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Environmental Technology Verification Program

Advanced Monitoring Systems Center

Test/QA Plan for Verification of Multi-Parameter Water Sensors

TEST/QA PLAN

for

Verification of
Multi-Parameter Water Sensors

April 4, 2007

Prepared by

Battelle
505 King Avenue
Columbus, OH 43201-2693

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Test/QA Plan for Verification of Multi-Parameter Water Sensors

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APPROVAL:

Name _____

Company _____

Date _____

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Uwe Michalak
Sensicore, Inc.
745 Phoenix Drive
Ann Arbor, MI 48108

Jeff Kauffman
City of Columbus Division of Power and Water (CDOPW)
910 Dublin Road
Columbus, OH 43215-9052

Ken Fritz
USEPA Facilities
26 West Martin Luther King Drive
Mail Code: 642
Cincinnati, OH 45268

Elizabeth A. Betz
U.S. Environmental Protection Agency-HEASD
National Exposure Research Laboratory
E205-01 EPA Mailroom
Research Triangle Park, NC 27711

Robert Fuerst
U.S. Environmental Protection Agency-HEASD
National Exposure Research Laboratory
D205-05 EPA Mailroom
Research Triangle Park, NC 27711

Amy Dindal
Ryan James
Zachary Willenberg
Battelle
505 King Ave.
Columbus, OH 43201

SECTION A

PROJECT MANAGEMENT

A4 VERIFICATION TEST ORGANIZATION

The verification test will be conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through the Environmental Technology Verification (ETV) Program. It will be performed by Battelle, which is managing the ETV Advanced Monitoring Systems (AMS) Center through a cooperative agreement with EPA. The scope of the AMS Center covers verification of monitoring technologies for contaminants and natural species in air, water, and soil.

The day-to-day operations of this verification test will be coordinated and supervised by Battelle personnel, with the participation of the vendor(s) who will be having the performance of their multi-parameter water sensors verified. There will be a laboratory and field component to this verification test. The laboratory testing will occur at the City of Columbus, Ohio Division of Power and Water (CDOPW). Staff from the CDOPW will participate in this test by preparing water samples with various levels of water quality parameters specified in this document, collecting drinking and surface water samples to be used as test samples, analyzing verification test samples with the technologies being verified, and conducting the reference analyses. The field component of testing will be performed by staff from the EPA National Exposure Research Laboratory (NERL) in Cincinnati, OH during an unrelated project which includes real-time water quality measurements of surface water in southern Ohio. Vendor representatives will operate their respective technologies throughout the test unless they provide training and give written consent for the verification staff to carry out these activities. Quality assurance (QA) oversight will be provided by the Battelle Quality Manager and the EPA AMS Center Quality Officer at their discretion. The organization chart in Figure 1 identifies the responsibilities of the organizations and individuals associated with the verification test. Roles and responsibilities are defined further below.

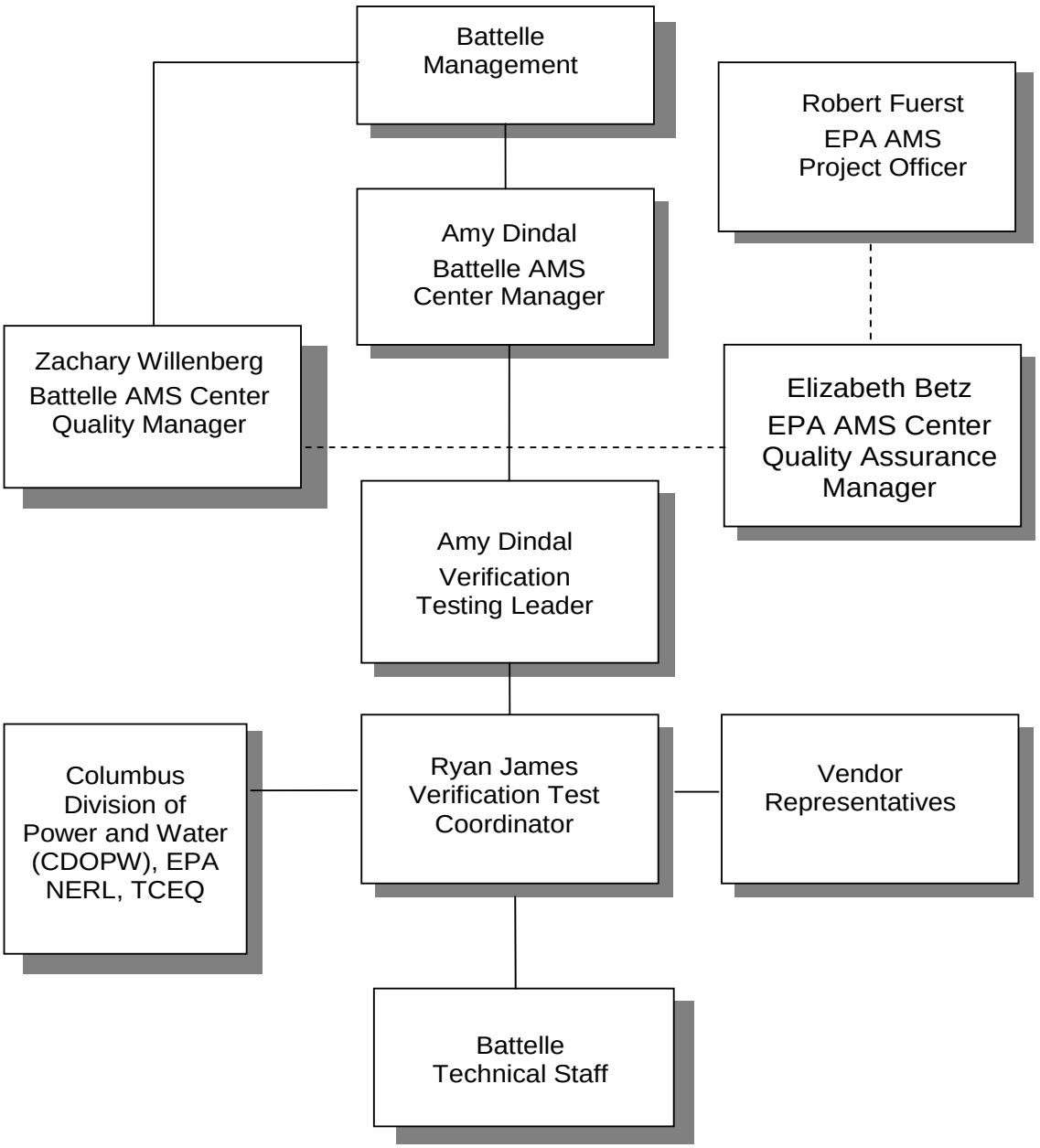

Figure 1. Organization Chart

A4.1 Battelle

Dr. Ryan James is the AMS Center Verification Test Coordinator. In this role, Dr. James will have overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. Specifically, he will:

- Assemble a team of qualified technical staff to conduct the verification test.
- Direct the team (Battelle, EPA, and CDOPW staff) performing the verification test in accordance with the test/QA plan.
- Prepare the draft and final test/QA plan, verification reports, and verification statements.
- Revise the draft test/QA plan, verification reports, and verification statements in response to reviewers' comments.
- Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary.
- Serve as the primary point of contact for vendor representatives.
- Coordinate distribution of the final test/QA plan, verification reports, and statements.
- Establish a budget for the verification test and manage staff to ensure the budget is not exceeded.
- Ensure that confidentiality of sensitive vendor information is maintained.

Ms. Amy Dindal is a Verification Testing Leader for the AMS Center and is also Battelle's manager for the AMS Center. Ms. Dindal will provide technical guidance and oversee verification testing. Specifically, she will:

- Support Dr. James in preparing the test/QA plan and organizing the testing.
- Review the draft and final test/QA plan.
- Review the draft and final verification reports and verification statements.
- Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test. Ensure that confidentiality of sensitive vendor information is maintained.
- Support Dr. James in responding to any issues raised in assessment reports and audits.
- Maintain communication with EPA's technical and quality managers.
- Facilitate a stop work order if Battelle or EPA QA staff discovers adverse findings that will compromise test results.

Battelle Technical Staff will work with the test collaborators to conduct the testing of the multi-parameter water sensor technologies. Battelle staff will be on-site at the CDOPW at various times throughout the verification test. The responsibilities of the technical staff will be to:

- Assist CDOPW in any and all aspects of performing the verification test as described in the test/QA plan. This could include test sample analysis and/or reference sample analysis.

Mr. Zachary Willenberg is Battelle's Quality Manager for the AMS Center. Mr. Willenberg or his designee will:

- Review the draft and final test/QA plan.
- Conduct a technical systems audit at least once during the verification test.
- Audit at least 10% of the verification data.
- Prepare and distribute an assessment report for each audit.
- Verify implementation of any necessary corrective action.
- Notify Battelle's AMS Center Manager to issue a stop work order if audits indicate that data quality is being compromised.
- Provide a summary of the QA/QC activities and results for the verification reports.
- Review the draft and final verification reports and verification statements.
- Ensure that all quality procedures specified in the test/QA plan and in the AMS Center Quality Management Plan[1] (QMP) are followed.

A4.2 Vendors

The responsibilities of the vendor representatives are as follows:

- Review the draft test/QA plan.
- Approve the test/QA plan prior to test initiation.
- Provide at lease two off-the-shelf multi-parameter water sensors for evaluation during the verification test.
- Provide all other equipment/supplies/reagents/consumables needed to operate their monitors for the duration of the verification test.
- Either supply a representative to operate their technology throughout the test, or provide written consent and instructions for Battelle staff to carry out these activities.
- Review the draft verification report and statement.

A4.3 EPA

EPA's responsibilities in the AMS Center are based in part on the requirements stated in the "Environmental Technology Verification Program Quality Management Plan" (EPA QMP)[2]. The roles of the specific EPA staff are as follows:

Ms. Elizabeth Betz is EPA's AMS Center Quality Assurance Manager. For the verification test, Ms. Betz will:

- Review the draft test/QA plan.
- Perform at her option one external technical systems audit during the verification test.
- Notify the EPA AMS Center Manager of the need for a stop work order if external audit indicates that data quality is being compromised.
- Prepare and distribute an assessment report summarizing results of external audit.
- Review draft verification reports and statements.

Mr. Robert Fuerst is EPA's Project Officer for the AMS Center. Mr. Fuerst will:

- Review the draft test/QA plan.
- Approve the final test/QA plan.
- Review the draft verification reports and statements.
- Oversee the EPA review process for the verification reports and statements.
- Coordinate the submission of verification reports and statements for final EPA approval.

Dr. Ken Fritz is an ecologist within the EPA Office of Research and Development, National Exposure Research Laboratory. Mr. Fritz will direct the field measurement component of this ETV test and in doing that will:

- Provide EPA technical staff to perform verification testing in the context of real-time field analyses.
- Provide data measured by the technologies being verified for all samples analyzed as well as the corresponding data measured from other technologies used during field analyses.

- Review portions of the draft verification reports to assure accurate descriptions of the field testing and to provide technical insights on verification results

A4.4 Texas Commission on Environmental Quality (TCEQ)

Ms. Christine Kolbe is an aquatic scientist at TCEQ. Ms. Kolbe will direct a second field measurement component of this ETV test and in doing that will:

- Provide TCEQ technical staff to perform verification testing in the context of real-time field analyses.
- Provide data measured by the technologies being verified for all samples analyzed as well as the corresponding data measured from other technologies used during field analyses.
- Review portions of the draft verification reports to assure accurate descriptions of the field testing and to provide technical insights on verification results

A4.5 Columbus (OH) Division of Power and Water

Mr. Jeff Kauffman is a water analyst at CDOPW. Mr. Kauffman will be Battelle's point of contact for the laboratory measurement component of this ETV test to be conducted at the CDOPW. In this capacity he will:

- Provide CDOPW technical staff to perform verification testing in the context of laboratory analyses including test sample preparation and collection, and analyses using the technologies to be verified.
- Perform reference analyses for the water quality parameters being measured during this verification test.
- Provide data measured by the technologies being verified for all samples analyzed as well as the data collected from the applicable laboratory reference methods.
- Document any unusual conditions that could substantively affect the outcome of the verification test.
- Review portions of the draft verification reports to assure accurate descriptions of the laboratory testing and to provide technical insights on verification results.
- Provide Battelle technical staff access to the CDOPW facilities in which testing is ongoing.

A5 BACKGROUND

The ETV Program's AMS Center does third-party verification testing of commercially available monitoring technologies that detect natural species and contaminants in air, water, and soil. A stakeholder committee of buyers and users of such technologies recommend the technology categories and technologies within those categories as priorities for testing. Multi-parameter water sensors were identified as a priority technology category through the AMS Center stakeholder process.

A6 VERIFICATION TEST DESCRIPTION AND SCHEDULE

A6.1 Summary of Technology Category

The multi-parameter water sensor technologies to be tested consist of sensors that measure several different water quality parameters from grab samples. This verification test will assess the performance of each sensor relative to key verification parameters including accuracy, precision, and inter-unit reproducibility. The accuracy measurements will include comparison to reference measurements where possible. In performing the verification test, Battelle will follow the technical and QA procedures specified in this test/QA plan and will comply with the data quality requirements in the AMS Center QMP[1].

A6.2 Verification Schedule

The verification test of multi-parameter water sensor technologies is planned to be completed during April and May of 2007. Because the field testing by EPA NERL was planned and scheduled well ahead of the development of the test/QA plan for this ETV test, the field testing was performed during the second week of September 2006, prior to approval of this test/QA plan. This was permitted because that portion of the verification test focused entirely on the technologies' ease of field portability and not as an evaluation of the sensors' quantitative performance. At the close of testing, individual reports will be drafted for each technology, reviewed, and submitted to EPA for final signature. All documents will be submitted to EPA in electronic (Microsoft Word and Adobe portable document format [PDF]) and hard copy formats.

A7 QUALITY OBJECTIVES

This verification test will evaluate the performance of multi-parameter water sensor technologies. This will include a comparison of the sensor results to the results of standard laboratory reference methods. The quality of the reference measurements will be monitored by the inclusion of blank, duplicate, and performance evaluation (PE) audit samples. The PE audit samples will be analyzed by an instrument that is different from the one used for the rest of the reference analyses or that was calibrated with a different set of calibration standards. These samples are meant to independently confirm that the reference measurements are being performed correctly with accurate results. Control limits on the duplicate and PE samples are given in Section B4.

A8 SPECIAL TRAINING/CERTIFICATION

Documentation on training related to standard analytical chemistry methodology is maintained for applicable Battelle or CDOPW technical staff in training files at the respective locations. The Battelle Quality Manager will verify the presence of appropriate training records prior to the start of testing. If the vendors request that Battelle or collaborator technical staff operate and maintain their sensors during the verification test, the vendors will be required to train the Battelle or collaborator technical staff prior to the start of testing. Battelle will document this training with a consent form, signed by the vendor, which states which specific Battelle technical staff have been trained to use their sensor. All technical staff will have a minimum of a bachelor's degree in science/engineering or have equivalent work experience.

A9 DOCUMENTATION AND RECORDS

The records for this verification test will be contained in the test/QA plan, the protocols, chain of custody forms, laboratory record books (LRB), data collection forms, electronic files (both raw data and spreadsheets), and the final verification report. All of these records will be maintained in the Verification Test Coordinator's office during the test and can be transferred to permanent storage at Battelle's Records Management Office at the conclusion of the verification test. All Battelle LRBs are stored indefinitely, either by the Verification Test Coordinator or Battelle's Records Management Office. The results from the reference measurements made by the CDOPW technical staff will be submitted to Battelle daily upon obtaining the results of the analyses. Section B10 further details the data recording practices and responsibilities.

SECTION B

MEASUREMENT AND DATA ACQUISITION

B1 EXPERIMENTAL DESIGN

This verification test will specifically address verification of multi-parameter water sensor technologies by evaluating the accuracy of the water quality measurements made by each technology in 1) ASTM Type II deionized (DI) water fortified with chemicals to provide various water quality measurements across the working range of the sensor, 2) finished drinking water, and 3) untreated source water samples. Precision of the sensors will be evaluated by analyzing replicate samples on one day and repeating some of the analyses over a period of several days. Two identical sensors will be tested simultaneously to compare their results. The drinking water analyzed by the multi-parameter water sensors will be from the Columbus, Ohio distribution system. Because only one geographical region is represented by the water system used for this verification test, this is not intended to be an exhaustive study or to represent all possible water types that could be tested.

The multi-parameter water sensors will be evaluated for 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 and across several days
- Inter-unit reproducibility - comparison of results from two identical sensors
- Field portability – operation during remote field site analysis
- Ease of use - general operation, data acquisition, set-up, demobilization, required maintenance

B1.1 Stage 1 – Field Analyses

The first stage of this verification test will evaluate the ease of using the multi-parameter water sensor technologies during a field water quality study with two collaborators. The ETV program is collaborating with 1) EPA NERL who conducted a short term field analysis campaign

during 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) the TCEQ who is going to conduct a similar sampling campaign in western Texas on the Rio Grande River. These studies are independent from the ETV test, but EPA, NERL, and TCEQ have agreed to collaborate by taking the technologies to be verified with them and performing single analyses at some of the measurement locations included in their studies. Because of the rugged terrain that the analysis teams traverse to make these measurements, no grab samples will be transported for reference analysis during this stage of the testing. However, the pH, conductivity, and temperature measurements made by the EPA (using other portable sensors) and TCEQ may be compared with the technologies being verified. However, the primary evaluation of sensor accuracy will take place during Stages 2 and 3.

B1.2 Stage 2 – Laboratory Testing of DI Water Samples

The second stage of the verification test will test the accuracy and precision of the sensors with respect to accepted laboratory reference methods. This will be done by preparing test solutions with water quality measurements that span the working range of the sensors. Table 1 gives the levels of each water quality parameter that will be analyzed. For example, the pH component of the sensors will be tested by preparing test solutions that cover the pH ranges from acidic (pH 4-6), neutral (pH 7), and alkaline (pH 8-10). Table 1 also shows groupings of the water quality parameters that will be evaluated by analyzing a single solution prepared for that purpose. The monochloramine and pH measurements will each be evaluated in unique solutions, but the other parameters will be grouped. The table also includes the key components and/or critical aspects of each solution's preparation. Three replicates of each of these test solutions will be analyzed blindly and in random order on each of three separate days to evaluate the short term repeatability over minutes or hours and the repeatability of the sensors over a multi-day period. Two identical sensors will be evaluated in the same way for the inter-unit reproducibility evaluation. The first set of analyses will be performed on Day 1 or 2, the second on Day 6 or 7, and the third on Day 12 or 13. The stability of the free chlorine solutions will require that they be prepared on each analysis day, but the other solutions should be stable so they will be prepared just once and then stored in closed containers in a refrigerator. These samples will be prepared from National Institute of Standards and Technology (NIST) traceable standards or other primary standards. However, to confirm that the solutions were prepared properly, at least one test sample

of each specific water quality parameter will be measured using the laboratory reference methods described in Section B.4.

Table 1. Stage 2 Test Sample Information

Parameter Grouping	Water Quality Parameter	Levels	Test Sample Preparation (all samples in DI water)
1	pH and temperature	5, 7, 10 (pH units)	Citrate, phosphate, and borate buffers, respectively, prepared at appropriate pHs
2	Alkalinity and Carbon Dioxide	22, 130, and 240 mg/L $CaCO_3$	Anhydrous sodium bicarbonate dissolved in DI water
3	Calcium	7, 50, and 90 mg/L	Calcium chloride (pH 8.3)
	Ammonia	0.1, 0.8, 1.5 mg/L	Ammonium chloride (pH 8.3)
4	Conductivity	100, 900, 1700 µS/cm	Sodium chloride (pH 9.0)
	Free Chlorine	0.2, 1.2, 2.2 mg/L	Sodium hypochlorite (pH 9.0)
	Oxidation / Reduction Potential	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 Solution #4 with a 15 minute reaction time (pH>9)

mg/L – milligram per liter

µS/cm – microSiemens per centimeter

B1.3 Stage 3 – Laboratory and Field Testing of Drinking and Surface Water Samples

The third stage of this verification test will evaluate the performance of the multi-parameter water sensors when analyzing samples of finished drinking water drinking water within the treatment process, and untreated surface and ground source water. Throughout the verification test, at least 10 samples (6 finished drinking water, 2 "in-process" water, and 2 source waters) will be collected. At least four of these samples will be analyzed upon collection and then immediately returned to the laboratory for reference analysis so that comparison between the two measurements is valid. When possible, the reference measurement will be performed at the location of the field measurement. In addition to these field measurements, all 10 samples will be returned to the laboratory for analysis using the technologies being verified and all of the reference analysis. Each of these samples will be analyzed in triplicate by the multi-parameter water sensors and then compared to the reference method results from these same samples. The

finished drinking water samples will be analyzed during days between the Stage 2 analyses. This will evaluate the degree to which the sensor response drifts throughout the lifetime of the sensor.

Table 2 summarizes the samples that will be analyzed in Stages 1-3 of this verification test and what reference sample analyses are being performed.

Table 2. Summary of Test Sample Analysis

Testing Stage	Minimum Number of Samples	Summary of Test Sample Analysis
1 – Field Analysis	10 samples with no replicate analysis	EPA will use the technologies for field analysis by analyzing one sample collected from at least 10 different locations. No reference measurements will be made, only a possible comparison with a handheld sensor routinely used by EPA.
2 – Laboratory Testing of DI Samples	45 samples analyzed in triplicate (7 blanks)	Each measurement level given in Table 1 will be analyzed in triplicate on three different days over a multi-day period. The first analysis will be performed on Day 1 or 2, the second on Day 6 or 7, and the third on Day 12 or 13. Reference measurements will be made on each solution on each day.
3 – Laboratory and Field Testing of Drinking and Untreated Source Water Samples	10 samples analyzed in triplicate (2 blanks)	CDOPW will collect and analyze (in triplicate) at least 10 total samples (6 finished drinking water, 2 "in-process" waters, and 2 source waters); reference measurements will be performed on each sample. Analysis of 4 of these 10 samples will occur at the field location, and samples will be returned to the laboratory immediately for reference analysis. When possible reference measurements will also occur at the field site.

B1.4 Statistical Analysis

B1.4.1 Percent Difference

Depending on the stage of testing, results from the analysis of drinking and source water samples by the multi-parameter water sensors will be compared to the results obtained from another sensor (Stage 1) or results obtained from a reference method (Stages 2 and 3). The results for each sample will be recorded, and the accuracy will be expressed in terms of the percent difference (%D), as calculated from the following equation:

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

where C_R is the value from each stage (as described above) with which each sensor measurement is being compared and C_S is the result from the sensor. This calculation will be performed for each of the parameters measured by each sensor. Ideally, if the sensor result and value being compared are the same, there would be a percent difference of zero. Percent difference will be assessed independently for each sensor provided by the vendor to contribute to the inter-unit reproducibility evaluation.

B1.4.2 Precision

Precision will be evaluated across two different time periods during this verification test. The first will evaluate the repeatability of the sensor across equivalent samples analyzed in triplicate on the same day and the second will evaluate the repeatability of the sensor across several days. In both cases, precision will be evaluated by calculating the standard deviations of both sets of repeated measurements:

$$S = \left[\frac{1}{n-1} \sum_{k=1}^{n} \left(C_s - \overline{C_s} \right)^2 \right]^{1/2} \quad (2)$$

where n is the number of replicate samples, C_s is the water quality parameter measured for the k^{th} sample, and $\overline{C_s}$ is the average water quality parameter measurement of the replicate samples. The multi-parameter water quality sensor precision at each concentration level will be reported in terms of the relative standard deviation (RSD), shown in Equation 3:

$$RSD = \left| \frac{S}{\overline{C_s}} \right| \times 100 \quad (3)$$

B1.4.3 Inter-Unit Reproducibility

The results obtained from identical units of each sensor will be compiled independently for each analyzer and compared to assess inter-unit reproducibility. The results will be interpreted using a two-sided *t*-test, a linear regression of the unit 1 results plotted verses the unit 2 results, or other appropriate comparison, to assess whether significant differences exist between the units tested. This evaluation will be conducted for Stages 2 and 3.

B1.5 Reporting

The statistical comparisons described above will be conducted separately for each of the sensors being tested, and information on the additional performance parameters such as ease of use, level of maintenance, calibration, and set-up/demobilization will be compiled and reported. Separate verification reports will be prepared for each sensor that is tested. Each report will show separate verification results from the duplicate sensors undergoing testing, along with calculations of the inter-unit reproducibility of the technology. For each test, the verification report will present the test procedures and test data, as well as the results of the statistical evaluation of those data.

All interaction with the sensors (such as during maintenance, cleaning, and calibration) will be documented at the time of the test and reported. In addition, descriptions of the data-recording procedures, use of vendor-supplied software, consumables used, and required reagents will be presented in the report. The verification report will briefly describe the ETV program, the AMS Center, and the procedures used in verification testing. These sections will be common to each verification report. The results of the verification test will then be stated quantitatively, as described in section B1.4 without comparison to any other technology tested or comment on the acceptability of the technology's performance.

B2 SAMPLE COLLECTION

As described above, Stage 1 testing of the multi-parameter water sensors will consist of an evaluation of the field portability of the technologies. Because of the remote locations at which these measurements will be made, no grab samples for reference method analyses will be collected. During Stage 2, test solutions that intentionally alter the water quality parameters across the working range of the sensor will be prepared. For confirmation of the accuracy of solution preparation, at least one of the levels of each water quality parameter measured will be analyzed by the laboratory reference method as well as by the technologies being verified. No sample collection will be required as the analysis will be performed on the excess test solution made from DI water. Stage 3 testing will use finished drinking water and source water samples collected by CDOPW staff. The drinking water samples will be collected in 500mL high density polyethylene containers from pumping or tank locations throughout the Columbus, Ohio water distribution system and the source water samples will be collected in a similar manner from the

source water intake at the Parsons Avenue (ground) and Dublin Road (surface) Columbus water treatment plants.

B3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Sample custody will be documented throughout collection and analysis of the test samples. A chain-of-custody form will include details about the sample such as the time, date, location, and person collecting the sample. The chain-of-custody form will track sample release from the sampling location to the analysis laboratory. Each chain-of-custody form will be signed by the person relinquishing samples once that person has verified that the chain-of-custody form is accurate. Upon arrival at the analysis laboratory, chain-of-custody forms will be signed by the person receiving the samples (if different from the sample collector) once that person has verified that all samples identified on the chain-of-custody forms are present. Copies of all chain-of-custody forms will be delivered to the Verification Test Coordinator and maintained with the test records.

B4 LABORATORY REFERENCE METHODS

Table 3 provides the standard laboratory methods that will be used for the reference analyses during this verification test. Also included in the table is each method's detection limit and the allowable percent difference (%D) for PE and duplicate reference samples. The analyses will be performed by CDOPW or Battelle technical staff. For reference measurements that are made at CDOPW, CDOPW is responsible for providing any necessary calibrated instrumentation, performing all method QA/QC, and providing calibration records for any instrumentation used. The CDOPW will provide Battelle all reference sample data daily upon obtaining results.

B5 QUALITY CONTROL AUDITS AND REQUIREMENTS

One duplicate sample analysis will be required by each standard reference method on each day that sample analyses are performed. The percent relative standard deviation (%RSD) of the duplicate measurements will be required to be within the acceptable tolerances provided in Table 3. Samples producing results not meeting these requirements shall be reanalyzed by the reference

method. If the results are still outside the required tolerance, the reference instrument will be recalibrated (if applicable) and/or the reference samples reanalyzed. If the outlying results persist, the repeat of the appropriate parts of the verification test or use of a different reference instrument may be considered. DI water blanks will be required each day for the ammonia, calcium, chlorine, and monochloramine reference

Table 3. Reference Methods

Parameter	Method	Method Description	Method Detection Limits	Acceptable Duplicate and PE Tolerance
Ammonia	SM 4500-NH_3[3]	ion selective electrode	0.03 mg/L	25%
Calcium	EPA 215.2[4]	titration	0.5 mg/L	25%
Conductivity	SM 2510[5]	probe	2 µmho	25%
Free Chlorine	SM 4500-Cl-G[6]	colorimetric	0.01 mg/L as Cl_2	25%
Monochloramine	SM 4500-Cl-G[6]	colorimetric	0.01 mg/L as NH_2Cl	25%
Oxidation Reduction Potential	SM 2580-B[7]	probe	NA	25%
pH	EPA 150.1[8]	probe	NA	±0.3 pH units
Temperature	EPA 170.1[9]	probe	NA	±1°C
Total Alkalinity	EPA 310.1[10]	titration	20 mg/L	25%

NA – not applicable due to nature of that water quality parameter

analyses. The blank reference method results for these water quality parameters are required to be less than the method detection limit. For the other measurements, there is no conclusive blank reading in DI water making the blank analysis of little use. One DI water blank will be analyzed using the technologies being verified for every 20 samples analyzed to confirm the absence of reagent contamination.

B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

The instruments used for the reference analyses (as allowed by the standard methods) will be tested and inspected as per the instrument manuals, the standard operating procedures of the CDOPW or the standard methods being used to make each measurement. If Battelle or CDOPW

staff operate and maintain the sensors during the verification test, it will be done as directed by the vendor. Otherwise, operation and maintenance will be the responsibility of the vendor.

B7 INSTRUMENT CALIBRATION AND FREQUENCY

The instruments used for the reference analyses (as allowed by the standard methods listed in Table 3) will be calibrated per the instrument manual, the standard reference methods being used to make each measurement or the standard operating procedures of the analysis laboratory. If the sensor being verified is being operated by Battelle or CDOPW, the vendor will provide the verification staff with a checklist of tasks to be completed daily to properly maintain each sensor. All calibrations performed will be documented by Battelle in the project LRB.

Calibration of the multi-parameter water sensors will be done for each measured parameter as often as suggested by the vendor. Vendors will be required to supply the necessary calibration solutions and devices specific to the sensors being verified. Balances and pipettes used during test solution preparation will be maintained and calibrated as required by the Battelle or CDOPW standard operating procedures which will be reviewed by the Battelle Quality Manager prior to the verification test.

B8 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

All materials, supplies, and consumables will be ordered by the Verification Test Coordinator or designee from Battelle or CDOPW. Where possible, Battelle will rely on sources of materials and consumables that have been used previously as part of ETV verification testing without problems. Battelle will also rely on previous experience or recommendations from CDOPW technical staff to guide selection of manufacturers and materials. The manufacturer's criteria for acceptance/purity will be required to be met.

B9 NON-DIRECT MEASUREMENTS

Data published previously in the scientific literature will not be used during this verification test.

B10 DATA MANAGEMENT

Various types of data will be acquired and recorded electronically or manually by verification staff during this verification test. Table 4 summarizes the type of data to be recorded. All data and observations for the operation of the sensors will be documented by the vendors or verification staff on data sheets or in LRBs. Results from the laboratory reference instruments will be compiled by verification staff in electronic format and submitted to the Verification Test Coordinator upon obtaining results.

Records received by or generated by any of the verification staff during the verification test will be reviewed by a Battelle staff member within two weeks of receipt or generation, respectively, before the records are used to calculate, evaluate, or report verification results. If a Battelle staff member generated the record, this review will be performed by a Battelle technical staff member involved in the verification test, but not the staff member that originally received or generated the record. The review will be documented by the person performing the review by adding his/her initials and date to the hard copy of the record being reviewed. In addition, data calculations performed by verification staff will be spot-checked by Battelle technical staff to ensure that calculations are performed correctly. Calculations to be checked include any statistical calculations described in this test/QA plan. The data obtained from this verification test will be compiled and reported independently for each multi-parameter water sensor. Results for multi-parameter water sensors from different vendors will not be compared with each other.

During the course of any assessment or audit, the Battelle Quality Manager will inform the technical staff of any immediate corrective action that should be taken. If serious quality problems exist, the Battelle Quality Manager will notify the Battelle AMS Center Manager who is authorized to stop work. Once the assessment report has been prepared, the Verification Test Coordinator will ensure that a response is provided for each adverse finding or potential problem, and will implement any necessary follow-up corrective action. The Battelle Quality Manager will ensure that follow-up corrective action has been taken.

Table 4. 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	EPA, Battelle, and CDOPW	Used to organize/check test results; manually incorporated in data spreadsheets as necessary
Calibration information	ETV data sheets and testing notebook	Prior to sample preparation	EPA, Battelle, and CDOPW	Manually incorporated in data spreadsheets as necessary
Multi-parameter water sensor results	Recorded electronically by each monitor and then downloaded and emailed to Verification Test Coordinator daily for CDOPW and weekly for EPA.	Recorded continuously.	EPA, Battelle, and CDOPW	Comma delimited text files.
Reference method procedures	ETV laboratory record books, or data recording forms	Throughout sample analysis process; sent to Battelle daily upon completion of analyses	EPA, Battelle, and CDOPW	Transferred to spreadsheets or laboratory record book

SECTION C

ASSESSMENT AND OVERSIGHT

C1 ASSESSMENTS AND RESPONSE ACTIONS

Every effort will be made in this verification test to anticipate and resolve potential problems before the quality of performance is compromised. One of the major objectives of the test/QA plan is to establish mechanisms necessary to ensure this. Internal quality control measures described in this test/QA plan, which is peer reviewed by a panel of outside experts, implemented by the technical staff and monitored by the Verification Test Coordinator, will give information on data quality on a day-to-day basis. The responsibility for interpreting the results of these checks and resolving any potential problems resides with the Verification Test Coordinator. Technical staff have the responsibility to identify problems that could affect data quality or the ability to use the data. Any problems that are identified will be reported to the Verification Test Coordinator, who will work with the Battelle Quality Manager to resolve any issues. Action will be taken to control the problem, identify a solution to the problem, and minimize losses and correct data, where possible. Battelle will be responsible for ensuring that the following audits are conducted as part of this verification test.

C1.1 Performance Evaluation Audits

A PE audit will be conducted to assess the quality of the reference measurements made in this verification test. Each type of reference measurement will be compared with an independent instrument or a NIST-traceable standard that is independent of those used during the testing as part of the PE audit. The results of the PE audit must be within the acceptable tolerances provided in Table 3. If the results do not meet this requirement, they will be repeated. If the outlying results persist, a change in reference instrument, and a repeat of the PE audit will have to be performed. This audit will be performed once at the start of the verification test, and will be the responsibility of the Verification Test Coordinator or designee.

C1.2 Technical Systems Audits

The Battelle Quality Manager will perform a technical systems audit (TSA) at least once during this verification test. The purpose of this audit is to ensure that the verification test is being performed in accordance with the AMS Center QMP[1], this test/QA plan, published

reference methods, and any standard operating procedures (SOPs) used by the CDOPW. In this audit, the Battelle Quality Manager, or designee, may review the reference methods used, compare actual test procedures to those specified or referenced in this plan, and review data acquisition and handling procedures. A TSA report will be prepared, including a statement of findings and the actions taken to address any adverse findings. The EPA AMS Center Quality Manager will receive a copy of Battelle's TSA report. At EPA's discretion, EPA QA staff may also conduct an independent on-site TSA during the verification test. The TSA findings will be communicated to technical staff at the time of the audit and documented in a TSA report.

C1.3 Data Quality Audits

The Battelle Quality Manager or designee will audit at least 10% of the verification data acquired in the verification test. The Battelle Quality Manager will trace the data from initial acquisition, through reduction and statistical comparisons, to final reporting. All calculations performed on the data undergoing the audit will be checked.

C1.4 QA/QC Reporting

Each assessment and audit will be documented in accordance with Section 3.3.4 of the AMS Center QMP[1]. The results of the TSA will be submitted to EPA. Assessment reports will include the following:

- Identification of any adverse findings or potential problems
- Response to adverse findings or potential problems
- Recommendations for resolving problems
- Confirmation that solutions have been implemented and are effective
- Citation of any noteworthy practices that may be of use to others.

C2 REPORTS TO MANAGEMENT

The Battelle Quality Manager, during the course of any assessment or audit, will identify to the technical staff performing experimental activities any immediate corrective action that should be taken. If serious quality problems exist, the Battelle Quality Manager is authorized to notify the Battelle AMS Center Manager who will issue the stop work. Once the assessment report has been prepared, the Verification Test Coordinator will ensure that a response is provided for each adverse finding or potential problem and will implement any necessary follow-up

corrective action. The Battelle Quality Manager will ensure that follow-up corrective action has been taken. The test/QA plan and final report are reviewed by EPA AMS Center QA staff and the EPA AMS Center program management staff. Upon final review and approval, both documents will then be posted on the ETV website (www.epa.gov/etv).

SECTION D

DATA VALIDATION AND USABILITY

D1 DATA REVIEW, VALIDATION, AND VERIFICATION REQUIREMENTS

The key data review requirements for the verification test are the collection of QC samples as outlined in the test/QA plan, a comparison of field data sheet comments against final data to flag any suspect data, and a review of final data to resolve any questions about apparent outliers. The QA audits, as described within this document are designed to assure the quality of this data.

D2 VALIDATION AND VERIFICATION METHODS

Section C of this test/QA plan provides a description of the validation safeguards employed for this verification test. Data validation and verification efforts include the analysis of QC samples as required in this document, and the performance of TSA and PE audits as described in Section C.

D3 RECONCILIATION WITH USER REQUIREMENTS

This test/QA plan and the resulting ETV verification report(s) will be subjected to review by the multi-parameter water sensor vendors, EPA, and expert peer reviewers. These reviews will assure that this test/QA plan and the resulting verification report(s) meet the needs of potential users of the multi-parameter water sensors. Performance data for the multi-parameter water sensors, collected under conditions where the quality control requirements for the duplicate and PE audit samples shown in Table 3 were met, will be presented in the final verification report without any further comment. Performance data and reference measurements that do not meet these criteria will be noted and a discussion of the possible impact of the failed requirements on the performance evaluation will be presented in the final verification report. The final verification report(s) will be submitted to EPA in MS Word and Adobe portable document format (PDF) and subsequently posted on the ETV website.

SECTION E

REFERENCES

1. Quality Management Plan for the ETV Advanced Monitoring Systems Center, Version 6.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, December 2005.

2. "Environmental Technology Verification Program Quality Management Plan", December 2002, EPA/600/R-03/021.

3. American Public Health Association, et al., SM 4500-NH_3 D Ammonia-Selective Electrode Method in *Standard Methods for the Examination of Water* and Wastewater. 20th Edition, Washington, D.C., 2005.

4. U.S. EPA, EPA Method 215.2, Calcium (Titrimetric, EDTA) in *Methods for Chemical Analysis of Water and Wastes*, EPA/600/4-79/020, March 1983.

5. American Public Health Association, et al., SM 2510 Conductivity in *Standard Methods for the Examination of Water* and Wastewater. 19th Edition, Washington, D.C., 1997.

6. American Public Health Association, et al., SM 4500-G Residual Chlorine in *Standard Methods for the Examination of Water and Wastewater*. 19th Edition, Washington, D.C., 1997.

7. American Public Health Association, et al., SM 2580-B Electrochemical Potential in *Standard Methods for the Examination of Water and Wastewater*. 19th Edition, Washington, D.C., 1997.

8. U.S. EPA, EPA Method 150.1, pH in *Methods for Chemical Analysis of Water and Wastes*, EPA/600/4-79/020, March 1983.

9. U.S. EPA, EPA Method 170.1, Temperature in *Methods for Chemical Analysis of Water and Wastes*, EPA/600/4-79/020, March 1983.

10. U.S. EPA, EPA Method 310.1, Alkalinity in *Methods for Chemical Analysis of Water and Wastes*, EPA/600/4-79/020, March 1983.