tracked the relative magnitude of the change in turbidity rather well for the first *E. coli* injection and the final aldicarb injection (data only available for one monitor); but, for the other two injections, the uncertainty of the background made it difficult to determine if a change occurred.

Figures 6-14 through 6-16 show the effect of the injections on pH, total alkalinity, and conductivity. The pH was clearly affected by both *E. coli* injections (as shown by both the reference and continuous measurements) and, to a lesser extent, by the aldicarb injections. This was also the case for total alkalinity. Both *E. coli* injections produced rather sharp downward spikes in pH and upward spikes in total alkalinity and conductivity. Note that a second *E. coli* injection was performed by T&E facility staff (not a part of the ETV test) immediately after the second *E. coli* injection. Its effect is observed in all three of these measurements. There was a downward trend in pH and total alkalinity (for both the reference and TitraSip™ measurement) during the aldicarb injection. Aldicarb had not altered the pH or total alkalinity during the Stage 2 injections, so this result was unexpected.



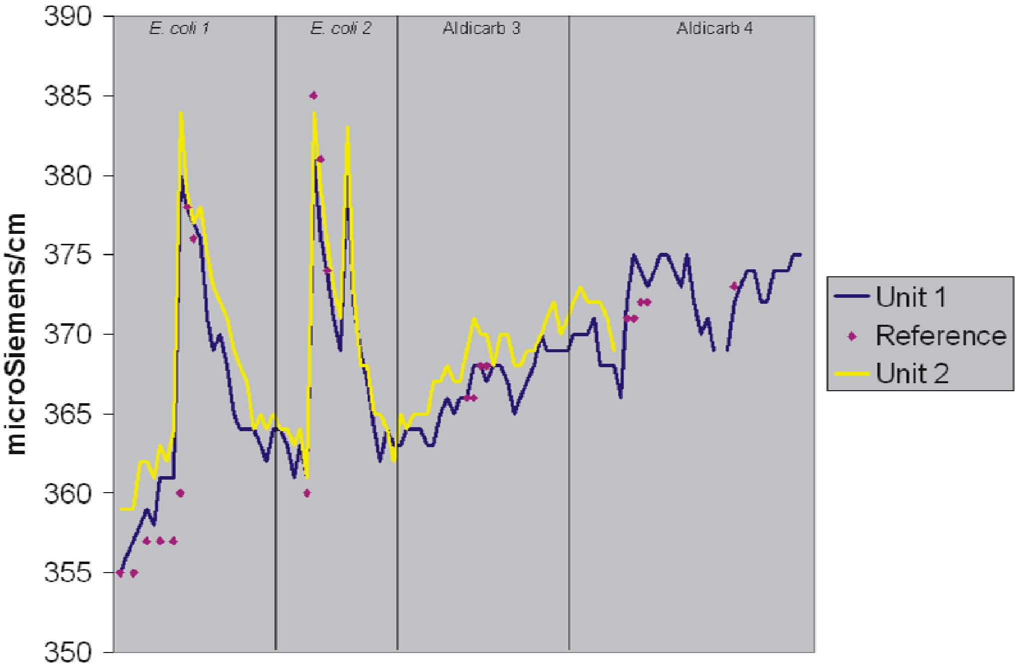
Each section of this figure represents the time between contaminant injection and the sensor's return to a baseline measurement (approximately 24 hours).

Figure 6-14. Stage 3 Contaminant Injection Results for pH



Each section of this figure represents the time between contaminant injection and the sensor's return to a baseline measurement (approximately 24 hours).

Figure 6-15. Stage 3 Contaminant Injection Results for Total Alkalinity



Each section of this figure represents the time between contaminant injection and the sensor's return to a baseline measurement (approximately 24 hours).

Figure 6-16. Stage 3 Contaminant Injection Results for Conductivity

6.5 Inter-unit Reproducibility

Two TitraSip™ units were compared throughout the verification test to determine whether they generated results that were similar to one another. This was done using the TitraSip™ 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 TitraSip™ 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.

As shown in Table 6-7, the pH, temperature, and total chlorine results had coefficients of determination greater than 0.94 and slopes within 6% of unity, indicating that their results were very similar and repeatable. Confirming that evaluation, the t-test p-values for the same three parameters were 0.85, 0.92, and 0.48, respectively, indicating that each unit was generating statistically similar results. The conductivity sensors had a coefficient of determination greater than 0.89, indicating that these data were highly correlated with one another; however, the slope values were approximately 9% and 16% from unity. This reflected the tendency of Unit 1 to

Table 6-7. Inter-unit Reproducibility Evaluation

Parameter	Slope	Intercept	r^2	t-test p-value
Conductivity	1.16	-38.1	0.896	0.110
pH	0.94	0.545	0.981	0.851
Total alkalinity	0.79	18.1	0.873	0.149
Turbidity	0.67	0.104	0.683	0.449
Temperature	1.06	-1.22	0.942	0.915
Total chlorine	1.06	0.03	0.958	0.481

experience negative spikes throughout the verification test. However, the difference between the two units was not consistent enough to cause the t-test to indicate a significant difference between the two units.

The total alkalinity and turbidity results from both units were not statistically different from one another. Therefore, none of the water quality parameter measurements of the TitraSip™ units were significantly different. These results were confirmed through visual observation of the figures throughout Chapter 6 because, when graphed, the data from both units were usually almost superimposed on each other. The only exception was total alkalinity, for which Unit 2 measurements were consistently higher than Unit 1; but, because of the variability of the Unit 1 measurements, they were not significantly different from each other.

6.6 Ease of Use and Data Acquisition

The TitraSip™ units required daily calibration by the verification staff. Once each day, the controller was manually rebooted, and an automatic “prime and purge” routine was performed to prepare the units for the upcoming day’s analyses. Analysis routines for the following 24 hours were programmed at this time. Other daily tasks included checking the levels of total chlorine and total alkalinity titration reagents and calibration standards for the pH, conductivity, and turbidity meters. The pH and conductivity meters were calibrated daily by using another automatic routine, while the turbidity meter was only calibrated once per week. Because the TitraSip™ units collect a sample from the flowing stream and then perform analyses on that water sample (conductivity, temperature, pH, turbidity, total alkalinity simultaneously, followed a few minutes later by total chlorine), they generate a complete set of results approximately every 30 minutes. Therefore, that is the maximum data collection frequency. These results were stored in a database that was downloaded into a delimited text file for import into Microsoft® Excel. The software used to program the calibration and analysis routines was easy to use. Note that this equipment appeared to be a bench-top instrument (as opposed to a field-deployable instrument that attaches to a wall).

A month-long period during Stage 3 required in-depth troubleshooting of Unit 1. Initially, the sample cell on that unit would not drain completely between analyses of separate pH calibration solutions. The most obvious way in which the problem made itself known was through decreased pH results (see Figure 6-3) and occasional very high outlying total chlorine results. Failed conductivity calibrations also made the problem evident. Because the TitraSip™ units each use a single sample cell for every analysis, any residual sample from a previous calibration or rinse solution can skew the results of subsequent analyses. The ETV staff worked with the

Man-Tech staff to resolve the drain problems. Once resolved, both TitraSip™ units functioned properly through the end of the verification test. Note that the method for conductivity calibration was altered near the beginning of Stage 2 of the verification test. This greatly decreased the percent differences of the conductivity results for the rest of the test.

Chapter 7
Performance Summary

Evaluation Parameter			Total Chlorine	Tem-perature	Conductivity	pH	Total Alkalinity	Turbidity
Stage 1—Accuracy	Units 1 and 2, range of %D (median)		-13.2 to 20.6 (7.5)	-9.1 to 52.5 (-0.04)	37.9 to 94.3 (57.5)(a)	-2.2 to 5.4 (0.6)	3.2 to 30.4 (11.5)	-65.2 to 0.6 (-45.2)
Stage 2—Response to Injected Contaminants	Nicotine	Reference	–	NC	NC	NC	NC	(b)
		TitraSip™	–	NC	NC	NC	NC	(b)
	Arsenic trioxide	Reference	–	NC	+	+	+	(b)
		TitraSip™	–	NC	+(c)	+	+	(b)
	Aldicarb	Reference	–	NC	NC	NC	NC	(b)
		TitraSip™	–	NC	NC	NC	NC	(b)
Stage 3—Accuracy During Extended Deployment	Units 1 and 2, range of %D (median)		-18.0 to 30.0 (2.7)	-15.7 to 3.7 (-3.1)	-2.8 to 5.2 (0.7)	-4.4 to 0.7 (-1.1)	-16.5 to 14.4 (5.7)	-96.7 to 155.3 (-37.3)
Stage 3—Accuracy After Extended Deployment	Unit 1, %D		1.0	-2.2	0.3	-1.0	-0.4	35.3
	Unit 2, %D		0.0	-1.9	1.1	-2.1	4.5	41.2
Stage 3—Response to Injected Contaminants	*E. coli*	Reference	–	NC	+	–	+	+
		TitraSip™	–	NC	+	–	+	(c)
	Aldicarb	Reference	–	NC	NC	–	–	+
		TitraSip™	–	NC	NC	–	–	(c)
Injection Summary	For a reason that is not clear, aldicarb and total alkalinity 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)		1.06 (0.03)	1.06 (-1.22)	1.16 (-38.1)	0.94 (0.545)	0.79 (18.1)	0.67 (0.104)
	r^2		0.958	0.942	0.896	0.981	0.873	0.683
	p-value		0.481	0.915	0.110	0.851	0.149	0.449
	All sensors generated results that were similar and repeatable between the units.							
Ease of Use and Data Acquisition	The TitraSip™ units required daily calibration, which involved operator intervention. Initially, the sample cell on Unit 1 did not drain completely between pH calibration solutions, but once the drain problem was resolved, both units functioned properly. Monitor results were recorded once every 30 minutes, which is the maximum data collection frequency.							

(a) Calibration procedure for the conductivity meter was changed after Stage 1, resulting in much lower percent differences throughout the remainder of the verification test.

(b) Relatively large uncertainties in the reference and continuous measurements made it difficult to determine a significant change.

(c) Duplicate injection results did not agree.

+/– = 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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