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Environmental Technology Verification Program

Advanced Monitoring Systems Center

Test/QA Plan for Verification of Nitrate Sensors for Groundwater Remediation Monitoring

ETV TEST/QA PLAN

for

Verification of Nitrate Sensors for Groundwater Remediation Monitoring

April 23, 2010

Prepared by

Battelle
505 King Avenue
Columbus, OH 43201-2693

SECTION A

PROJECT MANAGEMENT

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ETV Advanced Monitoring Systems Center

Draft Test/QA Plan

for

Verification of Nitrate Sensors for
Groundwater Remediation Monitoring

April 23, 2010

VENDOR ACCEPTANCE

Name _____

Company _____

Date _____

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A3 ACRONYMS AND ABBREVIATIONS

ADQ	audit of data quality
AMS	Advanced Monitoring Systems
ANOVA	analysis-of-variance
ARS	Agricultural Research Service
bgs	below ground surface
DI	deionized
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
IC	ion chromatography
ISE	ion-selective electrode
LRB	laboratory record book
MAE	mean absolute error
MCL	maximum contaminant level
MS/MSD	matrix spike/matrix spike duplicate
MSE	mean squared error
NELAC	National Environmental Laboratory Accreditation Conference
NIST	National Institute of Standards and Technology
NJDEP	New Jersey Department of Environmental Protection
NTU	nephelometric turbidity unit
OQA	Office of Quality Assurance
PE	performance evaluation
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
QCS	quality control sample
QMP	quality management plan
R^2	coefficient of determination
RFIC	Reagent-Free Ion Chromatography
SRM	standard reference material
TSA	technical systems audit
USDA	United States Department of Agriculture

A4 DISTRIBUTION LIST

Vendors

Gregg Gustafson
Instrumentation Northwest, Inc.
8902 122nd Ave. Northeast
Kirkland, WA 98033

EPA

Michael Brody
U.S. EPA/OCFO
Ariel Rios Building
1200 Pennsylvania Ave. NW, 2722A
Washington, DC 20460

John McKernan
Michelle Henderson
U.S. EPA
NRMRL/ORD/ETAV
26 W. Martin Luther King Dr., MS 208
Cincinnati, OH 45268

Battelle

Amy Dindal
Andrew Barton
Nicole Albers
Zachary Willenberg
Battelle
505 King Avenue
Columbus, OH 43201

Collaborators

Stuart Nagourney
New Jersey Department of Environmental Protection
Office of Quality Assurance
9 Ewing Street
Trenton, NY 08625

Thomas Moorman
USDA/ARS
National Laboratory for Agriculture and the Environment
Ames, Iowa 50010

A5 VERIFICATION TEST ORGANIZATION

The verification test will be conducted under 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. This verification will address sensors that provide real-time measurements of dissolved nitrate concentrations in groundwater in support of remediation activities.

The day to day operations of this verification test will be coordinated and supervised by Battelle personnel, with in-kind involvement from personnel of the United States Department of Agriculture (USDA) Agricultural Research Service (ARS). Laboratory testing will be conducted at the USDA ARS National Laboratory for Agriculture and the Environment in Ames, Iowa. Field testing will be carried out by Battelle personnel and USDA ARS personnel under Battelle's oversight at the test site in Ames, Iowa. The vendors will provide on-site assistance to Battelle during the laboratory testing and during startup and commencement of field testing. The vendors will provide Battelle and USDA personnel with instructions for use of their nitrate sensors and enough nitrate sensors for implementation of field and laboratory testing.

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. Quality assurance (QA) oversight will be provided by an auditor from the New Jersey Department of Environmental Protection (NJDEP) Office of Quality Assurance (OQA) with oversight from the Battelle Quality Manager and also by the EPA AMS Center Quality Manager, at her discretion.

A5.1 Battelle

Andrew Barton is the AMS Center's Verification Test Coordinator for this test. In this role, Mr. Barton will have overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. Specifically, Mr. Barton will:

- Prepare the draft test/QA plan, verification reports, and verification statements.
- Revise the draft test/QA plan, verification reports, and verification statements in response to reviewers' comments.
- Assemble a team of qualified technical staff to conduct the verification test.

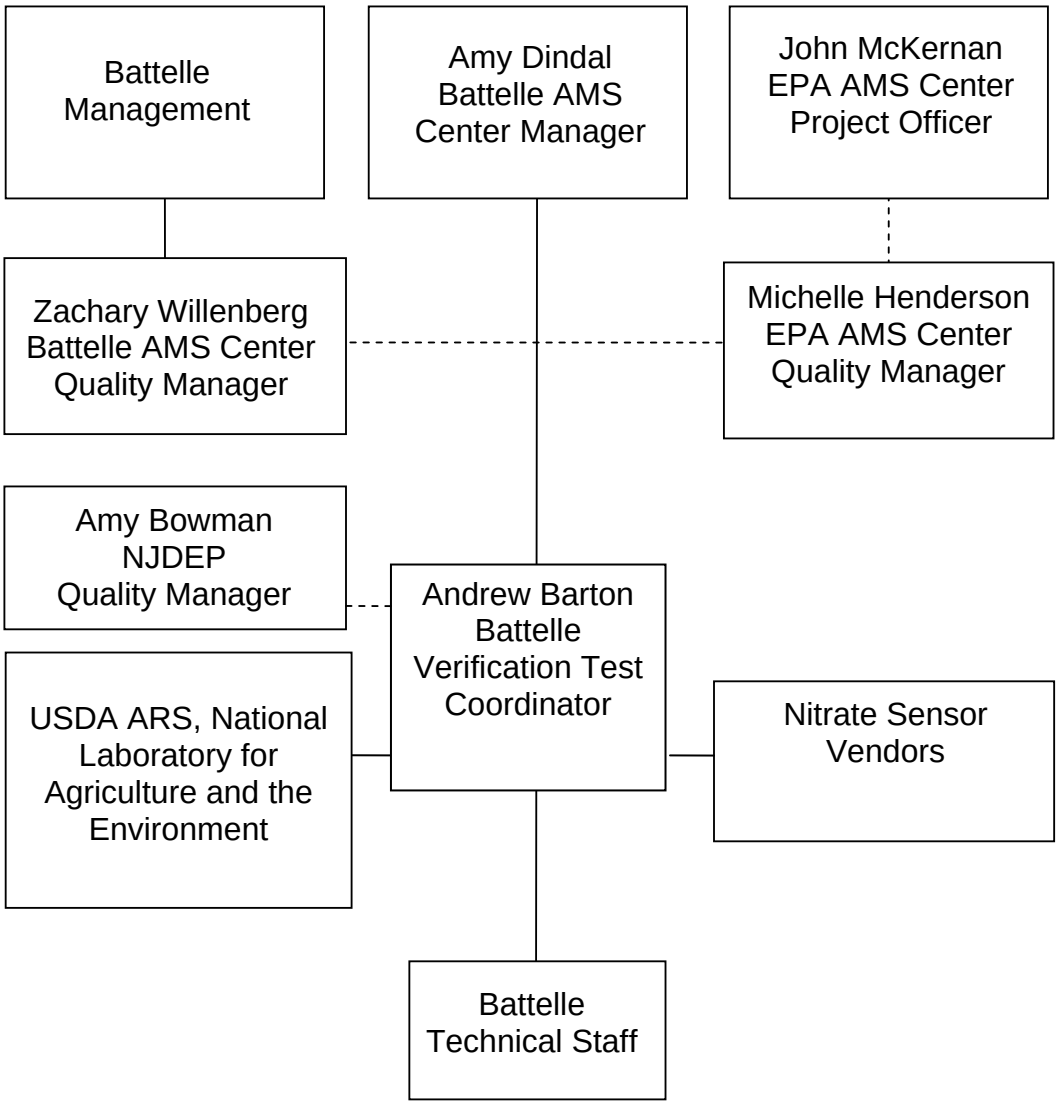

Figure 1. Organization Chart for the Verification Test

- Establish a budget for the verification test and manage staff to ensure the budget is not exceeded.
- Coordinate with the vendors for provision of nitrate sensors for testing.
- Direct Battelle technical staff in the laboratory testing and coordinate with Battelle and USDA ARS personnel for performance of the field testing.
- Direct the team in performing the verification test in accordance with this test/QA plan.

- Hold a kick-off meeting approximately one week prior to the start of the verification test to review the critical logistical, technical, and administrative aspects of the verification test. Responsibility for each aspect of the verification test will be confirmed.
- Ensure that all quality procedures specified in this EPA Quality Category III test/QA plan and in the AMS Center Quality Management Plan[1] (QMP) are followed.
- Serve as the primary point of contact for USDA ARS and vendor representatives.
- Ensure that confidentiality of sensitive vendor information is maintained.
- Assist vendors as needed during verification testing.
- Compile data from the first day of the verification test and provide the data to EPA for review.
- Become familiar with the operation of the nitrate sensors through instruction by the vendors, if needed.
- Prepare a deviation report for any departure from the test/QA plan during the verification, obtain the requisite EPA and vendor approvals, and distribute the approved report as specified in the AMS Center QMP.
- Respond to any issues raised in assessment reports, audits, or from test staff observations, and institute corrective action as necessary.
- Coordinate review and distribution of the final test/QA plan, verification reports, and verification statements.

Amy Dindal is Battelle's Manager for the AMS Center. As such, Ms. Dindal will oversee the various stages of verification testing. Ms. Dindal will:

- Review the draft and final test/QA plan.
- Attend the verification test kick-off meeting.
- 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.
- Maintain communication with EPA's technical and quality managers.
- Issue a stop work order if Battelle or EPA QA staff discover adverse findings that will compromise test results.

Technical staff from Battelle will support Mr. Barton in planning and conducting the verification test. The responsibilities of the technical staff will be to:

- Assist in planning for the test, and making arrangements for the receipt of and training on the nitrate sensors.
- Attend the verification test kick-off meeting.
- Conduct verification testing using the vendors' nitrate sensor technology.
- Perform statistical calculations specified in this test/QA plan on the technology data as needed.
- Provide results of statistical calculations and associated discussion for the verification reports as needed.
- Support Mr. Barton in responding to any issues raised in assessment reports and audits related to statistics and data reduction as needed.

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

- Review the draft and final test/QA plan.
- Attend the verification test kick-off meeting.
- Assist the NJDEP OQA auditor, as needed, in the conduct of the technical systems audit (TSA) during the verification test. The TSA will address both the laboratory and field components of nitrate sensor testing.
- Audit at least 10% of the verification data or designate other QA staff to conduct the data audit.
- Prepare and distribute an assessment report for each audit.
- Verify implementation of any necessary corrective action.
- Request that Battelle's AMS Center Manager issue a stop work order if audits indicate that data quality is being compromised.
- Provide a summary of the QA/quality control (QC) activities and results for the verification reports to Mr. Barton for review and submission to EPA in the final verification test report.
- Review the draft and final verification reports and verification statements.

A5.2 Nitrate Sensor Vendors

The responsibilities of the nitrate sensor vendors are as follows:

- Review and provide comments on the draft test/QA plan.
- Perform an initial site visit to coordinate logistics for the field verification test.
- Initially install and program nitrate sensors at the start of the field verification test and remove and field test (verify calibration) sensors at the end of the test.

- Provide a minimum of four and a maximum of seven nitrate sensors for evaluation during the verification test.
- Provide all other equipment/supplies/reagents/consumables needed to operate their technology for the duration of the verification test.
- Provide on-site assistance with sensor implementation during the laboratory testing and during startup and commencement of field testing.
- Supply training on the use of the technology, and provide written consent and instructions for test staff to carry out verification testing, including written instructions for routine operation of their technology.
- Perform/manage remote monitoring and dissemination of sensor data.
- Accept (by signature of a company representative) the final test/QA plan prior to test initiation.
- Review and provide comments on the draft verification report and verification statement for the nitrate sensor technology.

A5.3 USDA ARS National Laboratory for Agriculture and the Environment, Soil Microbiology and Environmental Quality Laboratory

The primary point of contact for USDA ARS will be Thomas Moorman. Mr. Moorman will lead USDA ARS personnel in meeting the following responsibilities for this verification:

- Provide laboratory space for the laboratory portion of the verification test.
- Provide access to and support at the field test site.
- Review and provide comments on the draft test/QA plan.
- Analyze all conventional groundwater field and associated QC samples for nitrate.
- Analyze conventional groundwater field and associated QC samples for nitrite as nitrogen (nitrate-N) until negligible concentrations (i.e., <1 mg/L) are verified in groundwater.
- Analyze all laboratory verification test and associated QC samples for nitrate.
- Provide sufficient personnel to collect weekly conventional groundwater samples at the test site according to procedures outlined in this test/QA plan.
- Modify conditions at the test site (if necessary) to ensure parameter variability.
- Review and provide comments on the draft verification report and verification statement for the nitrate sensor technologies.

A5.4 EPA

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

Michelle Henderson is EPA's AMS Center Quality Manager. For the verification test, Ms. Henderson will:

- Review the draft and approve the final test/QA plan.
- Attend the verification kick-off meeting, as available.
- Review checklists, reports, report responses, and closure statements of TSA, performance evaluation (PE) audits, and audits of data quality systems (ADQs) conducted by NJDEP, and/or Battelle.
- Perform an external TSA of field and/or laboratory activities, PE audits, and/or an audit of data quality during the verification test.
- Notify the EPA AMS Center Project Officer of the need for a stop work order if evidence indicates that data quality is being compromised.
- Prepare and distribute an assessment report summarizing results of the external audit performed.
- Review the first day of data from the verification test and provide immediate comments if concerns are identified.
- Review the draft and approve the final verification reports and verification statements.

John McKernan is EPA's Project Officer for the AMS Center. Dr. McKernan will:

- Review the draft test/QA plan.
- Approve the final test/QA plan.
- Attend the verification kick-off meeting, as available.
- Be available during the verification test to review and authorize any test/QA plan deviations by phone and provide the name of a delegate to the Battelle AMS Center Manager should he not be available during the testing period. Review the first day of data from the verification test and provide immediate comments if concerns are identified.
- Review the draft verification reports and verification statements.

- Oversee the EPA review process for the test/QA plan, verification reports, and verification statements.
- Coordinate the submission of verification reports and verification statements for final EPA approval.
- Post the test QA plan, verification reports, and verification statements on the ETV Web site.

A5.5 Verification Test Stakeholders

This test/QA plan and the verification report(s) and verification statement(s) based on testing described in this document will be reviewed by experts in the fields related to nitrate sensor technology. The following experts have been providing input to this test/QA plan and have agreed to provide a peer review:

- Stu Nagourney, NJDEP (also AMS Center stakeholder)
- Amy Bowman, NJDEP (TSA auditor)
- Charles Spooner, EPA Office of Water
- Kenneth Wood, Dupont (also AMS Center stakeholder)
- Michael Brody, EPA Office of the Chief Financial Officer

The AMS Center Water Stakeholder Committee also was apprised of the status of verification testing during periodic teleconferences and provided the opportunity to comment on the test design before it was implemented into this test/QA plan.

A6 BACKGROUND

A6.1 Technology Need

The ETV Program's AMS Center conducts third-party performance testing of commercially available technologies that detect or monitor natural species or contaminants in air, water, and soil. The purpose of ETV is to provide objective and quality assured performance data on environmental technologies, so that users, developers, regulators, and consultants can make informed decisions about purchasing and applying these technologies. Stakeholder committees of buyers and users of such technologies recommend technology categories, and technologies within those categories, as priorities for testing. Verification reports from previous tests are available at http://www.epa.gov/nrmrl/std/etv/verifiedtechnologies.html.

As a result of human activity (i.e., transportation, industrial processes, and agriculture) the annual transfer of nitrogen into biologically available forms has more than doubled.[3] Throughout the 2006-2011 EPA Strategic Plan are strategic commitments and measures that address emissions and concentrations of nitrogen and nitrogen compounds. This emphasis is continued in the recently released public review draft of this Strategic Plan Change Document, which can be found at http://www.epa.gov/cfo/plan/2006/entire_report.pdf. Based on the increase in biologically available dissolved nitrate, coupled with the potentially toxic effects of exposure at elevated concentrations, the EPA has set a maximum contaminant level (MCL) of 10 mg/L nitrate as nitrogen (nitrate-N) in drinking water.

Subsurface drainage from agricultural land commonly contains elevated dissolved nitrate concentrations, and contributes a substantial portion of base flow in rivers in areas of North America. In certain agricultural areas, drainage is promoted through the use of subsurface tiles (drainage tubes), which typically are joined to larger drains or deliver water directly into small streams. Concentrations of nitrate exiting subsurface tile drains frequently exceed 15 mg/L (3.4 mg/L nitrate-N) in spring and early summer.[4-9] This nitrogen export from Midwestern tile-drained watersheds is a contributing factor to the hypoxia problem in the Gulf of Mexico.[10] One strategy for reducing nitrate concentrations in this agricultural drainage is an "end of tile bioreactor", which is essentially an excavated cavity filled with wood chips. Tile drainage water is commonly routed through this structure; the wood chips naturally support populations of microorganisms that remove the nitrate through denitrification. Previous studies have shown that bioreactors and denitrification walls reduce nitrate concentrations in drainage water in a variety of settings.[11-14]

Underlying any approach to the reduction of nitrogen in the environment (i.e., groundwater) is the need to measure concentrations in a timely and useful manner. Monitoring of environmental contaminants in groundwater is currently a costly and often lengthy process that is accomplished by collecting samples from wells using labor-intensive techniques, preserving and then shipping the samples to an established laboratory where sample preparation, analysis and data reduction are performed. This process is time consuming and may not yield data for days or even weeks after sample collection, depending upon laboratory backlogs and report preparation timeframes. This verification test will evaluate a newer approach to monitoring of groundwater in a monitoring well, and in an end of tile bioreactor using environmental sensors. One of the objectives is to compare conventional grab (or discrete) groundwater sampling results (which are

often collected on a quarterly basis) to results collected on a continual basis using in situ sensors to better design an optimal monitoring groundwater strategy that focuses on ensuring adequate protection for human health and the environment.

A6.2 Technology Description

Environmental sensors are small, transportable analytical devices that provide data in real time, are rugged enough to withstand a wide range of weather conditions, operate remotely, acquire data continuously or on demand, and provide processed data directly to the user. Monitoring costs could be reduced by the use of sensors placed directly in a well, thereby eliminating sample collection and shipment costs, and reducing analytical costs and delays in data acquisition and reporting. Sensors ideally can collect large amounts of data on a continuous basis over time, with the sensor often placed in one location. Sensors can be used as a stand-alone to replace current methods or to supplement current methods. Networked sensors also can provide many more data points over a given time interval, thereby offering the potential to identify trends in data and to observe less frequent but environmentally significant events that cannot currently be observed by current sampling and analysis paradigms. The ETV verification described in this test/QA plan will explore the effectiveness and ease of use of nitrate sensors and quantify their response relative to conventional monitoring and laboratory analysis of dissolved nitrate in groundwater.

A submersible nitrate sensor is capable of collecting in-situ measurements of dissolved nitrate concentrations in groundwater. Although several types of nitrate sensors currently exist, this verification test will focus on submersible sensors equipped with a nitrate-specific ion-selective electrode (ISE) for monitoring dissolved nitrate concentrations. Nitrate-specific ISE sensors typically work on the principal of direct potentiometry, whereby two electrodes (a sensing electrode and a reference electrode) are contained within the sensor unit. The reference electrode is immersed in a solution of a constant nitrate concentration within the sensor housing, and ionic charge transfer between this solution and the sensing electrode is measured and converted to a concentration that is representative of a dissolved nitrate concentration of the aqueous solution being analyzed. Example ISE sensors are illustrated in Figure 2.

Submersible nitrate sensors are powered internally with alkaline batteries or with an auxiliary power supply for data intensive applications. The sensor can be programmed to measure and

collect data on a variety of time intervals, and can be connected to land-line modems that will transmit real-time data for immediate download.

A7 VERIFICATION TEST DESCRIPTION AND SCHEDULE

A7.1 Verification Test Description

The purpose of this test/QA plan is to specify procedures for a verification test applicable to commercial nitrate sensors. One aspect of the verification test is to compare dissolved nitrate concentrations in groundwater measured by the deployed sensors to nitrate concentrations collected using conventional groundwater monitoring techniques. In addition, a laboratory verification test will be performed to evaluate the performance of the nitrate sensors in response to simulated changes in field conditions. 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] This test/QA plan is an EPA QA Category III evaluation.

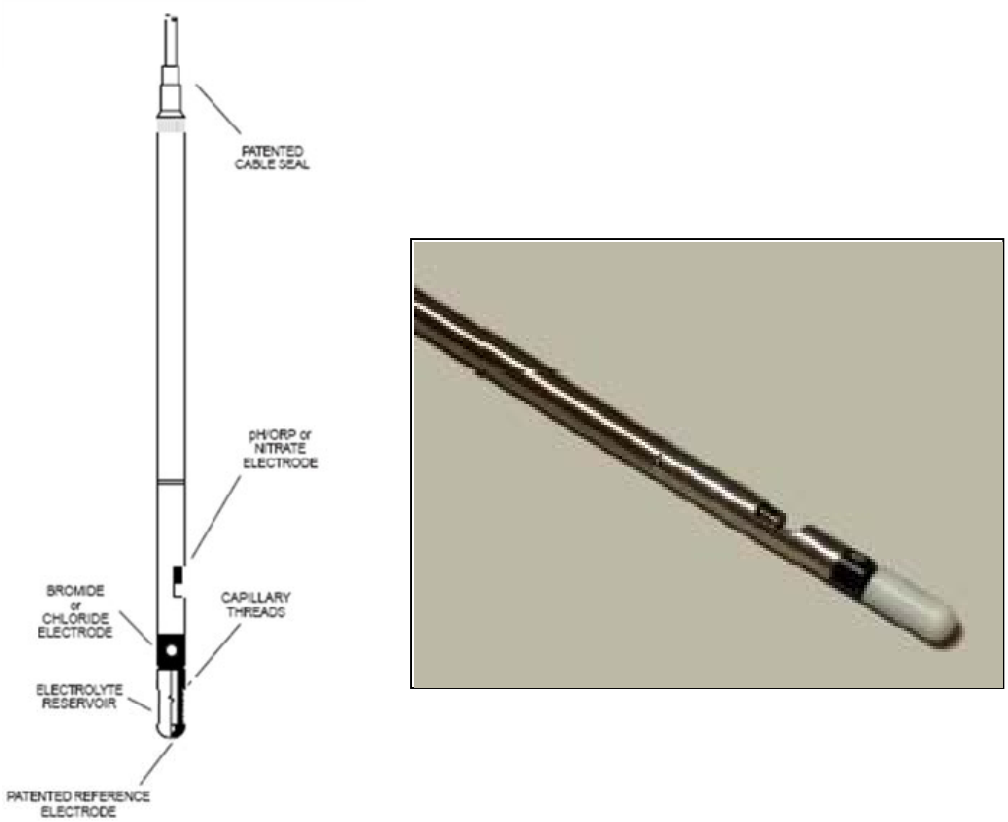

Figure 2. Example ISE Sensors

A7.2 Verification Schedule

Table 1 shows the planned schedule of activities for the verification testing and data analysis and reporting. Laboratory testing of the nitrate sensors will be initiated soon after final approval of this test/QA plan; field sensor deployment and field verification testing will take place simultaneously. As shown in Table 1, testing activities are planned to begin in the spring of 2010. Laboratory testing will commence first, and require approximately one week prior to field deployment and verification testing. Field testing will require approximately two months to complete. An ETV verification report will subsequently be drafted, and the report will be reviewed simultaneously by the participating technology vendors, NJDEP, USDA, and EPA, and subsequently by peer reviewers. The final reports will be submitted to EPA for final signature, and the final reports will be made publicly available on the EPA/ETV Web site.

Table 1. Planned Verification Schedule

Month and Year	Verification Activity	
	Testing	Data Analysis and Reporting
March 2010	Prepare for laboratory testing	Begin preparation of ETV report template
April 2010	Initiate and complete laboratory testing Initiate field testing using sensors[a] Perform field reference sampling	Compile data from laboratory testing Compile data from field verification testing Review and summarize laboratory operator observations
May-June 2010	Completion of field testing of sensors	Analyze laboratory test data Analyze field test data Review and summarize field operator observations
June-July 2010	None	Analyze field test data Prepare draft reports Internal review of draft reports
August 2010	None	Vendor/NJDEP/USDA/EPA review of draft reports Revision of draft reports Peer review of draft reports
September 2010	None	Revision of draft reports Submission of final reports for EPA approval

a: The start of field testing will be dependent upon weather conditions (i.e., whether groundwater is flowing in the test cell and the recent occurrence of a precipitation event).

A7.3 Test Facility

Laboratory analyses will be conducted in the USDA ARS laboratory in Ames, Iowa. In performing this verification test, Battelle and the USDA ARS laboratory will follow the procedures specified in this test/QA plan and will comply with quality requirements in the AMS Center QMP.[1] The USDA ARS laboratory that will be used is fully equipped for receiving, documenting, preparing, and performing calibrated measurement of dissolved nitrate concentrations in groundwater samples. The end of the tile bioreactor field site is located a few miles from the USDA ARS laboratory in Ames.

A8 QUALITY OBJECTIVES

This verification test is designed to evaluate the performance of sensors for measuring dissolved nitrate concentrations in groundwater. Laboratory verification testing will simulate field monitoring of nitrate in groundwater and will include an evaluation of sensor performance in accurately measuring nitrate concentrations in response to simulated variations in groundwater field conditions (e.g., nitrite, turbidity, and chloride). Nitrate and the selected interference parameters will be generated from stock solutions and injected at known concentrations to challenge the sensors. Conventional samples will periodically be collected during the laboratory testing and analyzed for verification of nitrate concentrations using ion chromatography (EPA 300.1). Field verification testing will consist of monitoring groundwater for nitrate using sensors and a conventional groundwater sampling technique. The conventional groundwater samples will be collected periodically during the field test and analyzed for verification of nitrate concentrations using ion chromatography (EPA 300.1). In addition to analyzing for nitrate, the groundwater samples will be analyzed for nitrite-N for one month or until negligible concentrations (i.e., <1 mg/L) are verified in groundwater for two successive monitoring events. The quality of the nitrate concentration data generated using the sensors will be documented by calibration data, and documentation of the QA activities carried out at the field monitoring site.

For consistency and understanding of reported nitrate concentrations, it should be noted that the nitrate sensors will be programmed to display and record concentrations as nitrate-N. The laboratory ion chromatography (IC) procedure also was written based on evaluating and reporting concentrations as nitrate-N. For comparison, 1 mg/L nitrate-N is equal to 4.4 mg/L nitrate, so 3 mg/L nitrate (the lower reporting limit of the nitrate sensor) is 0.68 mg/L nitrate-N.

QA/QC requirements will include a TSA, a PE audit, and an ADQ. The TSA will be conducted by Ms. Amy Bowman, NJDEP OQA. The inclusion of the PE sample will be conducted by Mr. Barton and the results of the PE audit will be reviewed by the Battelle Quality Manager who will also conduct the ADQ. The planned audit procedures are described in Section C1. The EPA Quality Manager also may conduct an independent TSA, PE audit, and/or ADQ at her discretion.

A9 SPECIAL TRAINING/CERTIFICATION

The Battelle Quality Manager or NJDEP auditor may verify the presence of appropriate training records prior to or during testing. Documentation of training related to technology testing, field testing, laboratory testing, data analysis, and reporting is maintained for all Battelle technical staff in training files at their respective locations. Battelle technical staff involved in this verification will have experience in operation of sensor calibration and monitoring equipment. In addition, the staff will have experience in operation and calibration of conventional groundwater monitoring equipment, including inter-well decontamination procedures. All Battelle and USDA personnel will receive on-site training by the vendor in the use of the nitrate sensors selected for this verification test.

A10 DOCUMENTATION AND RECORDS

The records for this verification test will be contained in the test/QA plan, laboratory record books (LRB), data collection forms, electronic files (both raw data and spreadsheets), the final verification report, or assessment reports. Nitrate sensor field test data will be uploaded to an internet (ftp) site that will be accessible with Windows®-based software. All of these records will be maintained by the Verification Test Coordinator during the test and will be transferred to permanent storage at Battelle's Records Management Office within two months of the finalization of the verification reports. Electronic files containing field and laboratory results will be disseminated to the project team on a bi-weekly basis. All Battelle LRBs are also stored indefinitely, either by the Verification Test Coordinator or within two months of the finalization of the verification reports in Battelle's Records Management Office. EPA will be notified before disposal of any files. Section B10 further details the data recording practices and responsibilities.

All written records will be in ink. Any corrections to notebook entries, or changes in recorded data, will be made with a single line through the original entry. The correction is then to be

entered, initialed, and dated by the person making the correction. In all cases, strict confidentiality of data from the vendor's technology will be maintained.

SECTION B

MEASUREMENT AND DATA ACQUISITION

B1 EXPERIMENTAL DESIGN

This test/QA plan addresses the verification of nitrate sensors through laboratory testing and field monitoring of nitrate concentrations in groundwater. Specifically, nitrate sensors will be evaluated for the following performance parameters:

- Accuracy
- Variability of readings
- Duplication of readings
- Effect of nitrite, turbidity, and chloride on nitrate sensor readings
- Operational factors including ease of use, downloading of data, timely dissemination of data, and use of nitrate sensors for real-time remote data collection.

Sensor probes for other parameters (e.g., specific conductance, temperature, pH, groundwater level, etc...) may be included with the nitrate sensor to better understand conditions within the test cell. These data will be reviewed to determine whether potential interference parameters may be affecting nitrate sensor readings. Prior to the deployment, critical interference parameter levels, above or below which the sensors may be compromised, will be established by the vendor using sensor technology criteria and water quality data from a groundwater sample collected from the test cell. Should these critical levels be exceeded at any time during the verification testing, nitrate sensor data will be immediately evaluated, the project team will be notified, the level and duration of exceedance will be noted, and appropriate action (i.e., sensor recalibration) will be taken. It should be noted that interference parameter sensor data will not be included in the verification report; only nitrate sensor data will be evaluated and reported.

Accuracy will be determined by comparing nitrate sensor readings to reference nitrate concentration measurements made in laboratory and field testing and analyzed in the laboratory using EPA-approved analysis methods (EPA Method 300.1 for nitrate). Variability will be assessed by observing the spread of nitrate sensor readings made at constant nitrate concentrations (equated to drift) using stock solutions in the laboratory. Nitrate sensor duplication of readings will be assessed by comparing nitrate sensor readings made by placing duplicate nitrate sensors in a single test cell in the laboratory so they are exposed to identical

concentrations simultaneously. The effect of nitrite, turbidity, and chloride on nitrate sensor readings will be assessed in the laboratory by comparing nitrate sensor readings exposed at constant nitrate concentrations but under varying degrees of nitrite, turbidity, and chloride. Operator observations will be recorded in all laboratory and field testing to assess operational factors of the nitrate sensors. Consistency of nitrate sensor readings over time will be assessed in the accuracy of nitrate sensor readings made in the field and in the laboratory over time, verified against laboratory analyses. The field testing evaluation (particularly the readings collected near the end of the field study) will serve to evaluate the effects of sensor fouling on the accuracy and duplication performance parameters.

B1.1 Test Procedures

The following sections describe the designed field and laboratory test procedures, and how these test procedures will be used to evaluate each of the performance parameters listed above.

B1.1.1 – Laboratory Testing

For laboratory testing, two test cells will be constructed using a 2-inch diameter, 4-foot high, clear plastic (i.e., polyvinyl chloride [PVC]) pipe with a stopcock installed six inches above the base. Two (2) bundled nitrate sensors will be deployed in the first test cell and one (1) sensor will be deployed in the second test cell, each suspended at a depth where the base of the sensor is six inches above the base of the test cell. The nitrate sensors will be calibrated prior to deployment (see Section B7) and programmed to collect nitrate concentration measurements at one minute intervals throughout the duration of the laboratory testing, which is expected to be approximately 2 days.

Phase 1 of the laboratory testing will consist of filling a two-liter (2 L) graduated cylinder with a mixture deionized (DI) water and an ionic strength adjustor exposed to air of normal temperature. Use of an ionic strength adjustor (ammonium sulfate) will create uniform background conditions in the test cells that will emulate field conditions, as natural waters have a background ionic strength. This addition will normalize the activity of the ionic strength of the solution and allow for sensor performance without the complication of calculating activity. The solution will be spiked with known nitrate concentration prepared from a concentrated stock solution to generate the desired nitrate concentration, using the following calculation to solve for the desired volume of stock solution:

$$C_1 \times V_1 = C_2 \times V_2$$

where: C_1 = concentration of stock solution (mg/L)
V_1 = volume of stock solution (L)
C_2 = desired nitrate or interference parameter concentration (mg/L)
V_2 = desired volume (L)

The solution in the graduated cylinder will be decanted into the two test cells (1 L per test cell) and this process will be repeated for each desired nitrate concentration. The nitrate concentrations will be randomly varied every 20 minutes, and will span the expected range of nitrate concentrations observed in the field test cell (roughly 1 to 12 mg/L nitrate-N [3-53 mg/L nitrate]) according to the schedule outlined in Table 2. Between each test, the test cell will be drained with the stopcock and flushed with DI water, allowing time for the nitrate sensors to re-equilibrate prior to spiking the test cells with subsequent nitrate solutions. A certified, concentrated liquid stock solution of sodium or potassium nitrite will be purchased from a laboratory supply company and appropriate volumes of the stock solution will be pipetted into the graduated cylinder to achieve the desired concentrations. The concentration-specific order of nitrate concentrations will be randomized to minimize the potential for error. It should be noted that the nitrate levels may vary slightly (i.e., ±5%) from the desired level; however, the integrity of the range in parameter levels, which is the objective of the laboratory testing, will still be maintained.

Phase 2 of the laboratory testing will evaluate the effects of known interferences (e.g., changes in nitrite, turbidity, and chloride) on the ability of the nitrate sensors to accurately measure nitrate concentrations. The effects of each of these parameters will be evaluated separately by varying the interference parameter within a specific range at varying nitrate concentrations (see Table 2). The parameter- and concentration-specific order of interference parameter evaluation will be randomized to minimize the potential for error. It should be noted that the interference parameter levels may vary slightly (i.e., ±5%) from the desired level; however, the integrity of the range in parameter levels, which is the objective of the laboratory interference parameter testing, will still be maintained.

Table 2. Summary of Nitrate Sensor Laboratory Testing

Phase	Interference Parameter	Nitrate-N Conc.[d] (mg/L)	Interference Parameter Level	Test Duration[a] (min)	No. of Conventional Samples Collected per Test Cell	Total No. of Conventional Samples[c]
1 (Nitrate Only)	None	1 (4.4)	Chloride = ND Temp. = ambient Nitrite = ND Turbidity = ND	20	1	2
		3 (13)		20	1	2
		6 (26)		20	1	2
		12 (53)		20	1	2
2 (Nitrate Plus Interference)	Chloride	1 (4.4)	100 mg/L	10	1	2
			500 mg/L	10	1	2
			2,500 mg/L	10	1	2
		3 (13)	100 mg/L	10	1	2
			500 mg/L	10	1	2
			2,500 mg/L	10	1	2
		12 (53)	100 mg/L	10	1	2
			500 mg/L	10	1	2
			2,500 mg/L	10	1	2
	Nitrite-N	1 (4.4)	1 mg/L	10	1	2
			2 mg/L	10	1	2
			4 mg/L	10	1	2
		3 (13)	1 mg/L	10	1	2
			2 mg/L	10	1	2
			4 mg/L	10	1	2
		12 (53)	1 mg/L	10	1	2
			2 mg/L	10	1	2
			4 mg/L	10	1	2
	Turbidity	1 (4.4)	1 NTU	10	1	2
			5 NTU	10	1	2
		3 (13)	1 NTU	10	1	2
			5 NTU	10	1	2
		12 (53)	1 NTU	10	1	2
			5 NTU	10	1	2
			Totals	***320***	***28***	***56***[b]

a: Duration indicates total time of test once nitrate and interference parameters have reached the desired levels; actual duration per test may be longer.
b: Total number of samples does not include reference sampling QC samples (see Section B5). It is estimated that approximately 15 reference QC samples will be collected in the laboratory verification test.
c: All samples will be analyzed for nitrate using EPA Method 300.1.
d: Equivalent nitrate concentrations in parentheses.
Note: The nitrate sensors will collect readings at one minute intervals throughout the entire laboratory test.
ND = non detect
NTU = nephelometric turbidity unit

During Phase 2 of the laboratory test, stock solutions of varying nitrate, nitrite, turbidity, and chloride concentrations will be generated in a manner similar to that described above. Certified, concentrated stock solutions of potassium nitrite (or similar), sodium chloride (or similar), and formazin (or similar for turbidity) will be purchased from a laboratory supply company and appropriate volumes of the stock solution will be pipetted into the graduated cylinder and subsequently into the test cells to achieve the desired concentrations. The interference parameter concentrations will be randomly varied every 10 minutes according to the schedule outlined in Table 2.

During laboratory testing, water samples will be collected from the test cells for laboratory analysis of nitrate concentrations using EPA Method 300.1. The laboratory analyses will be used to monitor changes in nitrate concentrations during the test, and will be compared to data collected using the nitrate sensors. The sampling frequency for the laboratory analyses is summarized in Table 2, with one conventional sample being collected for each nitrate concentration during Phase 1, and each interference parameter variation during Phase 2. Water samples will be collected from a stopcock installed in the plastic piping at a depth consistent with the sensor electrode. Water samples will then be collected by filling two 125 mL poly containers from discharge tubing attached to the stopcock. The water samples will be labeled and temporarily stored on site in a cooler at 4ºC prior to same-day delivery to the USDA laboratory for analysis. The laboratory will receive, process, analyze, and report results within 48 hours of sample collection. The procedure for collecting water samples and for sample preparation and shipment is included as Appendix A. Example field activities log sheets and field sampling logs are provided in Appendices B and C, respectively.

B1.1.2 – Field Testing

Field testing will consist of nitrate sensor deployment to monitor dissolved nitrate concentrations within an end of tile bioreactor located at the Kelly Farm research site in Ames, IA. A cross-section schematic of the site is shown in Figure 3, and illustrates the location of the inlet and outlet pipelines, and the three monitoring wells that are screened from 2 to 6 ft below ground surface (bgs). Reference sampling also will be performed using conventional groundwater monitoring techniques. The following subsections discuss the field testing components in more detail.

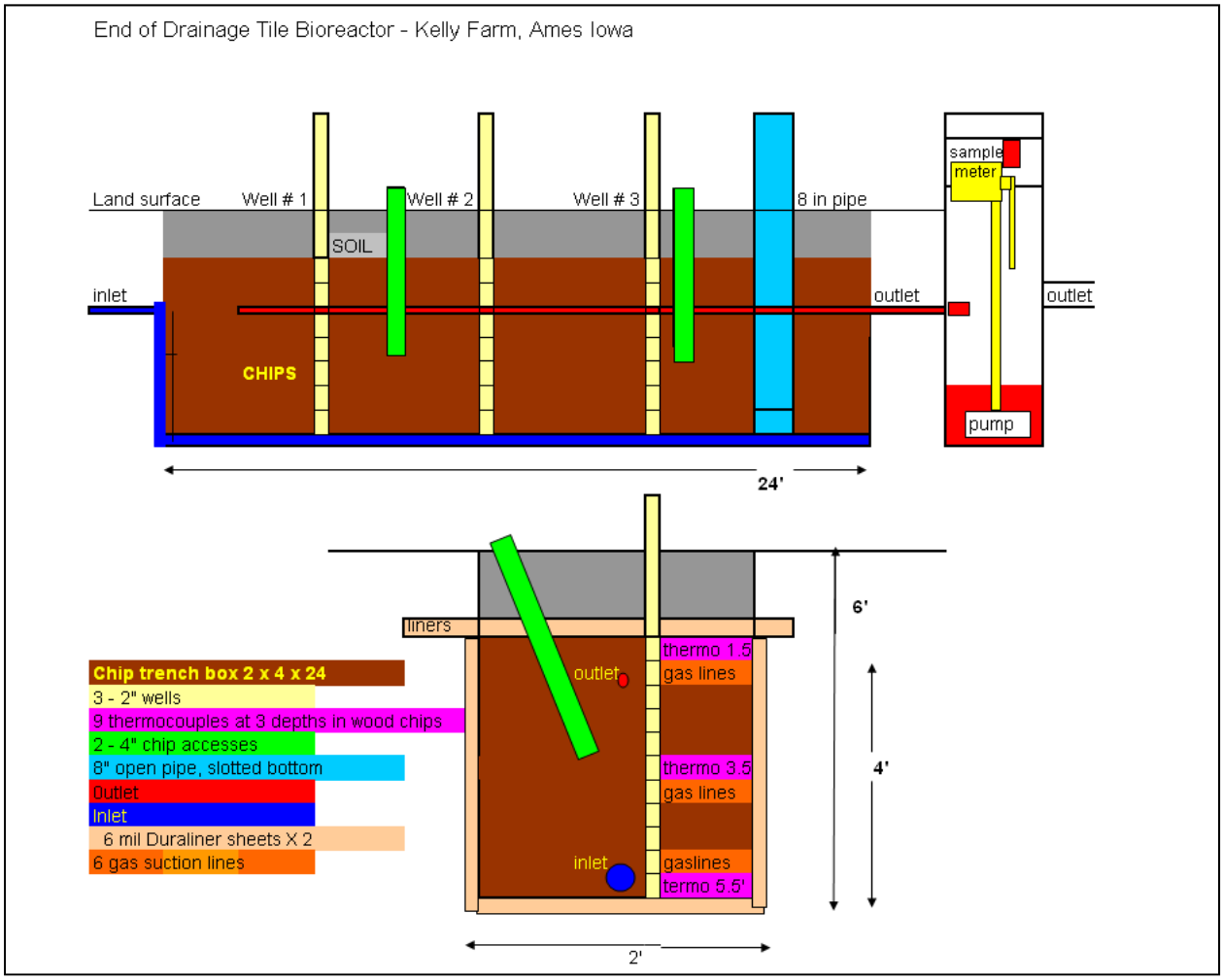

Figure 3. Schematic Cross Section View of End of Tile Bioreactor at Kelly Farm, Ames, IA

It should be noted that the quality and objectivity of the field evaluations conducted by USDA and Battelle will be assured by the efforts of Battelle technical and NJDEP QAO staff. The Battelle Verification Test Coordinator (Mr. Barton) will communicate the procedures and expectations for nitrate sensor evaluation to both the USDA and sensor vendor representatives by verbal and written means including this test/QA plan. That communication will be maintained before, during, and after the periods of field testing, and will continue in the data analysis phase of the verification.

Prior to field testing, a groundwater sample will be collected from one of the monitoring wells in the test cell and analyzed by the USDA laboratory for nitrate, the interference parameters

evaluated in the laboratory (nitrite, chloride, and turbidity), and other potentially interfering parameters such as bromide and sulfate. Information from these analyses will assist in programming the nitrate sensor prior to field deployment, and in evaluating the quality of the nitrate sensor data.

B1.1.2.1 – Field Testing Procedures – Nitrate Sensor

Nitrate sensors will be deployed to monitor dissolved nitrate concentrations at the bioreactor in the three 2-inch monitoring wells (Well #1, Well #2, and Well #3) and in the inlet sump. A nitrate sensor will be deployed in Well #1 and in Well #3 at a midpoint depth of 4 ft bgs. In Well #2, two nitrate sensors will be deployed at depths of 3 and 5 ft bgs to evaluate the existence of vertical gradients within the test cell. A nitrate sensor also will be deployed in the inlet sump approximately 90 ft upgradient of the upgradient edge of the bioreactor. Once the nitrate sensors have been calibrated (see Section B7), they will be deployed in the well for a period of two months and programmed to collect nitrate concentration measurements at a frequency of 15 minutes. Additional sensor testing/calibration will be performed once the nitrate sensors have been removed from the well at the end of the field test. The sensors will be equipped with wireless transmitters attached to the sensor cable that will be located at the top of the well casing and will transmit real-time data to a laptop located in a building on the Iowa State University Swine Nutrition Farm campus located approximately 300 yards to the southeast of the bioreactor. The data will be uploaded to the laptop and transmitted to a password protected Internet site using existing phone lines for immediate download by the project team.

B1.1.2.2 –Field Testing Procedures – Conventional Groundwater Monitoring

Concurrent with the nitrate sensor deployment within the bioreactor, field verification testing will be performed consisting of collecting groundwater samples, groundwater-level elevations, and inlet flow rates. Inlet flow rates will be measured in the inlet pipeline by USDA personnel using an in-line flow meter. Groundwater-level elevation data will be collected using a measuring tape/sounder that is lowered into the monitoring well until the depth to groundwater is reached and recorded. The conventional groundwater sampling technique will consist of sample collection using a peristaltic pump and dedicated Teflon® tubing. The dedicated tubing will be installed in the well so that the inlet is located at the same depth as the sensor electrode, and the open end at the surface will be capped to minimize fouling within the tubing. When collecting samples, the cap will be removed, the tubing will be attached to the peristaltic pump and the pump will be operated at the lowest allowable setting to extract groundwater from the well. One

to two pore volumes (within the Teflon® tubing) will be extracted from the well prior to sample collection; the volume of water will be calculated using the inner radius of the tubing and the thickness of the water column (inlet depth minus depth to groundwater). Groundwater samples will then be collected by filling two 125 mL poly containers from the discharge tubing. The groundwater samples will be labeled and temporarily stored on site in a cooler at 4ºC prior to delivery to the USDA laboratory for analysis. The laboratory will receive, process, analyze, and report results within 48 hours of sample collection. The procedure for collecting groundwater-level elevations and groundwater samples, and for sample preparation and shipment, is included as Appendix A. Example field activities log sheets and field sampling logs are provided in Appendices B and C, respectively.

The field reference monitoring schedule is presented in Table 3. Throughout the 2-month sensor deployment, groundwater monitoring (including collection of groundwater-level elevations, groundwater samples, and inlet flow rates) will be performed at each of the five monitoring locations on a weekly basis to simulate a more conventional groundwater monitoring approach. For two days at the beginning and two days at the end of the nitrate sensor deployment, more intensive hourly monitoring of the aforementioned parameters will be performed. The intensive monitoring at the beginning of the deployment is designed to provide initial verification of the sensor monitoring, whereas the intensive monitoring at the end of the test is designed to verify the accuracy of the unit after a significant deployment period where sensor biofouling within the well may be an issue. An attempt will be made to perform these intensive two-day sampling efforts immediately after a rainfall event to maximize the variation in nitrate concentrations in the bioreactor that is expected after such an event due to increased subsurface drainage routed through the inlet.

During field verification monitoring, approximately 252 groundwater and associated QA/QC samples will be collected for analysis of nitrate concentrations. It is anticipated that 64 samples will be analyzed during the weekly sampling and 94 samples during each of the 2-day intensive sampling events at the beginning and end of field testing (see Table 3). The number of QA/QC samples may vary based on unforeseen factors encountered during the field testing. It should be noted that the samples also will be analyzed for nitrite for one month or until negligible concentrations (i.e., <1 mg/L nitrite-N) are verified in groundwater for two successive monitoring events.

Table 3. Summary of Nitrate Sensor Field Verification Monitoring using Conventional Groundwater Monitoring Techniques

Sample Frequency	Duration	Anticipated Number of Field Samples	Associated QC Samples[a]	Total Number of Samples
Weekly	2 months	40	24	64
Hourly	2 days (beginning of deployment)	80	14	94
Hourly	2 days (end of deployment)	80	14	94

a: Estimated number of QC samples (see Section B5).

B1.1.3 – Evaluation of Test Parameters

Table 4 summarizes the types and numbers of samples that will be used to verify performance of each nitrate sensor. A summary of the sampling requirements in regard to the test performance parameters identified in Section B1 is presented in the following subsections.

Table 4. Summary of Nitrate Sensor Verification Samples

Sample Type	Responsible Organization	Approximate Number of Samples or Readings	Associated QC Samples	Uses
Phase 1 laboratory water samples	Battelle	80	Equipment rinsates "Field" duplicates Laboratory QA/QC	Accuracy, variability, duplication, user agreement.
Phase 2 laboratory water samples	Battelle	240	Equipment rinsates "Field" duplicates Laboratory QA/QC	Accuracy, duplication, effect of changes in water quality, user agreement.
Field groundwater samples	Battelle/USDA	200	Equipment rinsates Field duplicates Laboratory QA/QC	Accuracy, effect of changes in water quality, user agreement
User observations	Battelle/USDA	As needed	NA	Operational factors

B1.1.3.1 – Accuracy

Prior to deployment and testing, each nitrate sensor will be calibrated by the vendor; an example calibration procedure is presented in Appendix D. Immediately after calibration, the sensor will be programmed to take a few readings while the sensor is still in the reference standard(s) to

verify the accuracy of the initial calibration. The accuracy of the nitrate sensor in the field and in the laboratory will be determined by comparing nitrate sensor readings to simultaneous measurements made using conventional groundwater sampling techniques. The comparison of accuracy will be made statistically and graphically, by plotting nitrate sensor readings (concentrations) against the nitrate concentrations measured in groundwater samples collected using conventional techniques.

In the laboratory testing (as described in Section B1.1.1 and summarized in Table 2), nitrate concentrations will be generated from a concentrated stock solution. In Phase 1 of the laboratory testing, four nitrate concentrations (1, 3, 6, and 12 mg/L nitrate-N, or 4.4, 13, 26, and 53 mg/L nitrate), spanning the range of anticipated field concentrations, will be generated and evaluated with the nitrate sensors and conventional groundwater samples. In addition, concentrations of interference parameters will be introduced into the laboratory test cells in Phase 2 of the laboratory test to evaluate the ability of the nitrate sensor to accurately measure nitrate concentrations under a variety of hypothetical field conditions.

B.1.1.3.2 – Variability of Readings

Variability of nitrate sensor concentration readings refers to the consistency, or lack thereof, in reported nitrate concentrations with a constant nitrate concentration. Variability will be assessed in Phase 1 of the laboratory evaluation using the multiple readings (20) made by each of three sensors deployed in separate test cells at four reference nitrate concentrations (1, 3, 6, and 12 mg/L nitrate-N), as described in Section B1.1.1. Variability will be equated to drift and expressed as percentage change in concentration as a function of time compared to the reference concentrations.

B1.1.3.3 – Duplication

The degree of agreement of nitrate concentrations reported simultaneously using duplicate nitrate sensors will be assessed in the laboratory in the two test cells. As discussed in Section B1.1.1, the first test cell will house two nitrate sensors to evaluate intra-well duplication within the test cell, whereas the second test cell will house one nitrate sensor to evaluate inter-well duplication between the two test cells. The three nitrate sensors will be synchronized and programmed to record nitrate concentrations at one minute intervals throughout Phase 1 and Phase 2 of the laboratory test to allow direct comparison of nitrate concentration data.

B.1.1.3.4 – Effect of Changes in Water Quality

The effect of water quality (i.e., interference parameters) on nitrate sensor response to nitrate concentrations will be evaluated in Phase 1 and Phase 2 of the laboratory testing by exposing nitrate sensors to constant nitrate concentrations under different water quality conditions. The proposed laboratory testing schedule is described in Section B1.1.1 and summarized in Table 2. In Phase 1 of the laboratory test, nitrate concentration readings under ambient water quality conditions will be evaluated to formulate a baseline for comparison to the effects of changes in water quality due to the introduction of interference parameters (e.g., varying concentrations of nitrate, chloride, and turbidity). In Phase 2 of the laboratory test, three different constant nitrate concentrations will be used (1, 3, and 12 mg/L nitrate-N), spanning the range of suspected field concentrations. For each nitrate concentration, water quality will be modified as follows: chloride will be spiked at 100, 500, and 2,500 mg/L; nitrite will be spiked at 1, 2, and 4 mg/L nitrate-N; and turbidity will be spiked at 1 and 5 NTU. The ability of the nitrate sensors to accurately measure nitrate concentrations will be evaluated under each of these 24 different scenarios.

B1.1.3.5 – Operational Factors

Operational factors associated with use of the nitrate sensors will be evaluated based on the comments and observations of all users (Battelle and USDA) in the laboratory and field testing. Such observations may address the convenience of the nitrate sensors, the completeness of nitrate sensor readings (percent data collected), their reliability under differing conditions, the apparent consistency of nitrate sensor readings, and acceptability as a groundwater monitoring tool. Observations also will include any noted biofouling during (if sensors are to be inspected periodically) and at the end of the field testing period. In addition, data dissemination also will be evaluated, such as ease of data transmission, timeliness of data dissemination, ease of data downloading, and usability of downloaded data. In particular the observations of Battelle and USDA users will be important, as those users are likely to be the relatively non-technically trained users for which the nitrate sensors are designed. Cost for the nitrate sensor and associated data transmission equipment also will be reported.

B1.2 Statistical Analysis

Statistical comparisons will be made between nitrate concentrations measured using the nitrate sensor and those measured in the laboratory using EPA Method 300.1 from analysis of samples collected using the conventional groundwater sampling technique. It is assumed that the nitrate

concentration value represents the actual or target nitrate concentration present in the well against which the nitrate sensor concentration will be evaluated. The planned statistical comparisons are described in the following subsections.

B.1.2.1 – Accuracy

The accuracy of the nitrate sensor concentrations with respect to the laboratory measured concentrations will be assessed graphically and by evaluating the differences between paired concentrations (concentration residuals) from measurements collected simultaneously at the same location. The nitrate sensor concentration reading collected closest in time associated with the collection of the conventional monitoring sample will be used for paired comparison. Two statistical measurements will be used to assess the accuracy: (1) inference about the mean difference, and (2) estimation of the mean absolute error (MAE). The inference about the observed difference will include estimation of the mean difference and a statistical hypothesis about whether the mean difference is equal to or different from zero (using either a paired-sample t-test or a nonparametric equivalent). If the hypothesis test determines that there is a difference in two measurement methods, the estimated average difference will be used as an estimate of the *bias* for the nitrate sensors. The MAE will be calculated for the concentration differences as follows:

$$MAE = \frac{1}{\mathrm{n}}\sum_{\mathrm{j}=1}^{\mathrm{n}} |\text{laboratory concentration}_{\mathrm{j}} - \text{nitrate sensor concentration}_{\mathrm{j}}|$$

where *n* is the number of paired nitrate concentration measurements. The MAE will be used to represent the average absolute difference in the two measurement methods.

The accuracy estimates will be calculated separately for Phase 1 and Phase 2 of the laboratory evaluation and for the field evaluation. In addition, comprehensive accuracy estimates will be calculated using all of the paired data sets from the field and laboratory evaluation.

B1.2.2 – Variability of Readings

Variability of the nitrate sensor concentration readings will be evaluated using data from Phase 1 of the laboratory evaluation using the multiple readings (20) made by each of three sensors deployed in separate test cells at four reference nitrate concentrations (1, 3, 6, and 12 mg/L nitrate-N). Variability will be expressed as the standard deviation of the sensor concentration

readings calculated two ways: (1) using the reference concentrations as the average (mean) values for comparison, and (2) using the measured mean concentrations from the samples. Standard deviation values will be calculated for each of the four reference concentrations.

B1.2.3 – Duplication

The degree of agreement of nitrate concentrations reported simultaneously using duplicate nitrate sensors will be assessed in the laboratory evaluation. The first test cell will house two nitrate sensors to evaluate intra-well duplication within the test cell, whereas the second test cell will house one nitrate sensor to evaluate inter-well duplication between the two test cells. The degree of agreement between each pair of reported nitrate concentrations (inter-well and intra-well) will be assessed by calculating the intra-well mean square error (MSE) and inter-well MSE using a random-effects analysis-of-variance (ANOVA) model.

B1.2.4 – Effect of Changes in Water Quality

The effect of changes in water quality on nitrate sensor performance will be assessed using the data from Phase 2 of the laboratory evaluation (see Section B1.1.1) by calculating the accuracy, variability, and nitrate sensor duplication of readings (Sections B1.2.1 through B1.2.3) of the test data at each of the water quality conditions outlined in Table 2. Those results will be compared to indicate whether changes in nitrate, turbidity, and chloride concentrations have any apparent effect on the nitrate sensor performance at constant nitrate concentrations. Accuracy or variability results that differ by more than 5% or nitrate sensor duplication results that differ by more than 20% will be taken as evidence of a significant water quality effect, and will be thoroughly documented in the verification report.

B1.3 Reporting

The statistical comparisons described above will be conducted for the nitrate concentrations collected in the field and/or laboratory using the nitrate sensor and conventional groundwater monitoring, and user comments on the operational factors will be compiled and reported. A verification report will be prepared for the nitrate sensor that presents the test procedures and test data, as well as the results of the statistical evaluation of those data.

Operational aspects of the nitrate sensors will be recorded by testing staff at the time of use, and summarized in the verification report. The verification report will briefly describe the ETV program, the AMS Center, the test equipment and test conditions, and the procedures used in

verification testing. The results of the verification test will be stated quantitatively, without comment on the acceptability of the technology's performance. The draft verification report will first be subjected to review by the technology vendor, USDA, and NJDEP, and then revised and subjected to a review by EPA and/or other peer reviewers. The EPA comments and the peer review comments will be addressed in further revisions of the report, and the comments and responses will be tabulated to document the peer review process. The reporting and review process will be conducted according to the requirements of the AMS Center QMP.[1]

B2 REFERENCE SAMPLE COLLECTION

Reference sample collection in this verification test consists of laboratory analysis of water samples collected using a peristaltic pump in the laboratory test (see Section B1.1.1), and groundwater samples collected using a peristaltic pump during the field verification test (see Section B1.1.2.2 and Appendix A). These reference samples will then be compared with the corresponding readings collected concurrently with the nitrate sensors. In addition, the nitrate sensors will be calibrated against reference solutions prior to deployment in the laboratory and in the field as described in Section B7 and documented in Appendix D. The procedures and records of reference method calibrations will be reviewed for both laboratory and field testing as part of the TSA (Section C1.1).

B3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

For all samples collected by means of conventional groundwater sampling methods during the verification test, sample custody will be documented throughout collection, transport, shipping (if necessary), and analysis of the samples on standard forms used by the USDA ARS National Laboratory or forms provided by Battelle. Field activity logs (Appendix B), field sampling form data sheets (Appendix C), and sample custody forms (Appendix C) will be filled in by USDA and Battelle representatives. USDA ARS National Laboratory representatives conducting the laboratory portion will document sample custody from collection to analysis using the field sampling form data sheets (Appendix C). Copies of all data sheets will be retained by the respective organization that conducted the sampling and analysis, and the originals will be sent to Battelle by tracked shipment (FedEx or similar) for compilation of the data.

Real-time data collected with the nitrate sensors will be transmitted to a laptop located on the Iowa State University campus. The laptop will transmit the data to a password protected Internet

site via phone lines where it will be downloaded by the project team. All field data captured by the sensors, including any calibrations performed in the field, will be exported to a usable format and sent to Battelle by tracked shipment for compilation of the data.

B4 REFERENCE METHOD

All conventional groundwater samples collected will be analyzed following the laboratory reference method, ”Determination of Inorganic Anions by Ion Chromatography” (EPA Method 300.1) for determination of nitrate in the collected groundwater. Samples will be collected with adequate volume (125 mL) in glass or plastic containers that have been rinsed with DI water, preserved by refrigeration to 4°C ± 2°C and analyzed within 48 hours of collection. The collection of the samples will be the responsibility of USDA and Battelle staff. In laboratory analysis a Dionex ICS-2000 Reagent-Free Ion Chromatography (RFIC) System will be operated by USDA National Laboratory staff according to instrument procedures (Appendix E) and the manufacturers’ instructions, including those for warm-up and stabilization time before testing. The USDA Laboratory is responsible for coordinating the analysis of the samples with associated QA/QC. Calibration and maintenance documentation for the Dionex ICS-2000, and all results of the reference analyses will be provided to Battelle. A laboratory audit will be performed by the NJDEP according to guidelines provided by the National Environmental Laboratory Accreditation Conference (NELAC) Institute.

B5 QUALITY CONTROL REQUIREMENTS

Steps will be taken to maintain the quality of data collected during this verification test. The reference laboratory will follow their standard QA/QC protocols for analysis of quality control samples (QCSs) with each set of samples analyzed. QCSs producing results not meeting the laboratory’s standard requirements will be reanalyzed. If the results are still outside the required tolerance, the reference instrument will be recalibrated and the samples reanalyzed. If the outlying results persist, the affected data will be flagged and a repeat of the affected parts of the verification test may be considered. Sample results not meeting these requirements will be flagged and excluded from comparison to the nitrate sensor results.

During groundwater sampling activities, QC samples, including field duplicates, matrix spike/matrix spike duplicates (MS/MSD), and equipment blanks, will be collected to ensure the reliability of data. Duplicate groundwater samples will be collected at a frequency of one for

every 10 samples (i.e., 10%) to evaluate the reproducibility of analytical results. MS/MSD samples are used by the laboratory to evaluate the accuracy of its methods and equipment, and will be collected at a frequency of one for every 20 samples (i.e., 5%). Equipment blanks, also referred to as rinsate blanks, are collected to evaluate the potential for sample cross-contamination from the sampling equipment used. Equipment rinsate blanks will be collected daily, during sampling, for the groundwater sampling equipment to ensure that nondedicated sampling devices have been decontaminated effectively. A complete description of groundwater sampling QC samples is provided in Appendix A.

Quality of the laboratory reference nitrate (and nitrite) measurements will be ensured by a calibration of the Dionex ICS-2000 RFIC before any testing. A pre-testing calibration curve is prepared for each analytical run; the curve is expected to be linear with the coefficient of determination (R^2) greater than or equal to 0.995 before proceeding with analysis. Calibration is verified throughout the analytical run by inserting calibration check standards and reagent blanks with every set of 10 samples. The calibration and all verifications are incorporated into the run alongside the samples and visually evaluated by the instrument operator to meet the reference laboratory's QC criteria. The results of the analytical runs are copied into Microsoft® Excel files and the original files are retained at the laboratory work station. A complete description of the USDA National Laboratory's current Dionex ICS-2000 RFIC analytical procedures including equipment, standards, reagents, and calibration is included in Appendix E. Standard reference materials (SRMs) from the National Institute for Standards and Technology (NIST) shall be included as part of the regime to ensure laboratory testing. A minimum of 10% of samples shall be NIST SRMs with concentrations within the operational or working range of the test regime.

B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

The nitrate sensors used in the verification test will be tested, inspected, maintained, and calibrated prior to deployment by the technology vendor according to manufacturer specifications so as to meet the QC requirements stated in Section B5. Sample documentation for implementation of a nitrate sensor is included as Appendix D. The Dionex ICS-2000 system used to perform the laboratory nitrate analysis also will be tested, inspected, maintained, and calibrated so as to meet the QC requirements stated in Section B5. The Dionex ICS-2000 system analytical procedures are included as Appendix E. Other equipment, such as the water-level and

flow monitoring instruments, will be obtained from the Battelle Instrument Services Laboratory or the USDA laboratory and will have been inspected and calibrated within the past year.

B7 INSTRUMENT CALIBRATION AND FREQUENCY

The nitrate sensors will initially be calibrated prior to the laboratory test, and recalibrated between the laboratory and the field evaluation by the vendor (see Appendix D). No calibration verification is anticipated for the nitrate sensors during the evaluation; however, if calibration becomes necessary, the vendor will be consulted and the procedure will be thoroughly documented.

The instrumentation used by the reference laboratory for the reference analyses will be calibrated per the USDA procedures (Appendix E). Documentation of the instrument calibration, standard solutions and maintenance will be provided to Battelle. Other instrumentation used in this verification test, such as a multi-parameter water probe and balances, will have been calibrated within the 12 months prior to this verification test and documentation of the calibration provided to Battelle. If possible, the calibration will be verified immediately prior to use in this verification test.

B8 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

All materials, supplies, and consumables will be ordered by the Verification Test Coordinator or designee. Where possible, Battelle will rely on sources of materials and consumables that have been used previously as part of ETV verification testing without problems.

B9 NON-DIRECT MEASUREMENTS

Data published previously in the scientific literature will not be used to evaluate the vendor's technology during this verification test.

B10 DATA MANAGEMENT

Various types of data will be acquired and recorded electronically or manually by Battelle, USDA, and the technology vendor during this verification test. Table 5 summarizes the types of data to be recorded, how and by whom the data will be recorded, and how the data will be treated or used. Preprinted data sheets (Appendix B and C) will be used by USDA or Battelle staff to

Table 5. Summary of Data Recording Process

Data to Be Recorded	Where Recorded	How Often Recorded	Disposition of Data
Conventional field groundwater sampling data – groundwater-level elevations, purge volume, sample collection, inlet flow rates and field observations	Field activities log (Appendix B) Field sampling form (Appendix C)	Weekly for duration of field verification test (2 months); hourly for 2 days at beginning and 2 days at end of field test - each sampling event	Incorporated in verification report as necessary
Laboratory nitrate analyses data	Laboratory data sheets or recorded electronically by USDA	Each analysis	Converted to spreadsheet for statistical analysis and comparisons
Laboratory nitrite analyses data	Laboratory data sheets or recorded electronically by USDA	Each analysis (if above 1 mg/L for consecutive events)	Converted to spreadsheet for statistical analysis and comparisons (if above 1 mg/L for consecutive events)
Laboratory QA results	Laboratory data sheets or recorded electronically by USDA	Each analysis	Incorporated in verification report as necessary
Nitrate sensor readings - field	Data uploaded to laptop	Every 15 minutes for 2 months	Converted to spreadsheet for statistical analysis and comparisons
Sensor readings of temperature, water level, specific conductance	Data uploaded to laptop	Every 15 minutes for 2 months	Data retained but not to be used in comparative analysis for this verification
Nitrate sensor readings – laboratory test cell data	Data uploaded to laptop	Every 15 minutes for duration of test (~2 days)	Converted to spreadsheets for statistical analysis and comparisons
Conventional sampling - laboratory	Laboratory data sheets or recorded electronically by USDA	Periodically according to schedule in Table 2	Converted to spreadsheets for statistical analysis and comparisons
Laboratory conventional sampling QA results	Laboratory data sheets or recorded electronically by USDA	Coincide with laboratory conventional sampling	Incorporated in verification report as necessary

record sampling activities and observations in the field. All observations relevant to the laboratory testing of the nitrate sensor will be documented by USDA laboratory staff either electronically or in LRBs. Monitoring data from the field sensors will be transmitted in electronic format and made usable by windows-based software. If possible, it will be requested

that the files be provided to Battelle. The secondary probes connected to the nitrate sensor will be collecting data that will be recorded (such as water level and specific conductance); however, these readings will be supplementary and will not be verified in this evaluation.

All appropriate Battelle and USDA LRBs, record books and files will be forwarded (if necessary) to Battelle for permanent storage, either by the Verification Test Coordinator or Battelle's Records Management Office. EPA will be notified before disposal of any files. Battelle will provide technology test data and associated reference data (including records; data sheets; notebook records) from the first day of testing within one day of receipt to EPA for simultaneous review. The goal of this data delivery schedule is prompt identification and resolution of any data collection or recording issues. During the two-month field deployment, reference data from USDA will be sent on a weekly basis to the Battelle Verification Test Coordinator. Sensor data will be immediately available via an ftp site to the entire project team.

Records generated by any Battelle staff during the verification test will be reviewed by a Battelle staff member within two weeks of generation, before the records are used to calculate, evaluate, or report verification results. This review will be performed by a Battelle technical staff member involved in the verification test, but not the staff member who 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. Data entered from hard copy records into spreadsheets will be reviewed in hard copy within the two-week window. Spreadsheet entries will be checked as part of the ADQ (Section C1.3). In addition, any calculations performed by Battelle staff will be spot-checked by another Battelle technical staff member to ensure that calculations are performed correctly.

Field data sheets filled out by USDA, the technology vendor, or Battelle representatives will be reviewed by the lead USDA, technology vendor, or Battelle representative for completeness and consistency within one week after they are filled out. USDA will then retain copies of their respective data sheets and send the originals to Battelle. The Battelle Verification Test Coordinator will review all such data sheets immediately upon receipt. Any corrections needed in the forms will be implemented immediately, with consultation with the Battelle Quality Manager, as needed.

In addition to the Battelle Verification Test Coordinator performing a 100% data review and EPA's review of the first day's data, an audit of data quality will be conducted. This audit will consist of a review by the Battelle Quality Manager of at least 10% of the test data. During the course of any such audit, the Battelle Quality Manager will inform the technical staff of any findings and any immediate corrective action that should be taken. If serious data quality problems exist, the Battelle Quality Manager will notify the 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.

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 this test/QA plan is to establish mechanisms necessary to ensure this. The procedures 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 has 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. Independent of any EPA QA activities, Battelle will be responsible for ensuring that the audits described below are conducted as part of this verification test.

C1.1 Technical Systems Audits

An auditor from the NJDEP OQA will perform a TSA once during this verification test, in both the laboratory and field testing locations. The laboratory audit will be performed by the NJDEP according to guidelines provided by the NELAC Institute. 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, and the published reference method. In the TSA, the NJDEP QA auditor may review the reference method used, compare actual test procedures to those specified or referenced in this plan, and review data acquisition and handling procedures. In the laboratory, the NJDEP QA auditor may inspect the simulated test cells and test procedures, and view data records. This person also will check calibration certifications for test measurement devices. In the field the NJDEP QA auditor may inspect USDA site QA records, observe USDA sampling and analysis procedures, and review data records. The Battelle Quality Assurance Manager will communicate ETV specific QA requirements to the NJDEP QA auditor prior to the TSA. A TSA checklist will be prepared by the NJDEP QA auditor which will be reviewed and approved

by the Battelle and EPA Quality Managers prior to use in the TSA. A TSA report will be prepared by NJDEP, including a statement of findings and the actions taken to address any adverse findings. The NJDEP QA auditor will submit the audit report, 10 business days following the TSA, to the Battelle Verification Test Coordinator and the Battelle Quality Assurance Manager, who will distribute the report to the EPA. At EPA's discretion, EPA QA staff may also conduct an independent 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.

C1.2 Performance Evaluation Audit

A PE audit of the nitrate concentrations will be completed to confirm the accuracy of the laboratory nitrate analysis reference method (EPA 300.1). The PE audit will be performed by the Verification Test Coordinator, or designee. Prior to the laboratory and field investigations, up to five blind nitrate samples will be generated from a stock solution in the laboratory and sent to the USDA ARS National Laboratory for Agriculture and the Environment. The blind nitrate sample concentrations will be within the range of anticipated field concentrations. The associated reported laboratory nitrate concentration values will be verified against the blind sample concentrations to determine whether the concentration values are within an acceptable range. Results of the PE audit samples will be compiled by the Verification Test Coordinator and reviewed by the Battelle Quality Manager who will provide a copy to EPA within 10 business days of receipt of the laboratory report.

C1.3 Audit of Data Quality

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 spreadsheet entry, reduction and statistical comparisons, to final reporting. All QC data and all calculations performed on the data undergoing the audit will be checked. Results of the ADQ will be compiled and reviewed by the Battelle Quality Manager who will discuss findings in a written report distributed to the Verification Test Coordinator and EPA within 10 business days after completion of the laboratory report review.

C1.4 QA/QC Reporting

Each assessment and audit will be documented in accordance with Sections 3.3.4 and 3.3.5 of the AMS Center QMP.[1] The results of all audits will be submitted to EPA within 10 business days as noted above. 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

During the field and laboratory evaluation, any test/QA plan deviations will be reported immediately to EPA. The Battelle Quality Manager and/or Verification Test Coordinator, 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. A summary of the required assessments and audits, including a listing of responsibilities and reporting timeframes, is included in Table 6. If serious quality problems exist, the Battelle Quality Manager will notify the AMS Center Manager, who is authorized to stop work. Once the assessment reports have 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 EPA AMS Center program management staff. Upon final review and approval, both documents will then be posted on the ETV Web site (www.epa.gov/etv).

Table 6. Summary of Reports to Management

Assessment	Responsible Agency	Report Submission Timeframe	Receiving Agency
TSA	NJDEP OQA	10 business days after TSA is complete	Initially to Battelle VTC and subsequently to EPA
PE Audit	Battelle	10 business days after receipt of laboratory report	Initially to Battelle VTC and subsequently to EPA
ADQ	Battelle	10 business days after completion of the laboratory report review	Initially to Battelle VTC and subsequently to EPA

SECTION D

DATA VALIDATION AND USABILITY

D1 DATA REVIEW, VALIDATION, AND VERIFICATION REQUIREMENTS

The key data review requirements for the verification test are stated in Section B10 of this test/QA plan. The QA audits described in Section C1 of this document, including the audit of data quality, are designed to ensure the quality of the data. Data will be verified for completeness, correctness, and compliance with the procedures as written in this test/QA plan.

D2 VALIDATION AND VERIFICATION METHODS

Section C of this test/QA plan provided a description of the validation safeguards employed for this verification test. Data validation and verification efforts include the use of a Dionex ICS-2000, and the performance of TSA and data audits. An audit of data quality will be conducted by the Battelle Quality Manager to ensure that data review and validation procedures were completed, and to ensure the overall quality of the data. Any findings will be communicated to technical staff at the time of the audit and documented in a report.

D3 RECONCILIATION WITH USER REQUIREMENTS

The purpose of this test is to evaluate the performance of nitrate sensors. The data obtained should include thorough documentation to allow verification of the performance of each nitrate sensor. The data review and validation procedures described in the previous sections will ensure that data meet these requirements and are accurately presented in the evaluation reports generated from this test. Data for which incomplete recording cannot be resolved will be retained but will be flagged and not used for nitrate sensor verification.

This test/QA plan and the resulting ETV verification report(s) will be subjected to review by the technology vendors, USDA and EPA, and expert peer reviewers. These reviews will ensure that this test/QA plan and the resulting report(s) meet the needs of potential users of nitrate sensors. The final report(s) will be submitted to EPA in Microsoft® Word and Adobe PDF compliant format and subsequently posted on the ETV Web site.

SECTION E

REFERENCES

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Appendix A

Conventional Groundwater Sampling Procedures

Battelle

Environmental Restoration Department

GROUNDWATER PURGING AND SAMPLING PROCEDURES USING A PERISTALTIC PUMP

1.0 PURPOSE AND SCOPE

The purpose of this document is to define the equipment necessary and the standard operating procedure (SOP) for collecting groundwater samples using a peristaltic pump. This SOP describes the equipment, field procedures, materials, and documentation procedures necessary to collect groundwater samples. This SOP also contains information pertaining to the handling of groundwater samples, decontamination procedures to be completed during groundwater sampling, and procedures for the management of investigation-derived waste generated during this activity.

This procedure is to be followed during the ETV nitrate sensor evaluation field investigation, and any substantive modification to the procedure shall be approved in advance by the Field Team Leader(s), the Battelle Quality Manager and/or the Verification Test Coordinator, with subsequent notification of significant deviations to EPA.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Verification Test Coordinator is responsible for assigning appropriately-qualified field personnel for conducting the various activities to be completed at the site. The Verification Test Coordinator and Field Team Leader(s) is (are) also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for documenting and reporting deviations from the procedure or nonconformance to the Field Team Leader(s). Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on training, documented previous experience and health and safety training.

3.0 GROUNDWATER SAMPLING PROCEDURES

Groundwater samples will be collected from the bioreactor monitoring wells and from the inlet pipeline using a peristaltic pump. The following subsections document the procedures associated with groundwater sample collection using a peristaltic pump.

3.1 EQUIPMENT LIST

The following equipment list contains materials that may be needed to carry out the procedures contained in this portion of the SOP. Since multiple discrete activities are described in this SOP, not all materials on the equipment list may be required for each activity. Equipment used during groundwater sample collection includes the following:

- Appropriate Level D health and safety equipment (i.e., nitrile gloves and safety glasses)
- Permanent marker or grease pencil
- 5-gallon buckets
- Field logbook
- Appropriate decontamination equipment (i.e., DI water, Alconox®, and trash bags)
- Electronic water level indicator
- Peristaltic pump(s) (Geotech Series II Geopump variable rate peristaltic pump, or similar)
- Silicone tubing
- Teflon™-lined polyethylene tubing
- Polypropylene twine
- Laboratory-provided sample plastic ware or certified pre-cleaned plastic ware
- Coolers, ice, ice chests, and/or refrigerated storage unit

3.3 WATER LEVEL MEASUREMENT PROCEDURES

To provide information on groundwater flow and water levels within the bioreactor, depth to groundwater data will be collected from the monitoring wells and the inlet pipeline. The following steps will be followed to measure the depth to ground water in a monitoring well:

(1) Remove the flushmount lid or the lid to the stickup well casing.

(2) Remove the compression cap. Listen for signs of vapor lock, which can cause the groundwater surface to fluctuate until it achieves equilibrium with the atmosphere.

(3) Insert the probe of an electronic water level indicator equipped with a graduated tape.

(4) When the indicator signals contact with groundwater, the depth to groundwater will be recorded to the nearest 0.01 foot relative to the vertical survey datum assigned to the well (i.e., the top of casing or ground surface).

(5) If the contact signal fluctuates in a manner indicating that the groundwater surface is still rising in the well, the reading will not be recorded until the groundwater surface stabilizes.

3.4 GROUNDWATER PURGING AND SAMPLE COLLECTION

This section provides the step-by-step procedures for collecting groundwater samples from the monitoring wells. Observations made during groundwater sample collection should be recorded in the field logbook.

3.4.1 Purging

Prior to collecting groundwater sample volume from a monitoring well, a minimum volume of groundwater will be purged to ensure the collection of a representative sample. The following procedures will be followed to purge a monitoring well:

(1) Fresh silicone tubing will be installed in a peristaltic pump.

(2) The cap will be removed from the dedicated in-well Teflon™-lined polyethylene tubing.

(3) The dedicated in-well polyethylene tubing will be connected to the inlet end of the peristaltic pump, and an additional length of polyethylene tubing will be connected to the outlet end of the pump.

(4) The outlet tubing from the peristaltic pump will be routed to a 5-gallon bucket placed on a firm and level surface.

(5) The peristaltic pump will be engaged at a minimum sustained operation level and groundwater will be purged from the well equivalent to one polyethylene tubing purge volume (based on the depth to groundwater reading)

(6) The purge water will be consolidated as investigation-derived waste and decanted to ground surface outside of the bioreactor.

3.4.2 Groundwater Sampling

Once purging has been completed, groundwater sampling will be completed as follows:

(1) A “dirty hands”/ “clean hands” approach will be followed during actual sampling as outlined in U.S. EPA Method 1669 where all operations involving contact with the sample bottles and transfer of the sample from the sample collection device to the sample bottle are handled by the individual designated as “clean hands.” “Dirty hands” is responsible for preparation of the sampler (except the sample container itself) and for all other activities that do not involve direct contact with the sample.

(2) For all analyses the peristaltic pump will remain engaged and laboratory plastic ware will be filled directly through the pump.

(3) Groundwater retrieved will be slowly added to the appropriate sample plastic ware, taking care to avoid agitation and air bubbles.

(4) For each analyte, two sample containers will be filled per laboratory requirements and preserved as/if necessary.

(5) Samples will be stored on ice in sealed coolers or chests, and/or in a refrigerated storage container, and checked for preservation temperature of 4ºC, pending same-day delivery to the USDA laboratory.

4.0 SAMPLE HANDLING PROCEDURES

This section defines the procedures for labeling, containerizing, handling and shipping groundwater samples collected for analysis. These steps are essential, and could affect tracking, documentation, or integrity of samples. These procedures are intended to provide sufficient instructions for sampling personnel to follow equally, reliably, and consistently.

4.1 EQUIPMENT LIST

The following equipment list contains materials that may be needed to carry out the procedures contained in this portion of the SOP:

- Inert packing material
- Sample containers
- Sample labels
- Chain-of-Custody Forms
- Ice chest(s)/coolers
- Marking pens
- Shipping tape
- Sealable plastic bags
- Field logbook
- Ice or similar chilling source
- Paper towels or cloth.

4.2 SAMPLE LABELING

Each bottle used for sampling will have a preprinted label attached that is identical to the example label shown below. Whenever possible, field personnel will have the project identification, requested analyses and sample identification typed/printed onto the label before sampling. The date and time will be added at the time of sample collection. Where necessary, the label will be protected from damage with clear tape.

Nitrate Sensor ETV Study	
Sample ID:	
Date:	Time:
Analyses:	

Each field-collected sample will be assigned a unique sample ID that is documented on the sample container label and the field collection log form. This system provides a distinct link between the sample and the related collection information. Sample identification numbers will be in the format:

X-DDMM-TTTT

where,

DDMM is the date (day/month)
TTTT is the time (24-hour)
X is the sample location, where:

1	Well 1
2a	Well 2 – upper screen
2b	Well 2 – lower screen
3	Well 3
IN	Test cell inlet

4.3 SAMPLE CONTAINERS AND PRESERVATION

4.3.1 Sample Containers

Certified, pre-cleaned containers will be supplied from commercial suppliers or laboratories for the collection of all groundwater samples. Sample containers will be cleaned to the quality control standard defined in OSWER Directive #9240.0-05A. Certification of sample container quality per the OSWER directive will be kept in the project files. Two 125 mL poly containers will be filled for each sampling location.

4.3.2 Sample Preservation

No sample preservatives will be added, nor will any sample filtering be required during this investigation. Samples will be placed on ice after collection, and shipping containers will be packed with additional ice, if needed, prior to shipment via overnight carrier.

4.4 SAMPLE PACKAGING AND SHIPPING

Sample packaging and shipping will be performed as follows:

(1) After filling, securely seal sample bottle caps and complete the sample labels (if labels were not preprinted).

(2) Clean the outside of the samples bottles by wiping them off with a cloth or paper towel.

(3) Transfer the samples to an ice chest that will be used as a shipping container. For samples leaving the Site, use inert packaging material to cushion the samples and minimize the potential for breakage.

(4) If refrigeration is necessary, ice chests or coolers will contain ice or similar chilling sources sufficient to maintain 4º ± 2°C inside cooler during same-day transport to the laboratory.

(5) Complete chain-of-custody (COC) documentation, and place appropriate copies of the documents in a sealable plastic bag inside the ice chest (taped to the inside lid). Prior to sealing for shipment, the list of samples will be checked against the cooler/chest contents to verify the presence of each sample listed on the chain-of-custody.

(6) Transport the shipping container directly to the laboratory. Samples will be shipped within an appropriate timeframe after collection to ensure meeting all relevant sample and laboratory holding times.

4.5 SAMPLE TRACKING

All samples collected for analysis will be continuously tracked, in the field and in transit to the laboratory as follows:

(1) Individual sample bottles will be properly labeled and securely sealed before being placed in the container for shipment to the laboratory.

(2) All pertinent information will be entered on the COC form in the field (see Appendix C). COC forms must include the following, as required by guidance in SW-846, Test Methods for Evaluating Solid Waste (EPA, Third Edition, including Promulgated Update I, 1993, Chapter One): 1) the project name; 2) signatures of samplers; 3) the sample number, date and time of collection, preservatives, analyses to be performed, and grab or composite sample designation; and 4) signatures of individuals involved in sample transfer.

(3) The completed COC form will be signed, dated, enclosed in a sealable plastic bag and placed in the container prior to shipment (taped to the inside lid). A copy of the COC form will be retained by field personnel and an additional copy transmitted to the Verification Test Coordinator or the Verification Test Coordinator's designee.

(4) Samples will be considered in the sampler's custody while in sight, or locked in a secure area prior to delivery. If the person packing the container and verifying the sample list is different than the sampler, both the sampler and the packer will sign the COC form.

(5) Upon receipt at the laboratory, the designated laboratory sample custodian shall sign the COC form indicating receipt of the incoming field samples. The samples shall be checked against the COC form upon arrival at the laboratory. The receiving personnel will enter all arriving samples into a laboratory logbook and note any

problems or discrepancies between the samples and COC forms and sample container and seal conditions and report them immediately to the Verification Test Coordinator.

(6) A copy of the COC form shall be returned from the laboratory to the Verification Test Coordinator or the Verification Test Coordinator's designee. The original shall be retained by the laboratory's sample custodian.

5.0 DECONTAMINATION PROCEDURES

This section defines the procedures for cleaning reusable groundwater sampling equipment sufficiently to ensure that cross-contamination of samples does not occur. These steps are essential, and could affect the integrity of site sampling data. These procedures are intended to provide sufficient instructions for sampling personnel to follow equally, reliably, and consistently.

Throughout sample collection activities, care will be taken to avoid sample contamination. This will be accomplished through rigorous decontamination procedures and careful sample handling procedures, as follows:

(1) To the extent possible, non-contaminating materials (e.g., glass, stainless steel or Teflon™) will be used for groundwater sampling activities.

(2) All potential sources of contamination (e.g., airborne sources, personnel, or unclean equipment) will be avoided.

(3) To avoid cross-contamination in groundwater samples collected for chemical analysis, separate, pre-cleaned or new Teflon™-lined polyethylene tubing, silicone tubing and bailers will be used at each sampling location.

(4) The electronic water level indicator will be decontaminated by spraying the probe with a solution of water and non-phosphate detergent, followed by spraying with deionized water.

(5) If possible, gasoline or diesel engine powered equipment will be shut down at least one minute prior to sampling activities to eliminate the potential for contamination by exhaust gasses. If this is not possible, samples will be processed up-wind of the engines and care will be taken to avoid contamination from engine exhaust.

During all groundwater sampling and handling activities, field personnel will don appropriate personal protection equipment (PPE) (Level D) to avoid contact with potential contamination and also to avoid cross-contaminating samples. PPE will be changed as necessary to ensure that cross-contamination potential is minimized.

6.0 INVESTIGATION-DERIVED WASTE PROCEDURES

Implementation of groundwater sampling activities is expected to generate some amount of investigation-derived waste (IDW). Field sampling and sample preparation activities will be

conducted such as to minimize generation of waste materials (i.e., residual groundwater). In the field, trace amounts of residual groundwater from sampling equipment will be temporarily stored in 5-gallon buckets and decanted to ground outside the bioreactor footprint. All general solid waste (gloves, paper towels, used tubing, etc…) will be bagged or otherwise contained prior to disposal in standard refuse containers (dumpsters). Solid waste and wastewater generated during sample preparation at each laboratory will be managed in compliance with the organization's requirements.

7.0 FIELD QUALITY CONTROL

During groundwater sampling activities, QC samples will be collected to ensure the reliability of data.

7.1 FIELD DUPLICATES

Duplicate groundwater samples will be collected at a frequency of one for every 10 samples (i.e., 10%) for all analytes to evaluate the reproducibility of analytical results. If 10 samples are not collected during a sampling event, one duplicate sample per sampling event will be collected. Duplicate samples will be collected simultaneously with the base sample, and will be collected into identical sample plastic ware. Laboratory plastic ware for a particular analyte will be filled in alternating sequence between base sample and duplicate. Duplicate samples will be identified as "DUP" on the sample label.

7.2 MATRIX SPIKE/MATRIX SPIKE DUPLICATES

Matrix Spike/Matrix Spike Duplicate (MS/MSD) samples are used by the laboratory to evaluate the accuracy of its methods and equipment. MS/MSD samples will be collected at a frequency of one for every 20 samples (i.e., 5%). If 20 samples are not collected during a sampling event, one MS/MSD sample per sampling event will be collected. These samples typically require the collection of triplicate sample volume (i.e., one volume for base sample, one volume for MS and one volume for MSD), and will be collected into identical sample plastic ware as the base sample. MS/MSD samples are labeled identically for all volume collected, and will be properly identified as being a QC sample on the COC. No spiking of the MS/MSD will occur in the field.

7.3 EQUIPMENT BLANKS

Equipment blanks, also referred to as rinsate blanks, are collected to evaluate the potential for sample cross-contamination from the sampling equipment used. Equipment rinsate blanks will be collected daily, during sampling, for the groundwater sampling equipment to ensure that nondedicated sampling devices have been decontaminated effectively. Daily equipment blanks will be collected after collection of at least one field sample and after the equipment has been decontaminated. The equipment blank for groundwater sampling equipment will be laboratory-provided deionized water that is passed through or over the sampling equipment used to collect

samples (i.e., Teflon™ polyethylene tubing). Each equipment blank will be assigned a unique field sample identification number, and analyzed for nitrate.

8.0 DOCUMENTATION

8.1 FIELD NOTES

The Field Team Leader(s) or the Field Team Leader(s)' designee(s) is (are) responsible for documenting groundwater sampling and sample handling activities. Observations and data will be recorded on the Field Data Sheet (see Appendix C) and stored in the project notebook.

8.2 CHAIN-OF-CUSTODY DOCUMENTATION

All samples will be handled under strict chain-of-custody. COC forms will be provided by the selected analytical laboratory or will be Battelle's standard COC. Information to be included on the COC forms, and the procedures for tracking samples through the COC process, are included in the "Sample Tracking" section above.

Approvals

Author: _____ Date: _____

Verification Test Coordinator: _____ Date: _____

Battelle Quality Manager: _____ Date: _____

Appendix B

Field Activities Log

Battelle

ETV NITRATE SENSOR STUDY
FIELD ACTIVITIES LOG

Recorder:	Date:	Page ___ of ___
Personnel Present:	Weather:	

Time (00:00)	Activity

Appendix C

Field Sampling and Example Chain of Custody Forms

Battelle

ETV NITRATE SENSOR STUDY
FIELD SAMPLING FORM

Location:		Personnel:
Date:		
Well ID:		Weather:
Start Time:	End Time:	Time Sample Collected:
Depth to Water (ft):		Sample Inlet Depth (ft):
Volume Purged (mL):		Volume of Sample Collected (mL):
Condition of Dedicated Tubing and Cap:		
Notes:		
Signature of Recorder:		

Location:		Personnel:
Date:		
Well ID:		Weather:
Start Time:	End Time:	Time Sample Collected:
Depth to Water (ft):		Sample Inlet Depth (ft):
Volume Purged (mL):		Volume of Sample Collected (mL):
Condition of Dedicated Tubing and Cap:		
Notes:		
Signature of Recorder:		

EXAMPLE
SAMPLE CUSTODY RECORD Date _____
Page of

Battelle

Project No.:											Laboratory:
Project Name:											Address:
Project Manager:											
Phone:				**Testing Parameters**							Attn:
										Number of Containers	
Lab No.	Sample No.	Collection Date	Matrix								Observations, Instructions
											total # of containers

Relinquished by: Signature Date Time Printed Name Company	Received by: Signature Date Time Printed Name Company	Shipment Method: **Special Requirements or Conditions:** **Sample Disposition:**
Relinquished by: Signature Date Time Printed Name Company	Received by: Signature Date Time Printed Name Company	Distribution: 1. 2 copies to the Laboratory 2. 1 copy project manager 3. Return completed original to Battelle Marine Sciences Laboratory

Appendix D

Nitrate Sensor Implementation Document

Standard Operating Procedure for the AquiStar® TempHion™ Smart Sensor – pH, ISE, Redox (April 2010)

INTRODUCTION

What is the TempHion™ Smart Sensor?

The AquiStar® TempHion™ Smart Sensor is a submersible water quality sensor and datalogger capable of measuring pH, specific ions, redox, and temperature. Each unit comes with a thermistor based temperature element plus a combination of pH, ISE, or redox elements. (Contact INW for available combinations.)

The TempHion™ Smart Sensor is powered internally with two AA alkaline batteries or with an auxiliary power supply for data intensive applications. The unit is programmed using a laptop or desktop Windows® based computer via its RS485/RS232 adaptor and INW's easy-to-use Aqua4Plus software. Once programmed, the unit will measure and collect data on a variety of time intervals.

Several TempHions, or a combination of TempHions and other INW Smart Sensors, can be networked together and controlled from one location, either directly from a single computer or via a WaveData® Wireless Data Collection System.

The internal processor in the TempHion™ Smart Sensor allows for easy calibration, using the calibration utilities in Aqua4Plus. Once calibrated, this calibration data is stored in non-volatile memory within the Smart Sensor. When data is collected, this calibration information is applied to the data, resulting in highly accurate readings at a wide range of temperatures.

Initial Inspection and Handling

Upon receipt of your smart sensor, inspect the shipping package for damage. After opening the carton, look for concealed damage, such as a cut cable. If damage is found, immediately file a claim with the carrier. Check the label attached to the cable at the connector end for the proper cable length.

Do's and Don'ts

Do handle the device with care.

Do store in water or calibration solution and keep vertical once filled with reference solution.

Don't install the device so that the connector end is submerged.

Don't support the device with the connector or with the connectors of an extension cable. Use a strain relief device to take the tension off the connectors.

Don't allow the device to free-fall down a well as impact damage can occur.

Don't bang or drop the device on hard objects.

Theory-in-Brief

TempHion works on the principal of direct potentiometry, i.e., the same principal that governs any other pH or ISE electrode. In direct potentiometry, two electrodes - a sensing electrode and a reference electrode - are immersed in the solution that is being analyzed. TempHion is a "combination" electrode, which means that both the reference electrode and the sensing electrode are contained in one instrument body. (The majority of modern pH and ISE electrodes, particularly those intended for portable field use, are combination electrodes.) Together, the two immersed electrodes are analogous to a dry cell used to power a flashlight. To use or to measure the potential (voltage) of a dry cell, electrical connections must be made to both the positive and negative poles. The voltage measured is the "cell potential" and represents the difference between the electrochemical half-cell potentials of the two poles. In direct potentiometry, the two poles of the cell are represented by the sensing and reference half-cell electrodes.

The half-cell potential of a sensing electrode varies logarithmically with the concentration of the ion it is designed to sense. The reference electrode is designed to maintain a constant half-cell potential, against which the half-cell potential of the sensing electrode is measured.

The most common type of reference electrode used for pH/ISE measurements consists of pure silver metal coated with a layer of silver chloride (usually identified as a Ag/AgCl reference electrode). This is identical in concept (but not in construction) to the chloride sensing electrode used with TempHion. The constant half-cell potential of the reference electrode is established by immersing the solid state Ag/AgCl reference element in a solution of known and constant chloride content, known as the reference electrode filling solution. The reference half-cell potential will remain stable if the filling solution is in no way altered by contamination or dilution, which means that the capillary thread must maintain its integrity.

The filling solution must be in direct contact with the solution being tested to allow ionic charge transfer. Conventional reference electrodes designed to be submerged or under pressure typically use a ceramic or semi-permeable membrane to allow ionic charge transfer while at the same time acting as a physical barrier keeping the test solution and the filling solution from

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intermingling. These electrodes are electrically resistive and prone to fouling. While they are usually initially stable and accurate, fouling quickly leads to a noisy and unstable signal.

TempHion uses a long capillary pathway, initially filled with reference electrode filling solution, to separate the reference electrode chamber from the solution being analyzed. In addition, TempHion's reference electrode is filled without *any* air (which is compressible). With this construction, the principle mechanism that will eventually allow test solution to enter the reference chamber and contaminate the reference electrode filling solution is diffusion - an exceedingly slow mechanism. Further, while the capillary pathway is narrow by garden hose standards, its open cross-section is huge compared to the microscopic openings in a conventional porous ceramic fluid/fluid junction. It is therefore much less susceptible to fouling. Fluid expansion and contraction caused by temperature variations can augment the effects of diffusion. Nevertheless, TempHion's proven stability under actual field conditions is measured in weeks or months, rather than hours or days!

Figure 1 illustrates the construction of the TempHion™ reference electrode. Please note that the capillary pathway between the reference and test solutions is established using a modified screw thread. This means that the capillary can be easily opened up for cleaning, refilling, or other maintenance.

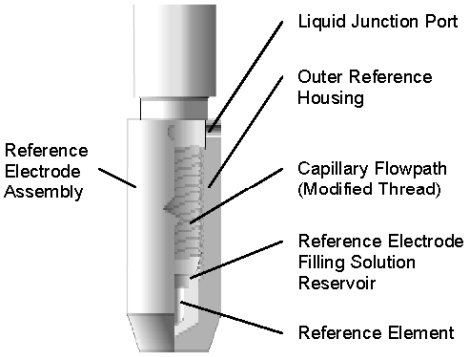

Figure 1: Reference Electrode Assembly: The modified thread provides a continuous liquid path between the solution in which the instrument is immersed and the reference element.

General Precautions

The rest of this document includes step-by-step instructions for setting up the TempHion™, calibrating it, and using it in the field. When reading and following the instructions in these sections, keep these very important considerations in mind:

- Do not handle the surfaces of the sensing electrodes. Oils from fingers can "blind" the reactive surface. Rough handling can scratch the reactive surface.
- Avoid long-term exposure of silver-based sensing electrodes to bright sunlight.
- Use calibration standards that are accurately prepared. Discard standards after use. Do not return the used standards to the bottles of "fresh" solution.
- When TempHion's reference electrode contains filling solution, TempHion must be stored in water to prevent evaporation of the filling solution.
- For any step-change in temperature (e.g., where calibration standards are at a different temperature than water to be tested) allow the instrument to come to complete thermal equilibrium before making measurements. Up to 30 minutes may be required.

SETUP AND INSTALLATION

Care and Filling of Reference Solution Reservoir

The TempHion's patented reference electrode is key to the TempHion's superior performance. The TempHion uses a long capillary pathway, filled with reference solution, to separate the reference electrode from the solution being analyzed. Proper care and filling of this reference solution reservoir is essential to accurate functioning of the sensor.

The TempHion is normally shipped with a bottle of INW Reference Solution. If you will be using a different solution, contact INW for any adjustments that may be needed.

Emptying and Cleaning the Reservoir

The TempHion is shipped fully assembled with the reservoir empty and the reference electrode chemically clean and dry. If you have just received your sensor from INW, you will not need to empty the reservoir. You should still, however, follow the instructions below for cleaning the electrode and reservoir cap.

Standard Operating Procedure for the AquiStar® TempHion™ Smart Sensor – pH, ISE, Redox (April 2010)

- Unscrew the reservoir cap. **Do not touch or scratch the sensing buttons or the reference electrode!**
- Empty any remaining filling solution from the cap.
- Thoroughly rinse the reference electrode and the inside of the cap with distilled or de-ionized water.
- There may be some crystallized residue inside the cap, on the electrode screw path, or on the electrode itself. If rinsing does not clear this away, then gently use a cotton swab or a soft toothbrush to remove the residue.
- Rinse the electrode assembly and cap thoroughly again after cleaning with the swab or brush.
- Gently, pat dry with a clean paper towel.

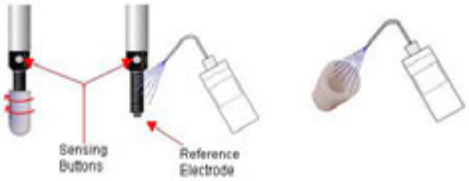

Figure 2: Careful rinsing of the electrode and reservoir cap to remove any contamination is essential for proper operation.

Filling the Reservoir

Once the reservoir has been emptied and cleaned, you are ready to fill the reservoir with reference solution.

- Rinse the reference electrode assembly and the inside of the cap with a small amount of the reference solution.
- Empty any remaining solution from the cap.
- Fill cap about half full with reference solution.
- Holding sensor vertically, replace reservoir cap. Some solution should spill from the top as you screw the cap on. This assures that no air bubbles are trapped inside.
  If any air bubbles are trapped, a proper electrical connection cannot be made and the sensor may read erratically!
- Once filled, keep the sensor upright in liquid to prevent the solution from drying out. A 1 to 10 ppm dilute chloride solution is recommended, but tap water will do. If you cannot keep sensor in liquid, see instructions below for storing dry.

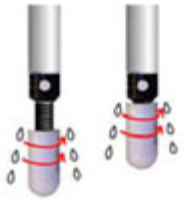

Figure 3: Excess filling solution spills over as the cap is tightened, forcing out any air bubbles.

CAUTION: Filling solutions are not considered hazardous, but they can be irritating to the skin. Protective gloves are advised. Rinse hands or gloves with fresh water.

Storing Sensor

For long-term storage, or when the sensor cannot be left in liquid, the sensor should be stored dry.

- Unscrew and empty the reservoir cap. **Do not touch or scratch the sensing buttons or the reference electrode!**
- Clean the cap and electrode assembly as detailed earlier in this application note.
- Let cap and electrode assembly dry thoroughly.
- Replace cap to protect electrode from scratching.

Battery Power

The TempHion sensors are shipped from the factory with fresh internal AA batteries. These batteries should last several months to a year when taking samples every 15 minutes. Actual battery life may depend on battery brand, battery age, temperature of the environment, usage schedule, and other factors.

Special note for TempHions with firmware version 0.16. Batteries in these units have a maximum life of about 30 days, **even if the TempHion is not yet deployed.** Heavy recording schedules can decrease that life, though you should be able to get at least 20 days of life in most circumstances.

Changing Batteries

Because changing the batteries involves opening the water-tight seal, **this must be done in a clean, dry environment to avoid contamination or moisture damage to the circuitry.**

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Standard Operating Procedure for the AquiStar® TempHion™ Smart Sensor – pH, ISE, Redox (April 2010)

Battery Type: Two standard AA Alkaline batteries.

Replacing the Batteries: Open the housing by removing the top-cap, as outlined below. The top-cap is the connector between the tube housing, the sensor and the cable.

1. Twisting gently, unscrew the top-cap.
2. Gently separate the top-cap from the body of the sensor. Top-cap remains attached to body via several colored wires.

   Caution! Pulling forcefully on the top-cap can pull the insides out of the sensor or snap the connections inside. Removing the circuit board or pushing on the surface of the pressure element **may void your warranty**.

   Note: O-rings provide a water-tight seal for the sensor housing. Take care not to nick or otherwise damage these O-rings.
3. Tip housing over and gently slide batteries out.
4. Insert new batteries - **positive terminals towards the top-cap**.
5. Replace and retighten top-cap.

Figure 4a: Gently separate the top-cap from the body of the sensor. Top-cap remains attached to body via several colored wires.

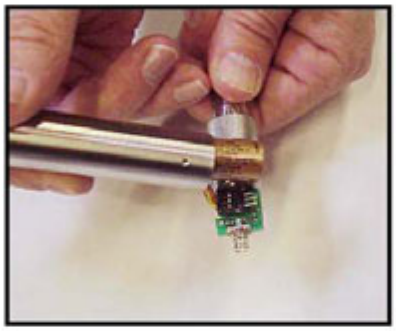

Figure 4b: Slide batteries out.

External Power

The TempHion can be powered from an external power supply, if desired. Twelve volt power supplies are available from INW. Alternately, you can connect any 6-13 VDC supply that can provide 15 mA. Connect to Vaux++ (white) and Ground (blue) or contact INW for auxiliary power connectors.

Computer Connection

The TempHion connects to a PC either via a serial port or via a USB port. The Smart Sensor cable is terminated with a weatherproof connector. For a serial port connection, connect the weatherproof connector to your PC or laptop serial port via the interface cable and an RS485/RS232 adapter, as shown below.

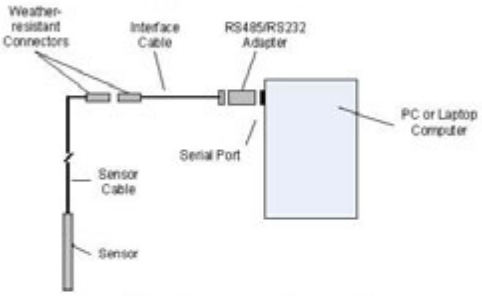

Figure 5: Serial Port Connection: Connect the weatherproof connector to your PC or laptop serial port via the interface cable and an RS485/RS232 adapter.

For a USB connection, connect the weatherproof connector to your PC or laptop USB port via the interface

cable, an RS485/RS232 adapter, and an USB to Serial Cable, as shown below.

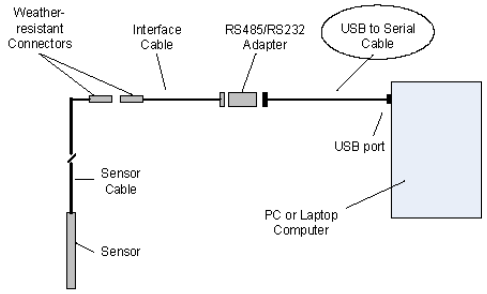

Figure 6: USB Port Connection: Connect the weatherproof connector to your PC or laptop serial port via the interface cable, an RS485/RS232 adapter, and an USB to Serial Cable

USB-to-Serial cables are readily available from many electronics and computer stores, as well as numerous sites on the Internet. INW has tested and recommends the Keyspan USA-19HS. It is available from INW or on the Internet. Install as follows:

- Plug into USB port
- Install the drivers provided with the particular unit
- Note new COM port number. (Right click on My computer. Select Manage. On left panel click on Device Manager. On right panel double-click on Ports. The new COM port should be listed.)
- Connect to the smart sensor (See Figure 6 above.)
- On the Aqua4Plus software, select the COM port noted above.

Aqua4Plus Software Installation

The TempHion™ comes with the Aqua4Plus host software to be installed on your PC or laptop. Use this software to calibrate the sensor, to program the datalogger, to retrieve data from the logger, to view collected data, and to export data to external files for use with spreadsheets or databases. Refer to the Aqua4Plus software manual for details on installing and using Aqua4Plus.

Calibration

Overview

The TempHion has two temperature channels and four millivolt channels. The millivolt channels can be configured to measure pH, redox, or various selected ions. Before leaving the factory, your sensor has been configured specifically for you. All unneeded channels have been disabled, and the active channels have been pre-configured. Disabled channels will not display in Aqua4Plus.

All active channels can be calibrated in the field. Temperature channels rarely need calibrating, however the millivolt channels should be calibrated before first use and every one to six months thereafter. It should also be calibrated if moving to a different sampling environment where readings will be significantly different than the current environment.

Environmental conditions of turbulence and temperature swings, as well as local likelihood for bio-fouling or mineral deposition, can vary considerably from site to site. Therefore, where the sensor is to be used for long-term monitoring, it is recommended that the calibration be initially checked frequently until a performance history is established.

Aqua4Plus provides an easy-to-use calibration calculator for performing one- or two-point in-field calibrations. Two-point calibrations are more accurate and should be used whenever possible. A Calibration Kit is available from INW, which includes a beaker, pipette, measuring beaker, and stand.

- In order for the TempHion Smart Sensor to calibrate and function correctly, the filling solution reservoir must be properly filled with reference solution. See previous section on filling reservoir.
- For best results, the filling solution reservoir should be filled at least 16 hours before calibrating.
- The sensor and all calibration buffers and solutions should be at the same temperature before and during calibration.
- Calibration can only be done when there are no sessions stored on the sensor. If there are any sessions stored on the sensor, upload any data you want and then erase the sessions before continuing. (Sessions Menu | Erase All Sessions).

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Field Calibration Window and Calculator

Field calibration is performed on each channel separately. To calibrate a specific channel, select Field Calibration from the Configure Menu, and then click on the channel to be calibrated. Follow directions below for each specific channel type.

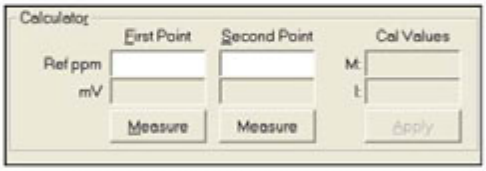

Figure 7: Use the field calibration calculator to calibrate each channel before deploying sensor.

Temperature Channel Calibration

The temperature channel rarely needs calibration. If needed, select Field Calibration from the Configure Menu. Click on Temperature, and then follow the instructions on the screen.

pH Channel Calibration

Preparing

- INW recommends pH buffers of 4, 7, and 10 for calibration. For a one-point calibration, select the buffer closest to the expected values in your samples. For a two-point calibration, select the two buffers that most closely bracket the expected values in your samples.
- For best results, look up the buffer's actual pH for the temperature closest to the buffer temperature during calibration. This information is available from the buffer manufacturer.

One-Point Calibration

--**First Calibration Point**--

- Prepare the buffer.
- Rinse sensor first with distilled water and then with small amount of the buffer.
- Place sensor in buffer. (Buffer must be deep enough to cover the sensing bulb in the slot in the black module on the sensor.)
- Allow time for sensor to stabilize.
- In the ***Ref pH*** box for the first point, enter the reference pH as noted in the preparation section above.
- Click first ***Measure*** button.
- When readings have stabilized to your satisfaction, click the ***OK*** button in the pop-up box.

--**Applying Calibration Values**--

- Observe ***I*** value in the right hand section of the calculator. This should be between 180 and 300.
- Click the ***Apply*** button to apply calibration values.
- The reference value, the computed I, and the sample temperature will be transferred to the calibration fields.
- Click ***OK*** to save the values to the sensor.

--**Verifying Calibration Values**--

- Using the Real Time Monitor, take a few readings while the sensor is still in the buffer. Be sure units are set to pH. Readings should be very close to your selected buffer.

Two-Point Calibration

--**First Calibration Point**--

- Prepare first buffer.
- Rinse sensor first with distilled water and then with small amount of first buffer.
- Place sensor in buffer. (Buffer must be deep enough to cover the sensing bulb in the slot in the black module on the sensor.)
- Allow time for sensor to stabilize.
- In the ***Ref pH*** box for the first point, enter the reference pH as noted in the preparation section above.
- Click first ***Measure*** button.
- When readings have stabilized to your satisfaction, click the ***OK*** button in the pop-up box.

--**Second Calibration Point**--

- Prepare the second buffer.
- Rinse sensor first with distilled water and then with small amount of second buffer.
- Place sensor in second buffer. (Buffer must be deep enough to contact stainless steel tube above the sensor section.)
- In the ***Ref pH*** box for the second point, enter the reference pH as noted in the preparation section above.
- Click second ***Measure*** button. (Note: measured temperature must be +/- 1 degree of first measured temperature or calibration will not be accurate!)
- When readings have stabilized to your satisfaction, click the ***OK*** button in the pop-up box.

--**Applying Calibration Values**--

- Observe the ***M*** and ***I*** values in the right hand section of the calculator. ***M*** should be between -50 and -60, and I should be between 180 and 300.

- Click the ***Apply*** button to apply calibration values.
- The reference values, the computed M and I, and the sample temperature will be transferred to the calibration fields.
- Click ***OK*** to save the values to the sensor.

--**Verifying Calibration Values**--

- Using the Real Time Monitor, take a few readings while the sensor is still in the buffer. Be sure units are set to pH. Readings should be very close to your selected buffer.

ISE Channel Calibration

(For Nitrate calibration see Nitrate Addendum at end.)

Introduction to ISE Calibration

INW recommends using the "known addition method" for preparing calibration solutions. Using this method, the sensor is placed in 100 mL of distilled or de-ionized water. A small amount of standard is added to create a known concentration. The first point is measured. An additional amount of the same standard is added to create a second known concentration. The second point is measured.

INW recommends the calibration standards listed below. The following instructions are based on using one of these standards. If you use different standards or prefer not to use the known addition method, you must use some other method to determine the concentration used for the first and second point when calibrating.

Recommended Standards

Bromide

- Molar NaBr (equates to 7990 ppm)

Chloride

- Molar NaCl (equates to 3550 ppm)
- 100 ppm
- 1000 ppm

Preparing

- Select a standard that you will be using for calibration.
- Place 100 mL of distilled water in a beaker.

Note: Temperature of the water ***must remain the same*** *throughout the calibration. Temperature of the sensor must also be this temperature prior to calibration.*

One-Point Calibration

--**Computing Calibration Value**--

- Rinse sensor with distilled water and pat dry.
- Place sensor in beaker of distilled water, as prepared above. (Solution must be deep enough to cover the sensing buttons.)
- Add 1 cc of selected standard to the water. Depending on which solution you are using, this will result in a concentration as shown below:
  - 0.1 Molar NaBr (Bromide) = 79.10 ppm
  - 0.1 Molar NaCl (Chloride) = 35.15 ppm
  - 100 ppm (Chloride) = 0.99 ppm
  - 1000 ppm (Chloride) = 9.90 ppm
- Stir to distribute standard evenly.
- Allow time for sensor to stabilize (15 - 20 minutes).
- In the ***Ref ppm*** box for the first point, enter the concentration you have chosen.
- Click the first ***Measure*** button. (Readings will be in mV).
- When readings have stabilized to your satisfaction, click the ***OK*** button on the pop-up box.

--**Applying Calibration Values**

- Observe the ***I*** value in the right hand section of the calculator. For Bromide, ***I*** should be between 0 and 40. For Chloride, ***I*** should be between 120 and 160.
- Click the ***Apply*** button to apply calibration values.
- The reference value, the computed I, and the sample temperature will be transferred to the calibration fields.
- Click ***OK*** to save the values to the sensor.

--**Verifying Calibration Values**--

- Using the Real Time Monitor, take a few readings while the sensor is still in the standard. Be sure units are set to ppm. Readings should be very close to your selected concentration.

Two-Point Calibration

--**First Calibration Point**--

- Rinse sensor with distilled water and pat dry.
- Place sensor in beaker of distilled water, as prepared above. (Solution must be deep enough to cover the sensing buttons.)

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- Add 1 cc of selected standard to the water. Depending on which solution you are using, this will result in a concentration as shown below:
  - 0.1 Molar NaBr (Bromide) = 79.10 ppm
  - 0.1 Molar NaCl (Chloride) = 35.15 ppm
  - 100 ppm (Chloride) = 0.99 ppm
  - 1000 ppm (Chloride) = 9.90 ppm
- Stir to distribute standard evenly.
- Allow time for sensor to stabilize (15 - 20 minutes).
- In the ***Ref ppm*** box for the first point, enter the concentration you have chosen.
- Click the first ***Measure*** button.
- When readings have stabilized to your satisfaction, click the ***OK*** button on the pop-up box.

--**Second Calibration Point**--

- Add 10 cc of the ***same*** standard to the water. Depending on which solution you are using, this will result in a concentration as shown below:
  - 0.1 Molar NaBr (Bromide) = 791.8 ppm
  - 0.1 Molar NaCl (Chloride) = 351.8 ppm
  - 100 ppm (Chloride) = 9.9 ppm
  - 1000 ppm (Chloride) = 99.0 ppm
- Stir to distribute standard evenly.
- Allow time for sensor to stabilize (15 - 20 minutes).
- In the ***Ref ppm*** box for the second point, enter the concentration you have chosen.
- Click the second ***Measure*** button.
- When readings have stabilized to your satisfaction, click the ***OK*** button on the pop-up box.

--**Applying Calibration Values**--

- Observe the ***M*** and ***I*** values in the right hand section of the calculator. ***M*** should be between -50 and -60. For Bromide, ***I*** should be between 0 and 40. For Chloride, ***I*** should be between 120 and 160.
- Click the ***Apply*** button to apply calibration values.
- The reference values, the computed ***M*** and ***I***, and the sample temperature will be transferred to the calibration fields.
- Click ***OK*** to save the values to the sensor.

--**Verifying Calibration Values**--

- Using the Real Time Monitor, take a few readings while the sensor is still in the standard. Be sure units are set to ppm. Readings should be very close to your selected concentration.

Redox Channels

- Call INW for instructions the first time you calibrate a TempHion redox channel.

Note on units: The unit "Eh" refers to readings in millivolts referenced to a hydrogen electrode. In other words, Eh represents millivolt readings that would have been obtained if using a hydrogen electrode. The units "mV" are direct millivolt readings from the sensor.

--**For Calibration You Will Need**--

- A beaker or bucket of a sample that is representative of what will be measured with the sensor.
- An alternate redox meter - such as an Orion or YSI meter.
- Distilled or deionized water.
- Paper towels.

--**Computing Calibration Value**--

Note: When calibrating a redox channel, do not use the built-in calculator in the Field Calibration Window. Instead, follow the instructions below.

1. Rinse sensor with distilled or deionized water, and then pat dry with clean paper towels.
2. Place the sensor in sample. (Solution must be deep enough to cover the sensing bulb.)
3. Using the alternate meter, take a redox measurement of that sample. Use either plain mV or Eh, whichever you normally use.
4. In Aqua4Plus - set display units to either mV or Eh, whichever you used for the above step.
5. Scan for and click on the sensor.
6. Open the field calibration window ***(Configure | Field Calibration)***.
7. Click on the redox channel, and then enter a zero in the offset box.

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8. Click ***OK***
9. Take two or three single readings using the Real Time monitor and note the redox value.
10. Subtract this value from the value read in the step 3.

--**Applying Calibration Value**--

11. Open the field calibration window.
12. Click on the redox channel, and then enter this value in the offset box.
13. Click ***OK***.

--**Verifying Calibration Values**--

14. Take another couple single Real Time readings. These should be close to the reading taken with the other meter.

Field Deployment

Once the TempHion™ Smart Sensor as been calibrated, it should be stored vertically in water or a calibration solution until it is placed in service at the field site.

1. Lower the sensor to the desired depth.
2. Fasten the cable to the wellhead using tie wraps or a weatherproof strain-relief system.
3. Secure the supplied cap on the weatherproof connector at the top of the cable.

Note that for shallow installations the liquid in which the sensor is submerged must, at all times, reach high enough to touch the metal tubing on the sensor.

Do not install such that the connector might become submerged with changing weather conditions. The connector can withstand incidental splashing but is not designed to be submerged.

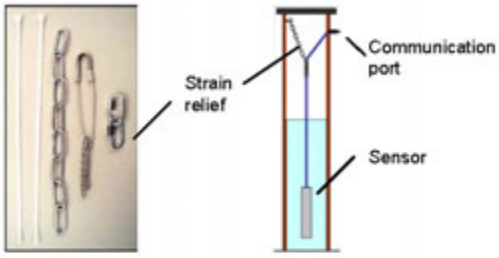

Figure 8: Typical Installation

OPERATION

Data Collection

Following is a brief overview on using Aqua4Plus to collect data. Please refer to the *Aqua4Plus Instruction Manual* for further details on configuring and using Aqua4Plus.

Real Time Monitor

- Click Single to get a single reading.
- Click Start to get a reading once a second.
- Click Stop to stop the reading.

Note: These are snapshot readings and are not recorded on the sensor.

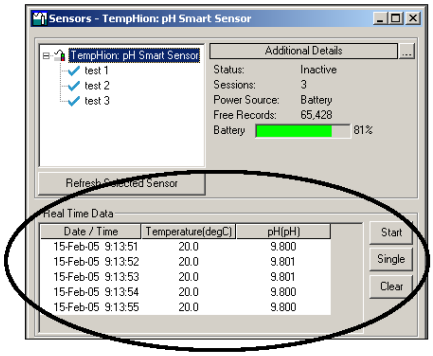

Figure 9: Real Time Monitor: Use the Real Time Monitor to view live readings from the sensor.

Setting up a Data Recording Session

Click the tool button. A Session Profile Window will open. Refer to the *Aqua4Plus Instruction Manual* for details in describing your session profile. Click the Start button to save the session to the sensor and begin recording.

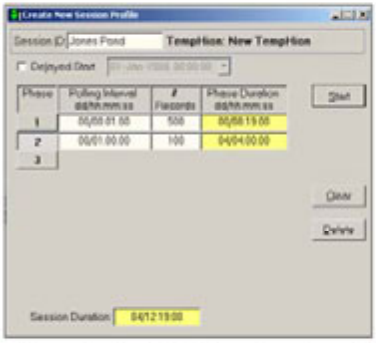

Figure 10: Session Profile Window: A session profile is a description of the test steps necessary for a particular test.

Retrieving Data from the Sensor/Datalogger

- Click on the session you want to upload.
- Click the tool button.
- Select a file location.
- Click Save.
- Click Start.

Figure 11: Click on the session you want to upload.

Viewing Data

- Click the tool button to view data as a table.
- Click the tool button to view data as a graph.
- Navigate to the desired file, then click the Open button. (If the File Open box does not appear, click the File Menu, then select Open.)

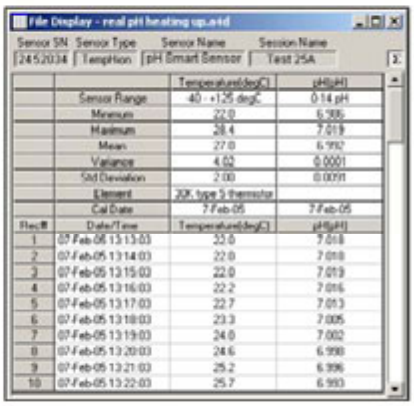

Figure126: The File Display Window displays data that has been uploaded to a disk file.

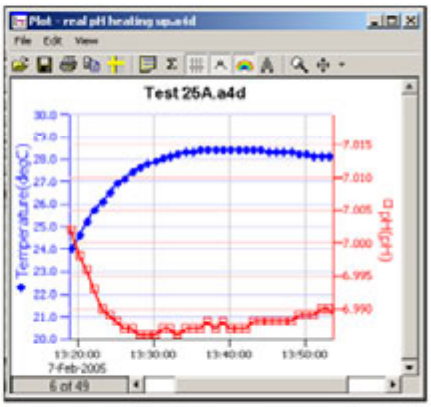

Figure 13: The uploaded data can also be displayed in a graph window.

Exporting Data to .csv or .xls Files

- Using the File Display window, open the file you want to export.
- Click on the tool button.
- Select a file location and enter a name for the file.
- Select a file type.
- Click Save.

Standard Operating Procedure for the AquiStar® TempHion™ Smart Sensor – pH, ISE, Redox (April 2010)

A Word About Units

Readings from the TempHion™ Smart Sensor can be displayed in various units. Select the units you want from the Options | Units menu.

pH:	pH or mV
ISE:	ppm or mV
Redox:	mVH or mV
Temperature:	Degrees Celsius, Fahrenheit, or Kelvin

When using pH, ppm, or mVH units, all readings are automatically compensated for temperature and all field calibration factors are applied. When using millivolts or ohms, only the actual millivolt or resistance values are displayed - no adjustments are made.

Standard Operating Procedure for the AquiStar® TempHion™ Smart Sensor – pH, ISE, Redox (April 2010)

APPENDIX

Wiring Information

Cable Type: 9-conductor, shielded

Shield	=	Ground
White	=	Vaux (6 to 13 VDC)
Brown	=	Digital out
Orange	=	Vbat+ (1.8 to 3.3 VDC)
Blue	=	Ground
Yellow	=	Comm D+
Purple	=	Comm D-

Operating Specifications

pH

Accuracy (typical)	± 0.2 pH units
Resolution	0.001 pH units

ISE

Accuracy (typical)	± 5% of reading
Resolution	0.1 ppm

Redox

Accuracy (typical)	± 5% of reading
Resolution	0.1 mVH

Temperature

Accuracy	± 0.5° C
Resolution	0.1° C

Time

Accuracy	± 6 sec/day	±2 sec/day (typical)

Recommended Operating Temperature Range 0° C to 40° C
Contact factory for extended temperature ranges.

Mechanical Specifications

Sensor

Length:	13.25" to 17.25" depending on configuration
O.D.	0.75"
Body Material	Delrin® and 316 stainless steel
Seal Materials	Viton® and Teflon®
Reference Electrode	Patented capillary liquid junction with Ag/AgCl electrode
Reference Electrolytes	TempHion - no heavy metals and non-contaminating
Thermistor	30K Ohm
pH Electrode	General purpose glass
Chloride Electrode	Solid state
Bromide Electrode	Solid state
Nitrate Electrode	Membrane
Redox	Platinum Ring

Cable

OD	0.28" maximum
Break Strength	138 lbs.
Weight	4 lbs. per 100 feet

Power Supply

Internal	2 AA Alkaline Batteries
Auxiliary	6 - 13 VDC, 15 Ma

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Standard Operating Procedure for the AquiStar® TempHion™ Smart Sensor – pH, ISE, Redox (April 2010)

NITRATE CALIBRATION ADDENDUM

(Letters in parentheses refer to screen shots on last page.)

1. Lab Computation of Slope and Offset (M & I)

a. You will need DI water, 2 molar ammonium sulfate as ionic strength adjuster (ISA), 100 ppm N-NO3 standard. NOTE: all liquids must be at the same temperature, as must the sensor, during calibration.

b. Preparation
   - i. Set Aqua4Plus to display ISE results in ppm.
   - ii. Prepare a beaker with 100 ml of DI water
   - iii. Add 1 ml of ISA (Ammonium Sulfate)
   - iv. Add 1 ml of 100 ppm N-NO3 standard to make a 0.98 ppm solution.

c. Slope and Offset for 1 – 10 ppm
   - i. Place sensor in prepared solution and allow to stabilize.
   - ii. From the Configure Menu, select Field Calibration
   - iii. In Field Cal window, enter 0.98 in 1st reference box(A).
   - iv. Click 1st measurement button(B). Click OK on popup when stable(C).
   - v. Add 10 ml of 100 ppm N-NO3 standard to increase solution to 9.82 ppm.
   - vi. Enter 9.82 in 2nd reference box(D).
   - vii. Click 2nd measurement button(E). Click OK on popup when stable(C).
   - viii. Note the new slope-M to the right(F) – write this down
   - ix. Note the new offset-I to the right(G) – write this down

d. Slope and Offset for 10 – 25 ppm
   - i. Leaving sensor in 9.82 ppm solution, enter 9.82 in 1st reference box(A).
   - ii. Click 1st measurement button(B). Click OK on popup when stable(C).
   - iii. Add 20 ml of 100 ppm N-NO3 standard to increase solution to 23.3 ppm.
   - iv. Enter 23.3 in 2nd reference box(D).
   - v. Click 2nd measurement button(E). Click OK on popup when stable(C).
   - vi. Note the new slope-M to the right(F) – write this down
   - vii. Note the new offset-I to the right(G) – write this down

e. Compute & record new slope and offset
   - i. Slope-M:
     1. Compute the new slope by taking the average of the two slopes you previously wrote down.
     2. Replace the current M value in the M box(J) **near the top** of the field calibration window with this new computed slope.
   - ii. Offset-I:
     1. Compute the new offset by taking the average of the two offsets you previously wrote down.
     2. Replace the current I value in the I box(K) **near the top** of the field calibration window with this new computed offset.
   - iii. Click OK(I) on the calibration window to save new values to sensor.

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Standard Operating Procedure for the AquiStar® TempHion™ Smart Sensor – pH, ISE, Redox (April 2010)

2. *In-Field 1-Point Calibration*

a. You will need a sample of your well water, 2 molar ammonium sulfate as ionic strength adjuster (ISA), 10 ppm N-NO3 standard. NOTE: all liquids must be at the same temperature, as must the sensor, during calibration.

b. Preparation

   i. Set Aqua4Plus to display ISE in mV.

   ii. Draw water from your sample well and put 100 ml in beaker.

   iii. Add 1 ml of ISA (ammonium sulfate)

   iv. Place sensor in beaker and allow to stabilize

c. Take first reading

   i. Using real time monitor, take a few readings with Aqua4Plus

   ii. Once readings are stable, write down the mV reading (E_1).

d. Take second reading

   i. Add 10 ml of 10 ppm N-NO3 standard

   ii. Using real time monitor, take a few readings with Aqua4Plus

   iii. Once readings are stable, write down the mV reading (E_2).

e. Compute and record new offset

   i. Take difference of mV readings from c and d above.

   ii. Using the formula to the right or looking up in a Q table or spreadsheet, determine Q factor.

   iii. Current concentration = Q factor * 10 ppm.

   iv. Set Aqua4Plus to display ISE in ppm

   v. In Field Cal window, enter Current Concentration. from step e iii., above, in 1st reference box(A).

   vi. Click 1st measurement button(B). Click OK on popup when stable(C).

   vii. Click Apply button(H) to move newly calculated offset-I to I box(K) near top of field cal window. (Slope-M will not change.)

   viii. Click OK(I) on the calibration window to save new offset to sensor.

f. Final calibration with sensor in well

   i. Place the sensor in the well and allow to stabilize.

   ii. In Field Cal window, enter Current Concentration. from step e iii., above, in 1st reference box(A).

   iii. Click 1st measurement button(B). Click OK on popup when stable(C).

   iv. Click Apply button(H) to move newly calculated offset-I to I box(K) near top of field cal window. (Slope-M will not change.)

   v. Click OK(I) on the calibration window to save new offset to sensor.

Q Factor

$$Q = \frac{p * r}{((1 + p)10^{\Delta E/S}) - 1}$$

where:

ΔE = $E_2 - E_1$
S = current slope
p = (volume of standard) / (volume of solution)
r = (volume of solution) / (volume of standard)

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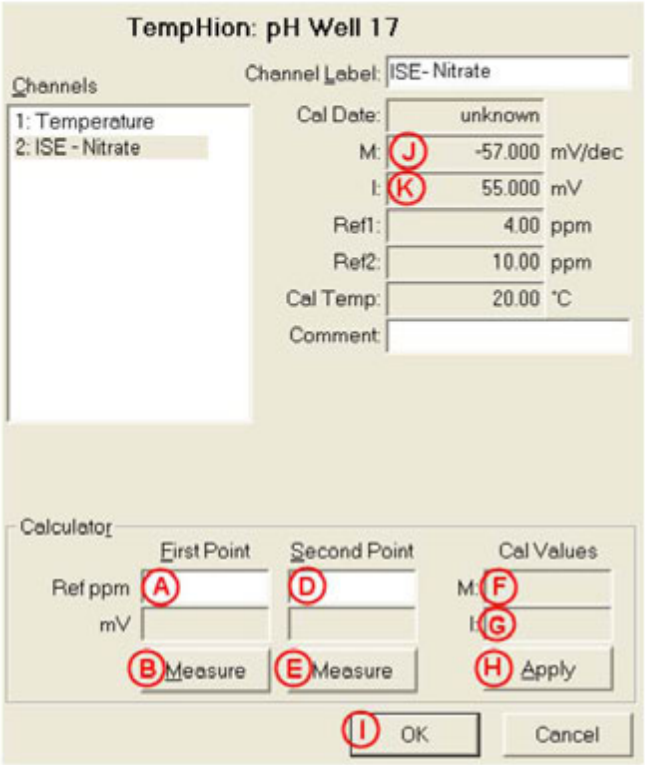
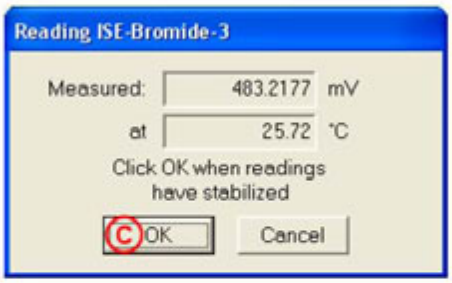
Standard Operating Procedure for the AquiStar® TempHion™ Smart Sensor – pH, ISE, Redox (April 2010)





Appendix E

Laboratory Test Procedures

USDA-ARS, National Laboratory for Agriculture and The Environment.
Method for Determination of Inorganic Anions in (Tile, River, Stream) Water & Aqueous Solutions by Ion Chromatography

Current analytical method (1/27/2010; B.D.)

The procedure was developed from EPA method 300.1 and Dionex Application Note 154.

Equipment:

The Dionex ICS-2000 Reagent-Free Ion Chromatography (RFIC) System consists of the following components: eluent generator, column heater housing an IonPac AS18 analytical column (4 x 250 mm) and IonPac AG18 guard (4 x 50 mm), dual piston pump, EluGen EGC-KOH Cartridge with CR-ATC and an anion self-regenerating suppressor (ASRS-Ultra II) in line with a digital conductivity detector. A Dionex AS40 autosampler is used to deliver samples to the ICS-2000. The ICS-2000 and autosampler are controlled by the Chromatography Workstation with Chromeleon 6.5 software.

Reagents

House deionized water is run through a Milli-Q system to achieve with 18 MΩ -cm resistivity or better, filtered through 0.22 um filter and degassed for 30 minutes with helium.

Anion solutions (nitrate-N, nitrite-N, phosphate-P, chloride, fluoride, sulfate and bromide) are purchased as 1000 ppm stocks in 125 ml volumes from Dionex. Anion solutions are stored in the manufacturers bottles at 4º C for not more than 6 months (EPA Method 300.1). New standards will be purchased for the ETV project.

Calibration Standards:

Calibration standards are prepared monthly by diluting the 1000 ppm stocks (described above) in deionized water. Calibrated pippettes (Rannin) and glass volumetric flasks are used. The concentrations for nitrate-N and nitrite-N standards are 1, 5, 10, 20, 30 and 40 ppm which covers the range of concentrations expected for the ETV project. We have obtained linear calibration curves with R^2 of 0.998-0.999 for nitrite and nitrate over a range of 1- 125 ppm. This is in agreement with Dionex Application Note 154 which claims linearity up to 100 ppm.

- 1.0 ppm NO_3-N Standard. Dilute 0.1 ml of 1000 ppm NO3-N stock into 100 ml deionized water.
- 5 ppm NO_3-N Standard. Dilute 0.5 ml of 1000 ppm NO3-N stock into 100 ml deionized water.
- 10 ppm NO_3-N Standard. Dilute 1.0 ml of 1000 ppm NO3-N stock into 100 ml deionized water.

- 20 ppm NO_3-N Standard. Dilute 1.0 ml of 1000 ppm NO3-N stock into 50 ml deionized water.
- 30 ppm NO_3-N Standard. Dilute 3.0 ml of 1000 ppm NO3-N stock into 100 ml deionized water.
- 40 ppm NO_3-N Standard. Dilute 1.0 ml of 1000 ppm NO3-N stock into 25 ml deionized water.
- 60 ppm NO_3-N Standard: Dilute 3.0 ml of 1000 ppm NO3-N stock into 50 ml deionized water

A new calibration curve is prepared for each run with at least 3 replicate standards at each concentration.. Calibration check standards (20 ppm, prepared as described above) are inserted every 10-12 samples in an analytical run. Laboratory reagent blanks (filtered deionized water) are included in each set of samples. We expect the calibration curve to be linear with an $R^2 >$ 0.98. Peaks for analytes of interest are integrated quantified using the Chromeleon software and visually inspected by the operator. Results are copied to Excell files, but the original Chromeleon files are retained on the work station.

Chromatography Conditions:

Column: AS18 analytical column (4 X 250 mm)

Eluent: 22 mM KOH

Eluent source technology: ICS-2000 with Continuous Regenerated Anion Trap Column (CR-ATC)

Flow rate: 1.0 ml/minute

Temperature: 30°C

Injection volume: 25 ul

Detection: Suppressed conductivity, ASRS ULTRA II, 4 mm, Auto Suppression Recycle Mode, 87 mA current

System Backpressure: <2500 psi

Sample Run Time: 20 minutes

Under these conditions the following analytes and their respective retention times (min) are obtained: Br (6.8), Cl (4.2), Fl (3.0), PO_4 (15.7), SO_4 (7.1), NO_3 (7.7), NO_2 (5.0), HCO_3 (5.9).

Sample Storage and Preparation:

Samples are stored on ice in the field for same-day shipment to be refrigerated in the laboratory, [1] 5-8 ml of fresh sample are filtered through 0.22 um filter into plastic scintillation vials, then

aliquoted into Dionex 0.5 ml PolyVials, fitted with black filtercaps and analyzed; or [2] 5-8 ml of fresh sample are filtered into plastic scintillation vials and frozen until ready for analysis (<14 days). The frozen samples are then thawed, aliquoted as described previously. If samples are refrigerated or frozen samples are warmed to room temperature prior to analysis. Unused samples will be refrozen or refrigerated for use as backup material if initial analysis fails QC and reanalysis is required.

Quality Control

In general Quality Control will be assessed as described in Method 300.1, Section 9, specifically containing the following elements. These apply only to the analysis of nitrate. For all other analytes only the calibration standards, calibration check standards and laboratory blanks will be used.

- Quality Control Standard. The QCS will be prepared by dissolving 0.6068 g sodium nitrate ($NaNO_3$, ACS grade reagent) in deionized water and dilute to 100 ml volume. To achieve a 1000 ppm NO_3-N standard. Dilute 1.0 ml of 1000 ppm NO_3-N of the QCS stock into 50 ml deionized water to make a 20 ppm QCS for analysis. A QCS standard is included in the analysis of each batch of samples after calibration standards. If the determined concentrations are not within 90% to 110% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of Precision and MDLs or continuing with on-going analyses.
- Initial Precision and Recovery – To establish the ability to generate acceptable precision results, the operator shall analyze 10 replicates of a mid-range standard (20 ppm), Using the results of the replicates compute the average percent recovery (X) and the standard deviation (s) for the analyte. Use the following equation for the calculation of the standard deviation.

  $$S=\left(\sqrt{\sum X^2-(\sum X)^2/n}\right)/(n-1)$$

- Where, n = Number of samples, x = concentration in each sample

  If the results meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If however, s and x do not meet criteria then system performance is unacceptable. In this event correct the problem, and repeat the test.
- Method Detection Limit. The MDL will be assessed at 0.5 ppm NO_3-N as described in Method 300.1. This will be compared to the MDL reported in Dionex Application Note 154.
- Laboratory Reagent Blanks. LRB are included in each analysis and consist of filtered deionized water.
- Laboratory Fortified Blanks. The LFB consist of deionized water containing 20 ppm NO_3-N. (Note these are identical in composition to calibration check standards). Control

limits described for LFB are detailed in Method 300.1, p 14. These are included approximately every tenth position in a series of sample analyses.

- Laboratory Fortified Sample Matrix. Field water samples will be divided after filtering and aliquating into Dionex PolyVials and stored in the refrigerator. After analysis to determine the "background" concentration these reserved samples will be spiked with NO3-N to achieve concentrations 2 to 3 times above background. For example a sample containing 10 ppm NO_3-N would be spiked with a highly concentrated solution to achieve 20 ppm NO_3-N with <2% change in sample volume.

  Recovery (R, %) is determined as $R=[C_F-C_B/S] \times 100$, where C_F and C_B are concentrations of the fortified field samples the concentration of the un-fortified field sample ("background"), respectively, and s is the concentration of the spike. Acceptable control limits are 57-125% recovery.

- Field or Laboratory Duplicates. We will perform duplicate analysis on 7% of the field samples in each analysis. Criteria for interpretation (acceptance if the relative percent difference is ± 10%) are as stated on Method 300.1. Samples falling outside the acceptable range will be re-analyzed and/or flagged as failing QC procedure.

- General Laboratory Procedures. Ranin pipettes are calibrated annually and measurements are checked by weight. Laboratory balances are checked at least monthly using standard weights. MSDS sheets are available for all reagents. Bound and numbered laboratory notebooks are used for each project.