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Environmental Technology Verification Report

SENSICORE, INC.
WATERPOINT 870

Prepared by
Battelle

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ETV ETV ETV

September 2007

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

SENSICORE, INC.
WATERPOINT 870

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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 environmental technology 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.

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List of Abbreviations

%D	Percent Difference
AMS	Advanced Monitoring Systems
ASTM	American Society for Testing and Materials
$CaCO_3$	Calcium Carbonate
CDW	Columbus, Ohio Public Utilities Division of Power and Water
cm	Centimeter
D	Absolute Difference
DI	Deionized
DW	Drinking Water
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification Program
IPW	“In-Process” Drinking Water
mg/L	Milligrams per liter
µS/cm	MicroSiemens per centimeter
mm	millimeters
NA	Not Applicable
NERL	U.S. EPA National Exposure Research Laboratory
NIST	National Institute of Standards and Technology
ORP	Oxidation Reduction Potential
PE	Performance Evaluation
QA	Quality Assurance
QC	Quality Control
QMP	Quality Management Plan
RSD	Relative Standard Deviation
SM	Standard Methods
SW	Surface Water
TCEQ	Texas Commission on Environmental Quality
TSA	Technical Systems Audit
WP870	Sensicore WaterPOINT 870

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 (EPA NERL) and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of the Sensicore WaterPOINT 870 (WP870), a multi-parameter water sensor. This test was carried out in collaboration with the Columbus, Ohio Department of Public Utilities Division of Power and Water (CDW).

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 WP870. Following is a description of the WP870, based on information provided by the vendor. The information provided below was not verified in this test.

Sensicore has developed a lab-on-chip micro-sensor array technology called the WaterPOINT 870 that incorporates chemical selective sensors and physical measuring devices on a single silicon chip. This panel of tests is used to chemically profile drinking water (and/or other liquids) in five minutes. This handheld system was designed for both municipal and industrial applications. It employs Sensicore's platform sensor chip with five membrane-based ion selective electrodes capable of detecting light metal ions and dissolved gases, two micro amperometric arrays for detecting free chlorine and monochloramine species, and electronic sensors for measuring oxidation-reduction potential (ORP), conductivity, and temperature. All of these sensors are incorporated on a single silicon substrate that is 4 millimeters (mm) × 5 mm in size and conveniently packaged in a semi-disposable unit that also contains its own reference electrode. In all, with the direct measurements and calculated values that can be obtained from the direct measurements, the system reports 16 different results as follows: pH, ORP, conductivity, total dissolved solids, free chlorine, monochloramine, free and total ammonia, chlorine-ammonia ratio, biocide-food ratio, carbon dioxide, total alkalinity, calcium, calcium hardness, total hardness, and Langelier Saturation Index. Only the direct measurements including pH, ORP, conductivity, free chlorine, monochloramine, free ammonia, calcium hardness, and total alkalinity results were verified during this test.

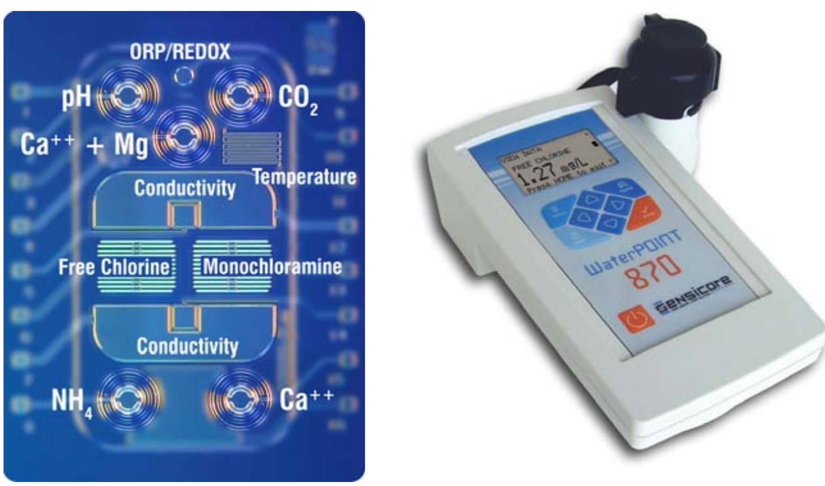

Figure 2-1 Schematic of a WP870 sensor (left) and a photo of the handheld unit (right)

The WP870 handheld system includes several features:

- Incorporates a single point calibration/QC check into every measurement;
- Calibrates all sensors via weekly two-point calibration;
- Transfer of results and sensor diagnostic and calibration information to computer via USB connection;
- Includes sample chain of custody information including time and date stamp, test location (including an optional GPS recording if desired) and a barcode recorder for identifying samples
- Software is menu driven and requires little training;
- Powered by rechargeable battery;
- Is compatible with WaterNOW software which is an online and secure data service utilizing 128-bit data encryption that helps the user understand data they have collected through unique visualization and comparison tools. It provides a means for the user to combine data from a variety of locations. Datasets from the WP870 analyzer can be uploaded through the internet or through email attachment. Subscriptions for the WaterNOW service start at $400 per month;
- Has dimensions of approximately 16 centimeters (cm) × 22 cm and weighs 1.75 pounds;
- Completes full analysis within five minutes;
- One time cost of $2,495 for the handheld unit, and $295 for every additional sensor chip (referred to as the "sensor" throughout this report) that is good for the analysis of 50 samples or for a duration of 30 days following the initial calibration, whichever comes first. New sensors include all necessary calibration solutions and sample buffers and conditioners required for the sample analyses. Note that each sample analysis provides results for all the above listed water quality parameters.

While not evaluated during this test, the WP870 has an Optical Module that includes the following capabilities:

- Turbidity measurements which meet US EPA Method 180.1
- 375 nm wavelength intrinsic color measurements following Standard Method 2120B
- Colorimetric measurements utilizing a red/green/blue light emitting diode and corresponding photodetectors to measure a variety of ampouled chemistries, including Total and Free Chlorine by Standard Method 4500 Cl-G.
- Total hardness ion selective electrode for the determination of hardness due to free calcium and magnesium.
- One time cost of $2,995 for the optic-enabled handheld unit, with sensor kits for free and monochloramine which are good for 90 analyses or up to 60 days ($295-$495), and ion selective electrode sensor kits which are good for 90 tests and up to 60 days ($225-$410).

Chapter 3
Test Design and Procedures

3.1 Test Overview

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Multi-parameter Water Sensors* including amendments 1-4[(1)] and adhered to the quality system defined in the ETV AMS Center Quality Management Plan (QMP).[2] Multi-parameter water sensor technologies consist of sensors that measure several different water quality parameters from grab samples. Throughout this test, the WP870 was challenged with a number of different types of water samples. For each sample, the WP870 generated all eight of the water quality parameters verified during this test. Those types of water samples included: 1) water samples that had been prepared in American Society for Testing and Materials Type II deionized (DI) water so the water quality parameters would cover the range of response for each parameter measured by the WP870, 2) finished drinking water samples, 3) surface water samples, and 4) water samples collected from within the water treatment process. In addition, the performance of the WP870 was evaluated over the lifetime (50 water samples or 30 days following initial calibration) of an individual sensor and handheld unit by first analyzing 15 samples prepared in DI water, then six finished drinking water samples, followed by another 15 samples prepared in DI water again. Some analyses were performed at a field location as well as in a laboratory.

The verification test for the WP870 was conducted from April through July 2007. This test was coordinated by Battelle, but conducted at the CDW and at various field locations. Technicians from both Battelle and CDW contributed to the testing effort. All reference measurements were performed on-site at the CDW laboratories.

The WP870 was verified by evaluating the following parameters:

- Accuracy – comparison to results from standard laboratory reference analyses for DI water, drinking water within the treatment process, finished drinking water, and untreated source water test samples
- Precision – repeatability from sample replicates analyzed on the same day
- Inter-unit reproducibility – comparison of results from two identical sensors and handheld units
- Field portability – operation during remote field site analysis
- Ease of use – general operation, data acquisition, set-up, consumables used, and purchase and operational costs.

3.2 Experimental Design

The verification test was organized into three stages that included: 1) samples prepared from DI water, 2) samples consisting of finished drinking water, surface water, or water within the drinking water treatment process, and 3) remote field analysis (qualitative testing only). Each stage of testing is described below as well as summarized in Table 3-1. As a reminder, the key component of the WP870 handheld unit is the sensor, a small chip that is inserted into the handheld unit and contains the functionality required for water quality parameter measurement. The software in the handheld unit keeps track and prevents more than 50 water samples to be analyzed per sensor and also prevents any analyses after 30 days following initial calibration. Therefore, the test sample matrix was designed to get the maximum amount of performance information from each sensor that was used. Six different sensors were used throughout testing.

Table 3-1. Test Sample Summary

Stage of Testing	Description and Number of Water Samples
Stage 1 Part 1 - Accuracy	Sensors 1 and 2: Three levels of the eight water quality parameters analyzed in triplicate using both sensors (72 individual results); as Table 3-2 shows, several of the water quality parameters were grouped into a single solution rather than requiring one solution for each water quality parameter, therefore, only a total of 45 water samples were analyzed by each sensor. All samples were compared to reference methods.
Stage 1 Part 2 - Performance Over Sensor Lifespan	Sensor 3: First, triplicate analysis of one level of solution groupings 1, 2, and 3 from Table 3-2 (12 results on 9 analyses), then triplicate analysis of six finished drinking water samples (18 analyses), and lastly, triplicate analysis of one level of solution groupings 1, 2, and 3 from Table 3-2 (12 results on 9 analyses). All samples were compared to reference methods. Sensor 4: Same as Sensor 3 only with solution groupings 4 and 5 from Table 3-2. All samples were compared to reference methods.
Stage 2 - Drinking, Surface, and "in-process" Water	Sensors 3 and 4: Six finished drinking water samples (analysis performed during Stage 1 Part 2) Sensors 5 and 6: Two surface water samples and two samples collected within the drinking water treatment process were analyzed in triplicate and compared to standard reference methods. Analyzed by the WP870 both at the collection location and after returning to the laboratory.
Stage 3 - Field Operation	Qualitative evaluation of operational performance when the WP870 is in use during field measurement scenarios

3.2.1 Stage 1 Laboratory Testing of DI Water Samples

Stage 1 consisted of two parts. The first part focused on testing the accuracy and precision of the sensors with respect to accepted laboratory reference methods. This was done by preparing test solutions with water quality measurements that spanned the working range of the sensor. Table 3-2 describes the levels of each water quality parameter that were analyzed. For example, the pH component of the WP870 was tested by preparing test solutions that covered the pH ranges from acidic (pH 5.4), to neutral (pH 7), to alkaline (pH 10). Table 3-2 also shows groupings of the water quality parameters that were evaluated by analyzing a single solution prepared for that purpose. The alkalinity, monochloramine, and pH measurements were each evaluated in unique solutions, but the other parameters were grouped in solution. The table also includes the key components and/or critical aspects of each solution's preparation. Each of these solutions was analyzed in triplicate on each of two sensors in order to thoroughly study the accuracy and precision of two different sensors installed on separate WP870 handheld units.

The second part of Stage 1 focused on testing the performance of the sensors over the vendor-specified lifetime of the sensors (30 days or 50 water samples) by testing one concentration level (the middle level) of the solutions given in Table 3-2, in triplicate twice, once near the start of the sensor's useful lifetime and once near the end. Between those analysis times, six finished drinking water samples were analyzed in order to challenge the sensor with more realistic samples between tests with samples prepared in DI water. If the sensors were susceptible to fouling due to analysis of drinking water samples, the second set of samples that had been prepared in DI water would be expected to exhibit diminished accuracy or precision. Because of the limitation of 50 samples per sensor, and because of the rigor of accuracy testing during the first part of Stage 1, this part of Stage 1 was split between two sensors in order to maintain the ability to perform triplicate analyses across the 30 day time period.

Table 3-2. Stage 1 Test Sample Information

Parameter Grouping	Water Quality Parameter	Levels	Test Sample Preparation (all samples in DI water)
1	pH	5.4, 7, 10 (pH units)	Citrate, Phosphate, and Borate Buffers
2	Alkalinity	22, 130, and 240 mg/L $CaCO_3$	Anhydrous sodium bicarbonate in DI water
3	Hardness	17.5, 125, and 225 mg/L $CaCO_3$	Calcium chloride
	Ammonia	0.1, 0.8, 1.5 mg/L	Ammonium chloride
4	Conductivity	100, 1100, 1700 µS/cm	Sodium chloride
	Free Chlorine	0.2, 1.2, 2.2 mg/L	Sodium hypochlorite
	Oxidation / Reduction Potential (ORP)	Use the free chlorine solutions to generate a range of oxidation reduction potentials.	
5	Monochloramine	0.2, 1.2, 2.2 mg/L	Addition of ammonium chloride to Sol. #4 with a 15 minute reaction time (pH>9)

mg/L – milligram per liter
µS/cm – microSiemens per centimeter

3.2.2 Stage 2 Laboratory and Field Testing of Drinking and Surface Water Samples

The second stage of this verification test focused on the performance of the WP870 when analyzing samples of finished drinking water, drinking water within the treatment process, and untreated surface water. Throughout the verification test (including the drinking water samples analyzed during the second part of Stage 1), six finished drinking water, two "in-process" water, and two source water samples were analyzed. The in-process and surface water samples were analyzed by the WP870 at a booster station within the CDW distribution system and then returned to the laboratory for reference analysis. In addition to the field measurements, all 10 samples were analyzed in the laboratory using the WP870. Each of these samples were analyzed in triplicate by the WP870 and then compared to the reference method results from these same samples.

3.2.3 Stage 3 Remote Field Analysis

The third stage of this verification test evaluated the ease of using the WP870 during a field water quality study with two collaborators. The ETV program collaborated with 1) personnel from EPA NERL who conducted a short-term field analysis campaign during September 2006 that consisted of measuring temperature, pH, and conductivity throughout Shayler's Run, a stream that flows into the East Fork of the Little Miami River in southern Ohio and 2) personnel from the Texas Commission on Environmental Quality (TCEQ) who conducted a similar sampling campaign in western Texas on the Rio Grande River in May of 2007. These studies were independent from the ETV test, but EPA NERL and TCEQ agreed to take the WP870 with them and perform single analyses at some of the measurement locations included in their studies. No grab samples were transported for reference analysis during this stage of the testing. Therefore, the focus of this part of the test was the evaluation of the practical aspects of using the WP870 under non-laboratory, field analysis conditions.

3.3 Laboratory Reference and Quality Control Samples

The WP870 was evaluated by comparing its results with standard reference measurements. The following sections provide an overview of the applicable procedures, analyses, and methods.

3.3.1 Reference Methods

The standard laboratory methods used for the reference analyses are shown in Table 3-3. Also included in the table are method detection limits and quality control (QC) measurement tolerances. CDW and Battelle technical staff performed the analyses for each of the water quality parameters. Any required instrumentation was calibrated as required by the reference method and those calibration activities were documented in the verification records. The CDW provided reference sample results within one day of the analysis. The monochloramine on the WP870 was measured directly while the monochloramine reference measurement was an indirect measurement based on the difference of total chlorine and free chlorine.

3.3.2 Reference Methods Quality Control Samples

As shown in Table 3-3, duplicate reference samples were collected and analyzed once daily during the verification test. Also, laboratory blanks consisting of DI water were analyzed with the same frequency. These blank samples were most important for the chlorine, ammonia, and monochloramine analysis because these were the only parameters that needed confirmation by the reference method of the lack of contamination. The other parameters produced a detectable result in DI water, so a blank sample could not be evaluated in a similar way. For those parameters, the performance evaluation (PE) audit confirmed the accuracy of the method and the absence of contamination. Tolerances for the PE audit comparisons and duplicate measurements had to be within the acceptable tolerances provided in Table 3-3 or corrective actions (as described in section B5 of the Test/QA plan) would be taken.

Table 3-3. Reference Methods

Parameter	Method	Instrument/ Description	Method Detection Limits	Acceptable Duplicate and PE Tolerance (%D)[a]
Ammonia	Standard Method (SM) 4500-NH_3[3]	Hach SENSion 1 Electrode	0.03 mg/L	25%
Hardness ($CaCO_3$)	SM 3500 - Ca- B[4]	EDTA titration	0.5 mg/L	25%
Conductivity	SM 2510[5]	YSI Datasonde	2 µS/cm	25%
Free Chlorine	SM 4500-Cl-G[6]	Hach Colorimeter	0.01 mg/L as Cl_2	25%
Monochloramine	SM 4500-Cl-G[6]	Hach Colorimeter	0.01 mg/L as NH_2Cl	25%
ORP	SM 2580-B[7]	Myron L Model 6P	NA	25%
pH	SM 4500-H^+-B[8]	YSI Datasonde	NA	±0.3 pH units
Alkalinity	SM 2320-B[9]	Sulfuric acid titration	20 mg/L	25%

NA – not applicable due to nature of that water quality parameter
[a]: %D defined in Section 4.1.1

3.4 Qualitative Evaluation Parameters

Operational factors such as general operation, data acquisition, set-up, demobilization, consumables used, purchase and operational costs, and ease of use were evaluated based on observations by Battelle, CDW, U.S. EPA NERL, and TCEQ staff. A laboratory record book was maintained at the host facility and was used to enter daily observations on these factors. Qualitative observations were made in logbooks during the field analyses.

Chapter 4
Quality Assurance/Quality Control

QA/QC procedures were performed in accordance with the QMP for the AMS Center[5] and the test/QA plan for this verification test.[1] QA/QC procedures and results are described below.

4.1 Audits

Three types of audits were performed during the verification test: a PE audit of the reference methods, a technical systems audit (TSA) of the verification test procedures, and a data quality audit. Audit procedures are described further below.

4.1.1 PE Audit

A PE audit was conducted to assess the quality of the reference measurements made in this verification test. Each type of reference measurement was compared with a National Institute of Standards and Technology (NIST)-traceable standard reference water sample or a standard that was obtained independently from the standard used to calibrated the reference instrument. The NIST-traceable standard reference water samples had certified values of alkalinity, chlorine, conductivity, hardness, and pH that were unknown to the analyst. The PE audit for ammonia was evaluated with a second source of ammonia, and that for ORP was performed with separately obtained stocks of Light solution, a solution that generates an ORP of approximately 450 millivolts. These samples were analyzed in the same manner as the rest of the reference analyses to independently confirm the accuracy of the reference measurements. As Table 4-1 shows, all PE audit results were within the acceptable differences provided in Table 3-3. The percent difference (%D) was calculated using the following equation:

$$\%D = \frac{C_N - C_R}{C_R} \times 100\% \qquad (1)$$

where C_R was the reference method result and C_N the NIST value for each respective water quality parameter.

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 monochloramine, all parameters were within the differences defined in Table 3-3. No corrective action was taken for the one monochloramine measurement (45.2% D) that was outside the acceptable difference because the absolute difference between the concentrations measured in those two duplicate samples was very small (0.07 mg/L) and the rest of the duplicate measurements were well within the acceptable tolerance of 25 %D. In addition, it should also be noted that because pH units are measured on a logarithmic rather than linear scale, the quality control metric for that parameter was the absolute unit rather than percent difference. The pH PE audit was completed after one attempt that was within, but nearly outside of, the acceptable range, therefore it was repeated.

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

	PE Audit Results			Reference Method Duplicate Analysis	
Parameter[(a)]	**Standard Value**	**Reference Method Result**	**%D**	**Average of Absolute Values of %D**	**Range of %D**
Alkalinity (mg/L)	36.2	35.0	-3.3%	2.51	0.0 to 5.7
Ammonia	0.60	0.56	-6.7%	3.08	1.5 to 6.9
Chlorine (mg/L Cl_2)	4.29	4.38	2.0%	2.80	0.0 to 6.2
Conductivity (µS/cm)	665	656	-1.4%	0.42	0.0 to 1.9
Hardness (mg/L $CaCO_3$)	136	137	0.7%	3.14	0.0 to 11.8
Monochloramine (mg/L)	NA	NA	NA	6.39[a]	0.0 to 18.2[a]
ORP (millivolts)	476	447	6.1%	1.19	0.0 to 5.1
pH[b]	7.05	7.00	0.05 pH units	0.02 pH units	0.00 to 0.04 pH units

[a] Removed outlier of 45.2%D because absolute difference was only 0.07 mg/L. %D was driven by small average concentration.
[b] Repeated measurement since original nearly failed acceptance criteria.
NA – No reliable traceable standard solution or method to compare reference method result.

4.1.2 Technical Systems Audit

The Battelle Quality Manager performed a TSA during the test to ensure that the verification test was performed in accordance with the AMS Center QMP, the test/QA plan, and published reference methods. 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 Data Quality Audit

At least 10% of the data acquired during the verification test were audited. The data was traced 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 QA/QC Reporting

Each audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center.[(5)] Once the audit reports were 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 submitted to the EPA.

4.3 Data Review

Records generated in the verification test received a one-over-one review before these records were used to calculate, evaluate, or report verification results. Data were reviewed by a Battelle technical staff member involved in the verification test. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Chapter 5
Statistical Methods

The statistical methods used to evaluate the quantitative performance factors listed in Section 3.1 are presented in this chapter. Qualitative observations were also used to evaluate verification test data.

5.1 Accuracy

Throughout this verification test, results from the WP870 were compared to the results obtained from analyses by the reference methods. The %D between these two results was calculated from the following equation:

$$\%D = \frac{C_m - C_R}{C_R} \times 100\% \qquad (2)$$

where C_R is the result determined by the reference method and C_m is the result from the WP870 units. Ideally, if the WP870 unit and reference method measurements were the same, there would be a percent difference of zero. For pH, which is measured on a logarithmic scale, and in cases when the water quality parameter levels were near the detection limit, the absolute difference from the reference measurement was used to evaluate accuracy.

5.2 Precision

The precision of the WP870 was evaluated by calculating the percent relative standard deviation (RSD) of each set of the triplicate samples that were measured during the verification test. The RSD is defined as the standard deviation of the results of the three replicates divided by the average result of the three replicates. Because pH is measured on a logarithmic scale, the RSD of pH was not calculated.

5.3 Inter-unit Reproducibility

The results obtained from two identical WP870 sensors were compared to assess inter-unit reproducibility. For each sample analysis during this verification test (119 samples), the triplicate results from each WP870 sensors were compared to evaluate whether the two WP870 sensors were generating similar results. This was done by performing a paired t-test with the assumption that the data from each WP870 sensors had equal variances. A probability of less than 0.05 indicated a significant difference between the two WP870 sensors. Results found to be statistically different from the two units were noted, in terms of the separate readings and absolute difference of the two units.

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 sensors. Stage 1 focused on the accuracy and precision of the WP870 when test samples were prepared in a DI water matrix as well as the performance of the WP870 throughout the expected lifetime of a sensor (30 days or 50 samples). Stage 2 focused on the accuracy and precision of water samples that were either raw surface water, water within the process of being treated within the water treatment system, or finished drinking water. Some of these samples were also analyzed at a field location as well as at the laboratory in order to evaluate their performance in both locations. Six different sensors were used throughout Stages 1 and 2. The results are given so it is clear what sensor is being used. Stage 3 was a qualitative evaluation of the operational aspects of the WP870 when it was used during two field analysis trips.

6.1 Accuracy and Precision

6.1.1 Stage 1 Laboratory Testing of DI Water Samples

Table 6-1 shows the water quality parameter levels that were prepared in each solution, the laboratory reference method result, the average result of the triplicate analyses by the WP870, the percent difference (%D) (or absolute difference (D) for pH only) for each parameter level, and the relative standard deviation for each set of replicate samples. All samples were analyzed by two WP870 units, identified as Sensor 1 and Sensor 2. For each level of alkalinity (except the lowest level of Sensor 2), conductivity, hardness, and ORP, the %Ds were all less than 10%. The %D for ammonia ranged from -19.9% to -23.8% for the higher two concentration levels and was 47.1% for the lowest concentration level. The absolute difference between the average WP870 result for ammonia and the reference measurement was only 0.05 mg/L, therefore, the rather large percent difference was driven in part by the small concentrations being considered. For free chlorine, the %Ds generated by each sensor were -41.2% and -29.4% for the lowest concentration sample, 11.5% and 11.8% for the middle concentration, and 23.6% and 26.8% for the highest concentration sample. For all the concentration levels of monochloramine across both sensors, the %Ds ranged from 12.7% to 28.4%. As mentioned previously, because pH is on a logarithmic scale, the absolute difference between the average result and the reference measurement was determined and used to evaluate the performance of the WP870 as a pH sensor. During Stage 1, the WP870 differed from the reference method by -0.05 and -0.08 for the pH 5.4 sample, 0.13 and 0.21 for the pH 7.0 sample, and -0.25 and -0.01 for the pH 10 sample. The RSD for each set of replicate samples is also given in Table 6-1. With the exception of the lowest free chlorine concentration, every triplicate set of samples exhibited

Table 6-1. Stage 1 Accuracy and Precision Results for the WP870

Water Quality Parameter	Test Level	Reference	Sensor 1			Sensor 2		
			Avg.	%D or D	%RSD	Avg.	%D or D	%RSD
Alkalinity (mg/L $CaCO_3$)	22	25	26	4.0%	3.8%	20	-20.0%	5.0%
	130	128	119	-7.3%	1.3%	122	-4.7%	3.0%
	238	238	225	-5.6%	8.7%	243	2.1%	7.2%
Ammonia (mg/L NH_3)	0.10	0.10	0.15	47.1%	0.0%	0.15	47.1%	0.0%
	0.80	0.81	0.63	-23.0%	4.0%	0.62	-23.8%	4.3%
	1.50	1.64	1.32	-19.7%	1.2%	1.31	-19.9%	0.9%
Conductivity (µS/cm)	100	106	106	0.3%	0.5%	112	5.7%	0.9%
	1100	1096	1126	2.7%	0.3%	1126	2.7%	0.1%
	1700	1540	1582	2.7%	0.2%	1548	0.5%	1.4%
Free chlorine (mg/L Cl_2)	0.20	0.17	0.10	-41.2%	26.5%	0.12	-29.4%	22.0%
	1.20	1.13	1.26	11.5%	2.9%	1.26	11.8%	4.4%
	2.20	1.98	2.45	23.6%	2.5%	2.51	26.8%	3.8%
Hardness (mg/L $CaCO_3$)	17.5	18	18	0.0%	0.0%	17	-5.6%	0.0%
	125	128	138	7.8%	1.9%	139	8.6%	3.3%
	225	234	247	5.7%	2.9%	256	9.3%	3.0%
Mono-chloramine (mg/L NH_2Cl)	0.20	0.21	0.24	12.7%	2.4%	0.24	15.9%	6.3%
	1.20	1.14	1.33	17.0%	3.0%	1.36	19.3%	1.3%
	2.20	1.91	2.35	23.0%	1.1%	2.45	28.4%	3.5%
ORP (millivolts)	[a]	551	500	-9.2%	7.6%	510	-7.5%	8.4%
		702	683	-2.8%	5.5%	684	-2.6%	2.4%
		694	688	-0.8%	6.3%	705	1.6%	4.0%
pH	5.40	5.34	5.29	-0.05	n/a	5.26	-0.08	n/a
	7.00	6.88	7.01	0.13	n/a	7.09	0.21	n/a
	10.00	9.87	9.62	-0.25	n/a	9.86	-0.01	n/a

[a] ORP test levels not set, but allowed to vary with free chlorine concentration.

RSDs that were below 10%, and in most cases less than 5%. Presumably, the increased variability for the lowest concentration of free chlorine is due to it being closer to the detection limit of the WP870.

The second part of Stage 1 focused on the performance of the sensors over their 30 day (or 50 sample) lifespan while attempting to simulate a measurement scenario in which the WP870 may be used for by a water utility or other end user. To do this, one concentration level of each water quality parameter (solutions prepared in DI water) was analyzed near the start of the sensor's lifetime, then six finished drinking water samples were analyzed to simulate how the sensor may actually be used, and then the same concentration level of each water quality parameter (again prepared in DI water) was analyzed again. These analyses covered approximately 30 days and utilized almost all of the 50 samples that each sensor is able to measure.

Table 6-2 presents the %D from the reference method both before and after the analysis of six finished drinking water samples. Instead of comparing the absolute results from before the drinking water samples were analyzed, the %Ds were used for the basis of comparison because the solutions were prepared once again prior to the second analysis and the reference analyses were also performed again. Therefore, the appropriate comparison is with respect to the reference method result at that time and not the absolute water quality parameter measurement performed at least several days prior using a different solution. The %Ds for alkalinity and ORP changed by 20.4% and 15.3%, respectively, while the other water quality parameters did not change any more than 10%. The results for alkalinity and ORP both indicated a smaller difference after the drinking water analyses than before. The pH result also improved from a difference of 0.18 from the reference method to a difference of just 0.04 during the second analysis. In addition to evaluating the %Ds for each parameter, the RSDs can also be evaluated in this way as results might be expected to become less repeatable as the sensor nears the end of its lifespan. However, there was little consistent change in %RSDs from before to after the analysis of the finished drinking water. In most cases, the %RSD either did not change more than a few percent or decreased somewhat during the second analysis.

Table 6-2. Stage 1 Performance Across Sensor Lifespan

Water Quality Parameter	Sensor	Test Level	Description	%D or D	%RSD
Alkalinity (mg/L $CaCO_3$)	3	130	Pre-DW	-11.7%	9.3%
			Post-DW	8.7%	3.6%
Ammonia (mg/L NH_3)	3	0.8	Pre-DW	-20.6%	5.9%
			Post-DW	-19.6%	4.7%
Conductivity (µS/cm)	4	1100	Pre-DW	-0.3%	0.2%
			Post-DW	2.8%	0.9%
Free chlorine (mg/L Cl_2)	4	1.2	Pre-DW	20.9%	4.3%
			Post-DW	19.7%	1.5%
Hardness (mg/L $CaCO_3$)	3	125	Pre-DW	-1.3%	13.3%
			Post-DW	1.6%	0.0%
Monochloramine (mg/L NH_2Cl)	4	1.2	Pre-DW	11.1%	1.6%
			Post-DW	19.3%	5.0%
ORP (millivolts)	4	700	Pre-DW	-11.4%	4.6%
			Post-DW	3.9%	6.8%
pH	3	7.01	Pre-DW	0.18	n/a
			Post-DW	0.04	n/a

6.1.2 Stage 2 Results for Drinking and Source Water Samples

Table 6-3 shows the results for the finished drinking water samples that were referred to in the second part of Stage 1. The six drinking water samples were collected at various locations within the CDW distribution system. The amount of ammonia in these samples was below the detectable level of the reference method (0.05 mg/L) so the results for ammonia are not shown. Conductivity and ORP were the most accurate with average %Ds of mostly less than 5%. Alkalinity generated average %Ds that ranged from -19.5% to 8.0% and hardness resulted in average %Ds that ranged from -17.0% to 2.3%. The pH measurements were always within 0.22 pH units of that of the reference measurement. The Columbus, Ohio water system, from which these samples were collected, is not a chloraminated system and therefore, there is only a small concentration of monochloramines in the water (~0.2 mg/L). Because of this, even small deviations from the reference concentration can cause %D to become artificially high due to the small reference concentration (see Equation 2). Therefore, the difference between the monochloramine concentration and the reference result is reported here as absolute concentration

Table 6-3. Stage 2 Finished Drinking Water (DW) Results

Water Quality Parameter	Test Matrix		Sensor 3			Sensor 4		
		Reference	Avg.	%D or D	%RSD	Avg.	%D or D	%RSD
Alkalinity (mg/L $CaCO_3$)	DW1	29	31	8.0%	24.0%	25	-13.8%	10.6%
	DW2	48	46	-4.9%	3.3%	40	-16.7%	4.3%
	DW3	45	39	-13.3%	0.0%	37	-18.5%	1.6%
	DW4	43.5	38	-12.6%	2.6%	37	-14.9%	7.2%
	DW5	50.5	47	-6.9%	6.4%	41	-19.5%	3.8%
	DW6	35	31	-11.4%	3.2%	29	-18.1%	4.0%
Conductivity (µS/cm)	DW1	257	260	1.4%	0.4%	259	1.0%	0.7%
	DW2	455	451	-0.9%	0.4%	458	0.7%	0.7%
	DW3	481	481	-0.1%	0.5%	488	1.5%	0.9%
	DW4	479	483	0.8%	0.2%	486	1.5%	1.0%
	DW5	501	498	-0.6%	0.2%	513	2.4%	0.4%
	DW6	335	336	0.2%	0.2%	345	2.9%	0.2%
Free chlorine (mg/L Cl_2)	DW1	1.14	0.98	-14.3%	2.6%	0.96	-15.8%	3.8%
	DW2	1.23	1.00	-18.7%	5.0%	0.98	-20.3%	3.7%
	DW3	1.47	1.05	-28.3%	3.1%	1.00	-32.2%	3.2%
	DW4	1.19	0.93	-22.1%	3.3%	0.90	-24.4%	5.1%
	DW5	0.77	0.55	-28.1%	12.0%	0.62	-19.0%	9.8%
	DW6	0.92	0.74	-19.9%	6.7%	0.80	-12.7%	2.6%
Hardness (mg/L $CaCO_3$)	DW1	67	63	-6.0%	3.2%	63	-6.0%	0.0%
	DW2	106	88	-17.0%	4.1%	90	-14.8%	10.0%
	DW3	101	95	-5.6%	2.2%	103	2.3%	1.5%
	DW4	102	92	-10.1%	5.4%	97	-4.6%	11.3%
	DW5	75	65	-13.8%	3.6%	66	-11.6%	3.1%
	DW6	77	71	-8.2%	2.2%	71	-7.4%	2.1%
Monochloramine (mg/L NH_2Cl)	DW1	0.16	0.06	-0.10	63.8%	0.12	-0.04	44.7%
	DW2	0.26	0.19	-0.07	21.7%	0.25	-0.01	18.7%
	DW3	0.22	0.36	0.14	18.2%	0.44	0.22	11.6%
	DW4	0.27	0.22	-0.05	25.4%	0.32	0.05	17.4%
	DW5	0.15	0.22	0.07	41.6%	0.18	0.03	31.0%
	DW6	0.26	0.19	-0.07	22.9%	0.18	-0.08	31.5%
ORP (millivolts)	DW1	604	603	-0.1%	8.6%	655	8.4%	3.4%
	DW2	674	669	-0.8%	1.7%	682	1.1%	0.5%
	DW3	676	692	2.5%	1.3%	694	2.7%	1.0%
	DW4	685	646	-5.7%	5.0%	665	-2.9%	2.7%
	DW5	622	654	5.1%	1.2%	656	5.5%	1.4%
	DW6	646	670	3.7%	0.8%	676	4.6%	0.6%
pH	DW1	7.68	7.70	0.02	n/a	7.78	0.10	n/a
	DW2	7.62	7.69	0.07	n/a	8	0.10	n/a
	DW3	7.75	7.80	0.05	n/a	7.79	0.04	n/a
	DW4	7.68	7.90	0.22	n/a	7.85	0.17	n/a
	DW5	7.7	7.80	0.10	n/a	7.83	0.13	n/a
	DW6	7.73	7.82	0.09	n/a	7.84	0.11	n/a

units rather than a %D. All the monochloramine measurements were within 0.22 mg/L of the reference measurement. Lastly, the free chlorine results were unique from the others because they consistently exhibited a negative %D that ranged from -14.3% to -32.2%.As for the precision of these finished drinking water results, with the exception of the monochloramine results which were impacted by the low concentration, almost all of the %RSDs were below

Table 6-4. Surface (SW) and "In-Process" (IPW) Drinking Water – Field and Laboratory Results

Water Quality Parameter	Test Matrix	Reference[a]	Sensor 5			Sensor 6		
			avg	%D or D	%RSD	avg	%D or D	%RSD
Alkalinity (mg/L $CaCO_3$)	IPW1 (Field)	61	49	-19.1%	12.9%	47	-22.4%	3.2%
	IPW1 (Lab)	61	50	-18.6%	7.6%	49	-20.2%	4.3%
	IPW2 (Field)	116	92	-20.4%	13.4%	113	-2.3%	2.5%
	IPW2 (Lab)	116	85	-26.4%	2.4%	108	-7.2%	10.0%
	SW1 (Field)	190	197	3.5%	7.2%	184	-3.2%	2.4%
	SW1 (Lab)	190	175	-7.7%	6.1%	170	-10.7%	0.3%
	SW2 (Field)	169	130	-23.3%	6.2%	164	-3.0%	2.7%
	SW2 (Lab)	169	135	-20.1%	10.9%	145	-14.2%	3.6%
Conductivity (µS/cm)	IPW1 (Field)	558	566	1.4%	0.2%	576	3.3%	1.7%
	IPW1 (Lab)	558	565	1.3%	0.4%	572	2.4%	1.4%
	IPW2 (Field)	651	674	3.6%	0.2%	685	5.3%	1.0%
	IPW2 (Lab)	651	664	2.0%	0.3%	679	4.4%	1.3%
	SW1 (Field)	650	662	1.8%	0.2%	683	5.0%	0.7%
	SW1 (Lab)	650	663	2.1%	0.2%	675	3.8%	0.4%
	SW2 (Field)	636	650	2.1%	0.5%	671	5.5%	0.3%
	SW2 (Lab)	636	643	1.2%	0.4%	665	4.5%	0.5%
Hardness (mg/L $CaCO_3$)	IPW1 (Field)	89	80	-10.5%	0.7%	78	-12.7%	4.1%
	IPW1 (Lab)	89	78	-12.4%	1.3%	76	-14.6%	7.0%
	IPW2 (Field)	162	143	-11.5%	2.2%	152	-6.2%	1.1%
	IPW2 (Lab)	162	146	-9.9%	1.8%	153	-5.6%	4.1%
	SW1 (Field)	193	168	-13.1%	3.6%	189	-2.1%	5.7%
	SW1 (Lab)	193	169	-12.6%	1.2%	159	-17.4%	4.8%
	SW2 (Field)	170	145	-14.9%	3.4%	155	-8.6%	14.0%
	SW2 (Lab)	170	146	-13.9%	0.8%	159	-6.7%	5.6%
ORP (millivolts)	IPW1 (Field)	301	77	-74.4%	3.4%	117	-61.1%	3.1%
	IPW1 (Lab)	301	65	-78.5%	7.1%	123	-59.0%	15.1%
	IPW2 (Field)	352	157	-55.5%	7.1%	207	-41.3%	10.9%
	IPW2 (Lab)	352	157	-55.5%	13.5%	240	-31.9%	10.3%
	SW1 (Field)	250	90	-64.1%	5.0%	157	-37.2%	6.6%
	SW1 (Lab)	250	85	-65.9%	2.4%	160	-36.1%	4.2%
	SW2 (Field)	312	223	-28.5%	34.5%	219	-29.8%	2.4%
	SW2 (Lab)	312	145	-53.5%	14.1%	209	-32.9%	27.5%
pH	IPW1 (Field)	8.67	8.88	0.21	n/a	8.88	0.21	n/a
	IPW1 (Lab)	8.67	8.92	0.25	n/a	8.88	0.21	n/a
	IPW2 (Field)	7.07	6.83	-0.24	n/a	6.82	-0.25	n/a
	IPW2 (Lab)	7.07	6.90	-0.17	n/a	6.93	-0.14	n/a
	SW1 (Field)	7.77	7.71	-0.06	n/a	7.71	-0.06	n/a
	SW1 (Lab)	7.77	7.72	-0.05	n/a	7.76	-0.01	n/a
	SW2 (Field)	7.65	7.77	0.12	n/a	7.76	0.11	n/a
	SW2 (Lab)	7.65	7.76	0.11	n/a	7.81	0.16	n/a

[a] The reference value is from a single measurement for each water sample.

10%. Table 6-4 shows the results for the surface water as well as water samples collected from within the water treatment process. Both surface water samples (SW1 and SW2) were collected at the raw water (Scioto River) intake at a CDW treatment plant. The in-process waters (IPW 1 and IPW2) were taken from within that plant. IPW1 was collected at the end of the recarbonation process and IPW2 was collected at the end of the coagulation process. Each of these samples was analyzed at a CDW booster station that was near where the samples were collected as well as returned to the laboratory for analysis by the WP870 and the laboratory reference method in order to compare the performance of the WP 870 when the measurements were made at a field location and in the laboratory. The reference measurement results for free chlorine, monochloramine, and ammonia were below the detection limits so those water quality parameters were not included in this data set. Conductivity was most accurate with average %Ds that ranged from 1.2% to 5.5%. Hardness generated average %Ds that ranged from -17.4% to 3.6% and alkalinity resulted in average %Ds that ranged from -26.4% to 3.5%. The pH measurements were always within 0.25 pH units of that of the reference measurement. The ORP results for all of the surface water samples and the in-process water samples had relatively high average %Ds from the reference method compared with all of the other water quality parameters and all of the other water samples. The %Ds ranged from -78.5% to -28.5%. The reason for these relatively large differences was not clear, but it seems likely that some constituent of the water sample that is removed during the water treatment process inhibited the ORP sensing component of the WP870. The precision of the WP870 in these matrices as expressed in %RSD for each set of replicates was 10% or less in 70 out of the 80 sets that were analyzed.

The difference in the average %D between the laboratory and field measurements was small in most cases. In only four instances did the difference between average %Ds exceed 10% and in each of those instances, the field result was closer to the reference measurement result than was the laboratory result. Similarly, for pH, the average results determined at the laboratory did not differ from those determined in the field by more than 0.11 pH units.

6.2 Inter-unit Reproducibility

Throughout the first part of Stage 1 and all of Stage 2 of this verification test, two WP870 sensors were used to analyze each test sample. Two types of data were used to compare the two units equipped with separate sensors that have a lifespan of either 50 samples or 30 days. To do this, the data were evaluated in two ways. First, a paired t-test was performed on each set of replicate results to determine if there was a statistical difference between each of the sets of replicate data. However, when t-tests are applied to very repeatable data (as was the case here for some parameters), it is possible for extremely small differences to be considered significant. Therefore, to provide some perspective to the t-test results, the absolute difference between the averages from each unit was also reported. For example, in one instance during Stage 2, the conductivity results for Sensors 3 and 4 were reported as 336 µS/cm and 345 µS/cm, respectively, an absolute difference of only 9 µS/cm. Because of the precision of this particular replicate measurement, the results were reported as significantly different. Table 6-5 gives the results for each of the samples for which the pairs of sensors were determined to generate significantly different results. Overall, out of 106 pairs of triplicate results using separate units, only 19 pairs were determined to be significantly different from one another by a paired t-test. The reference method result, the average result from each sensor, and the absolute difference between the average results from the two sensors are shown in the table. Replicate results for samples with non-detectable reference measurement results were not included in this evaluation.

Table 6-5. Surface with Significantly Different Results Between Sensors

Stage	Water Quality Parameter	Matrix	Reference[a]	Sensor 1,3, or 5 Avg.	Sensor 2,4, or 6 Avg.	Absolute Difference
Stage 1 (Sensors 1&2)	pH	DI Water	5.34	5.29	5.26	0.03
		DI Water	6.88	7.01	7.09	0.08
		DI Water	9.87	9.62	9.86	0.25
	Alkalinity (mg/L $CaCO_3$)	DI Water	25	26	20	6
	Conductivity (µS/cm)	DI Water	106	106	112	6
	Free chlorine (mg/L Cl_2)	DI Water	0.17	0.10	0.12	0.02
	ORP (low)	DI Water	551	500	510	10
Stage 2 (Sensors 3 & 4)	Alkalinity (mg/L $CaCO_3$)	DW2	48	46	40	6
		DW3	45	39	37	2
		DW5	50.5	47	41	6
	Conductivity (µS/cm)	DW5	501	498	513	15
		DW6	335	336	345	9
Stage 2 (Sensors 5 & 6)	Alkalinity	SW2 (Field)	169	130	164	34
	Conductivity (µS/cm)	SW1 (Field)	650	662	683	21
		SW1 (Lab)	650	663	675	12
		SW2 (Field)	636	650	671	21
		SW2 (Lab)	636	643	665	22
	ORP (millivolts)	IPW1 (Field)	301	77	117	40
		IPW1 (Lab)	301	65	123	58
		IPW2 (Field)	352	157	207	50
		IPW2 (Lab)	352	157	240	83
		SW1 (Field)	250	90	157	67
		SW1 (Lab)	250	85	160	75
	pH	SW1 (Lab)	7.77	7.72	7.76	0.04
		SW2 (Field)	7.65	7.77	7.76	0.01
		SW2 (Lab)	7.65	7.76	7.81	0.05

[a] The reference value is from a single measurement for each water sample.

6.3 Operational Factors

The verification staff found that the WP870 was easy to use both in the laboratory setting, where most of the quantitative results were collected, and in the various field environments. The WP870 procedure for calibration as well as measurement of samples includes the addition of either calibration solutions or water samples to the sample tube, containing approximately 7-8 mL, attached to the handheld unit. All functions of the WP870 were controlled from the menus displayed on the handheld unit. Full calibrations of the WP870, which took approximately 15-20 minutes, were required to be performed on a weekly basis or whenever a new sensor was installed into the handheld unit. Upon selection of the calibration option on the menu, text displayed on the screen guided the operators through the calibration process. The instructions detailed which calibration and rinse solutions needed to be added to the sample reservoir and the amount of time that should be allowed for each solution. The calibration solutions were provided by Sensicore in disposable containers and were clearly labeled so that the on-screen instructions directing the use of specific solutions were easily understood.

The sensor was easily installed into the handheld unit by unscrewing the top of the sample tube and inserting the sensor so that the electrical leads matched up with those on the handheld unit. It is important to note that once a sensor is installed in the handheld unit and calibrated for the first time (therefore hydrated) it is required to remain hydrated. This is done by filling the sample tube with a storage solution provided by Sensicore between uses and 24 hours before a sensor's first use. Each sensor is only able to be used for 50 sample analyses and within 30 days after its first calibration. That total limit of samples does not include the calibration analyses that are performed. The software will not allow any analyses to be performed after the 50 sample maximum has been reached and the number of samples analyzed on a sensor is displayed following each sample analysis. Also, the software will not allow any samples to be analyzed after the 30 day time limit.

The WP870 also required daily calibrations (called "quick calibrations" in the software), that took approximately 5 minutes, to ensure that the sensor was maintaining an appropriate calibration. Similar to the full calibration, the quick calibration was guided by on-screen instructions that were very easy to understand. For sample analysis, the operators selected the measurement option and the menus guided the analysis of water samples in an identical fashion. For each sample, approximately 6 mL of the water sample was added to the sample tube and then 3 drops of 3 different reagents (provided by Sensicore) were added to the sample tube throughout the measurement cycle. Following the analysis of a sample, the operators were prompted for a series of sample identification information in order to link the collected data with the appropriate sample. The full analysis process took approximately 5 minutes for each sample analyzed. Following the measurement of samples, the data (comma-delimited) were exported from the handheld unit to a personal computer using a USB cable and software provided by Sensicore. The data were then transferred to a spreadsheet for analysis.

Stage 3 of the verification test focused on the evaluation of the practical aspects of operating the WP870 in a non-laboratory, field environment. As described in Section 3.2.3, WP870 units were used on water sampling and analysis field studies by the TCEQ and EPA NERL. In addition, Stage 2 included some samples that were analyzed near the surface water intake or within a water treatment plant. The operators who completed this aspect of the testing documented various aspects of the WP870 that stood out to them.

During the TCEQ sampling campaign, the WP870 battery was fully charged before leaving on the trip and measurements were made at nine different locations over seven days. The low battery indicator did not appear until the seventh day, which was three days longer than Sensicore had informed the TCEQ to expect. Operators noted that both the calibration and sample measurement screens on the handheld unit walked them right through the process. The screens were easy to read in an outdoor environment and the on-screen directions were very straightforward. Operators noted that the only thing that takes a bit of getting used to is setting up the users and sample locations ahead of time using the software, so instead of taking some time to learn, they just recorded that information in a sample log book and linked it with a default sample number given by the WP870.

The EPA NERL operators reported that the carrying case was adequate in size to hold everything needed for calibration and sample analysis and was relatively lightweight and easy to carry across difficult terrain. They noted that, in general, the technology was easy to use in the field, but would suggest that calibration would be more efficiently done in the lab so as to not waste time in the field if on a day-long trip. The operators said that the WP870 was easily operated on the ground (e.g., on sloped banks along streams or uneven surfaces of streamside boulders and bedrock) with only approximately one square foot required. Overall, both the TCEQ and EPA NERL operators agreed that one drawback of the WP870 is the limited number of samples that each sensor can measure before disposal.

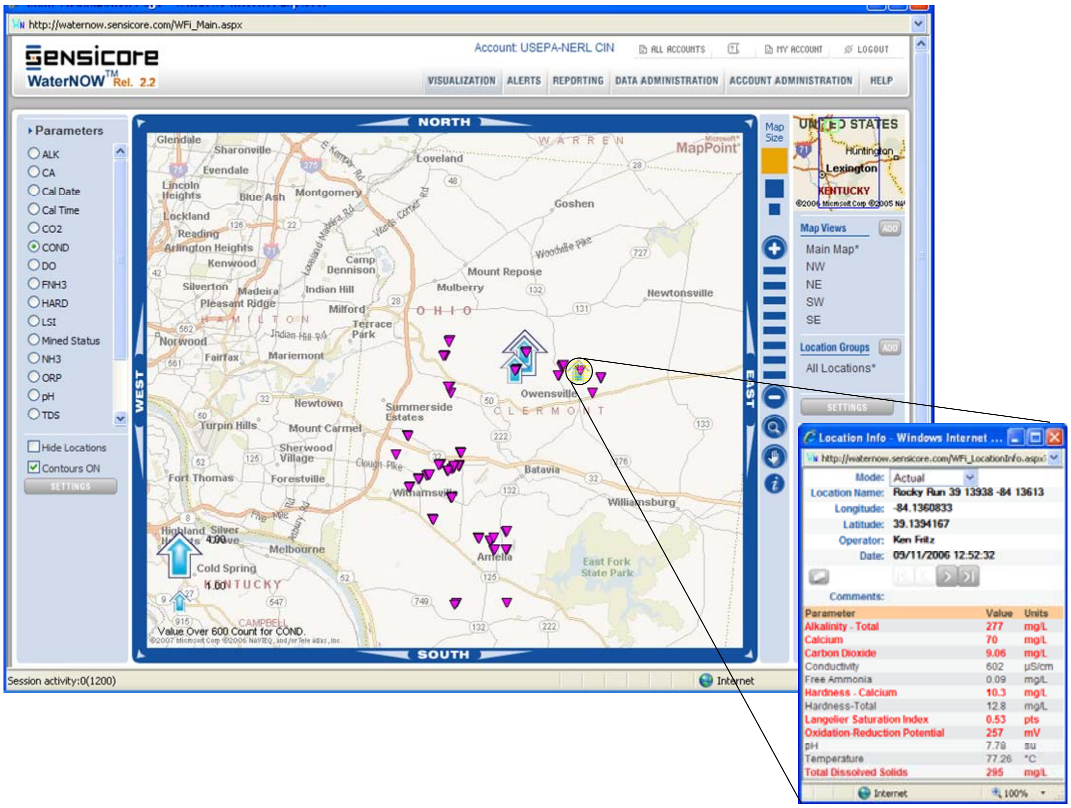

Figure 6-1 Screen Shot of EPA NERL WP870 Data on WaterNOW Software

The EPA NERL operators worked with Sensicore to load their data onto Sensicore's WaterNOW software which is an online and secure data service utilizing 128-bit data encryption that helps the user understand their data through unique visualization and comparison tools. The sample results from 80 locations were uploaded with the latitudinal and longitudinal coordinates to the NERL online account. The software provides a graphical representation of selected parameters, with a variety of contouring tools (area, pipeline, location) available to study the relationships between locations and sample levels. Figure 6-1 shows a map of EPA NERL's conductivity data. In this example visualization, the sampling locations are shown with triangles and then arrows indicate locations that are above a selected level (in this case, a conductivity measurement of 600 µS/cm) that is entered by the user. Different sized arrows reflect the number of occurrences that the selected level was exceeded at a location. The inset graphic shows that the rest of the sample data is available by clicking on the location. This software tool was not rigorously evaluated during this ETV test, but was utilized by the EPA NERL staff who found it to have a lot of potential as a data evaluation tool for water quality data from several locations.

Chapter 7
Performance Summary

The table below summarizes the results from the ETV testing of the WP870. The range of accuracy results are given along with summaries of other verified performance parameters.

Water Quality (WQ) Parameter	Stage 1 WQ Levels (test samples prepared in DI water)	Stage 1 Accuracy - %D from Ref.	Stage 2 Accuracy - %D from Ref. (drinking, surface, and "in-process" water)
Alkalinity	22, 130, and 240 mg/L $CaCO_3$	-20 to 4.0	-26.4 to 8.0
Ammonia	0.1, 0.8, 1.5 mg/L	-23.8 to 47.1	Ref. result below detection limit
Conductivity	100, 1100, 1700 µS/cm	0.3 to 5.7	-0.9 to 5.5
Free Chlorine	0.2, 1.2, 2.2 mg/L	-41.2 to 26.8	-32.2 to -12.7
Hardness	17.5, 125, and 225 mg/L	-5.6 to 9.3	-17.4 to 2.3
Monochloramine	0.2, 1.2, 2.2 mg/L	12.7 to 28.4	<0.22 mg/L from reference
ORP	550 and 700 millivolts	-9.2 to 1.6	-5.7 to 8.4 (DW) -78.5 to -28.5 (SW and IPW)
pH	5.4, 7, 10 (pH units)	-0.25 to 0.21 (pH units)	-0.25 to 0.25 (pH units)

Overall Precision	Excluding the monochloramine results for the DW, out of 216 triplicate measurements, 16 (7.4%) had %RSDs of greater than 10%.
Inter-unit Reproducibility	Out of 106 pairs of triplicate results using separate units, 19 pairs were determined to be significantly different from one another by a paired t-test. It seems most of these differences were relatively small, driven mostly by extremely small variability
Field Portability	The difference between the average %D between the laboratory and field measurements in Stage 2 was small in most cases. In only four instances did the difference between average %Ds exceed 10% and in each of those occurrences, the field results were closer to the reference measurement result than the laboratory result. Similarly, for pH, the results determined at the laboratory did not differ by more than a pH of 0.11.
Operational Factors	The verification staff found that the WP870 was easy to use both in the laboratory setting, where most of the quantitative results were collected, and in the various field environments in which the WP870 was used. The WP870 procedure for calibration as tube as measurement of samples includes the addition of either calibration solutions or water samples to the sample tube attached to the handheld unit. Overall, operators from both TCEQ and U.S. EPA NERL who used the WP870 for field analysis considered it to be an easy to use instrument. However, the operators also noted that the instrument is limited in that each sensor can analyze 50 samples over 30 days.

Chapter 8
References

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Appendix

Sensicore Comment on WP870 Improvements

In an entirely separate effort, but ongoing simultaneously to the ETV test, Sensicore was working to improve the Sensicore WP870. The following is a description of some of the improvements that have been made. This information has not been independently verified.

Affect of Cleaning (Activation) Cycle on Precision and Accuracy of Free Chlorine and Monochloramine Results on the WP870

Free available chlorine and monochloramine species are reduced at the surface of a platinum array by applying a known potential difference, relative to the Ag/AgCl reference electrode located on the WP870 sensor. Current generated in this process is proportional to the concentration of chlorine species present. Calcium, magnesium and other dissolved species may deposit on the array through the normal use of the instrument during repeated measurement cycles. The calibration cycle of the WP870 has a built in activation cycle which uses the rinse and conditioner solution of the sensor kit to electrochemically clean the array surfaces and leave the array in a know state for calibration and measurements.

The activation cycle was modified by including the use of the sample buffer solution (already contained in the sensor kit of the unit) to drop the pH to a value which more efficiently promotes the removal of adverse deposits. Using the new activation cycle, the results of a single study on free chlorine performed on laboratory prepared test solutions showed that the difference from the reference method was 5.6% ± 8.2% (N=48) compared with -7.1 ± 15% (N=104) previously. The most notable improvement was in the reproducibility. Contact Sensicore about details of this and other possible improvements that may have been implemented since this testing was completed.