

Protocols for the Performance Verification of In Situ pH Sensors

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Questions and comments should be directed to: Dr. Tom Johengen
ACT Chief Scientist
CILER-University of Michigan
4840 S. State Street
Ann Arbor, MI 48108 USA
Email: Johengen@umich.edu

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Protocols for the ACT Performance Verification of In Situ pH Sensors

1. Background on ACT Technology Evaluations

ACT has initiated a Performance Verification of commercially available in situ pH sensors for four reasons: 1) an increasing awareness of the need to monitor pH to assess ocean acidification and changes in the carbon chemistry speciation in coastal and estuarine ecosystems; 2) development of instrument packages to help in the maintenance and enforcement of water quality standards, 3) pH sensors and sensor packages are already available but vary in performance (see ACT workshop, *In-situ measurement of dissolved inorganic carbon speciation in natural waters: pH, pCO₂, TA and TCO₂*, Honolulu Hawaii, February 2005); 4) verification testing of these instruments is feasible within a reasonable timeframe with existing ACT capabilities and funding.

These test protocols delineate how ACT will evaluate the performance characteristics of *in situ* pH sensors through the collection and analysis of quality-assured environmental data. The goal of ACT's verification program is to provide industry with an opportunity to have a third-party (ACT) test their instruments in the field and under controlled laboratory settings, and to provide users of this technology with an independent and credible assessment of instrument performance. ACT will also use this opportunity to promote this emerging technology to the scientific and management communities. The instrument performance characteristics examined in the verification reflect the needs of the broader research and management communities.

ACT does not certify technologies, nor guarantee that technologies will always operate at the verified standards, especially under conditions other than those used in testing; ACT does not seek to determine regulatory compliance; does not rank technologies, nor directly compare performance between specific instruments; ACT does not label, nor list technologies as "acceptable" or "unacceptable;" and does not seek to determine "best available technology" in any way. ACT will avoid all potential language that implies "winners or losers". Thus, although the following protocols will be used to test all instruments tested in this program, there will be no direct comparisons of instruments. After the tests are complete, Instrument Performance Verification Statements for each instrument will be released to the public.

2. Technical Advisory Committee

These *Protocols for the Performance Verification of in situ pH Sensors* were developed under the guidance of our external Technical Advisory Committee and in collaboration with accepted applicants and ACT staff. The members of the Technical Advisory Committee are as follows:

Dr. Robert Byrne, University of South Florida
 Dr. Andrew Dickson (Chair), Scripps Institution of Oceanography, University of California, San Diego
 Dr. Burke Hales, Oregon State University
 Mr. Scott McLean, Oceans Networks Canada, University of Victoria
 Dr. Kenneth Pratt, National Institute of Standards and Technology
 Dr. Chris Sabine, NOAA Pacific Marine Environmental Laboratory
 Dr. Simone Alin, NOAA Pacific Marine Environmental Laboratory
 Dr. Rik Wanninkhof, NOAA Atlantic Oceanographic and Meteorological Laboratory

3. Introduction to Technology

There are four important reasons for measuring pH continuously from coastal moorings. The first is to monitor pH as a naturally changing environmental parameter and as measure of CO₂ as a pollutant developing acidification in coastal and open ocean ecosystems. Near continuous measurements of pH can provide some understanding of CO₂ fluxes, their variability and their forcing parameters. The second reason involves estimating the changes in saturation state of the water with respect to carbonate minerals and the impact on calcifying ecosystems. Surface pH measurements in conjunction with direct measurements of one other parameter of the marine CO₂ system (pCO₂, TA or total DIC) can be used to calculate saturation state (for CaCO₃ minerals such as calcite and aragonite). A third important use is to infer net community production in shallow waters, and thus further understanding how the carbon cycle is affected by climate change parameters such as temperature, and CO₂. Changes in pH can occur on a wide range of time scales ranging from hourly, to seasonal and inter-annual. All the DIC parameters are potentially being altered by progressive ocean acidification. Thus it is vital to further promote, develop and improve measurement capabilities for seawater pH. A fourth reason is to measure and monitor pH for enforcement of effluent discharge into natural waters.

Participants at an earlier ACT workshop on *DIC parameters in natural waters* recognized that the required certainty and reproducibility of pH measurements varies 100-fold, depending on the application (items 1-4 above). Specifically, workshop participants concluded that an accuracy of 0.1 pH unit was typically required for compliance issues but 0.01 would improve data for regulation. Furthermore, an accuracy of 0.01 for field pH measurements was generally considered adequate for assessing dissolved inorganic carbon changes and speciation in natural waters; however, there was interest in improving the precision and reducing the uncertainty of these measurements for ongoing research applications. At the time of the workshop, participants also concluded that in-situ measurements of pH, TA and DIC were not yet ready for moored applications; however, in the ensuing 6 years there has been a dramatic increase in the use of pH instruments for moored applications. Based on this increase in the use of pH sensors, we believe it is now appropriate to conduct a performance verification to help to identify useful technologies.

4. Objectives of the pH Sensor Performance Verification

The fundamental objectives of this Performance Verification are to: (1) highlight the potential capabilities of particular in situ pH sensors by demonstrating their utility in a range of coastal environments, (2) verify the claims of manufacturers on the performance characteristics of commercially available pH sensors when tested in a controlled laboratory setting, and (3) verify performance characteristics of commercially available pH sensors when applied in real world applications in a diverse range of coastal environments.

ACT recently performed a customer needs and use assessment on pH sensors. Scientists, resource managers, and other users of these technologies were asked about their current use or application of these instruments, their perceptions of limitations or problems with the technology, and the most important criteria they use when selecting a sensor or instrument package. The results of these assessments, conclusions from the past DIC workshop, and discussions with the Technical Advisory Committee were used to identify the main applications and key parameters that ACT will evaluate in this Technology Verification.

Over 170 coastal resource managers, environmental health agency representatives, manufacturers, and scientific researchers were surveyed regarding their needs, uses and current practices of making pH measurements in the environment. Overall, 42 individuals responded to the survey, all of which are using, or manufacturing, in situ pH sensors. The types of pH sensors being used varied between potentiometric (45%), ion-selective field-effect transistor (32%), and spectrophotometric (indicator dye) 20%, but with a quarter of respondents using more than one type. The greatest area of use among respondents was academic research (76%) followed by state and federal resource management (40%). The environmental applications were broad with coastal ocean greatest (74%), followed by estuarine (64%), followed by open-ocean (41%), and followed by freshwater (38%). Correspondingly, these environments included temperature ranges from -5 to 50 °C, with medians of 5 °C and 28 °C when responses were binned into low and high ranges. Similarly, salinities ranged from 0 – 100 psu, with low and high bin medians of 15 and 35, respectively. The range of pH measured by the respondents in these applications was between 4.0 and 11.0, with low and high bin median values of 7.0 and 8.3. Remote deployment was the most common method of use (74%), followed by depth profiling (50%), then hand-held portable use (48%), then flow-through systems (26%). Respondents used a variety of calibration procedures including commercial buffers (68%), CO₂ chemistry (35%), seawater CRMs (23%), pH indicator dyes (18%), and supplied by manufacturer (13%). The four areas where respondents expressed the greatest concern over the use of in situ pH sensors were ruggedness (49%), calibration life (46%), level of measurement uncertainty (43%), and reliability (41%). The complete needs and use assessment reports can be found at: www.act-us.info/customer_needs.php.

4.1. Definition of Performance Parameters being Evaluated

- **Accuracy (or Uncertainty)** – uncertainty will be estimated by repeated comparisons between instrument measurements and reference water sample pH determinations as determined by an indicator dye. Standard buffers and Certified Reference Materials for low and high ionic strength solutions will be supplied by the National Institute of Standards and Technology (Kenneth Pratt, NIST) and Scripps Institution of Oceanography (Andrew Dickson, SIO) to calibrate and monitor the accuracy of the reference sample analysis.
- **Precision (or Repeatability)** – Precision will be determined by repeated measures during the pre and post laboratory calibration, and burst sampling during the test.
- **Stability** – Stability will be determined by an evaluation of the difference in instrument readings and reference samples over time a 2-3 month laboratory mesocosm test at varying temperature and salinity conditions and during the two-month long field deployments.
- **Reliability** – Reliability of instruments will be determined by: 1) examining the percent of useful data recovered versus percent of data expected, and 2) by performance evaluation of pre- and post-measures of reference standards to quantify total drift during field deployment periods. Comments on the physical condition of the instruments (e.g., physical damage, flooding, corrosion, battery failure, etc.) will also be recorded.

5. Summary of Verification Approach

The ACT verification of in situ pH sensors will occur in two separate test components. The first component will involve extended laboratory/mesocosm tests conducted over 2-3 months, under well-controlled conditions designed to minimize biofouling while covering a broad range of water temperatures, salinities, and pH. The second component will involve field-based deployments of 2-3 month duration at three to four coastal ocean and freshwater sites. The test approach and analytical methods for the laboratory test are outlined below. Details of the field test will be determined following further discussions with the Technology Advisory Committee and participating manufacturers after reviewing the results of the laboratory test. ACT will convene another protocol development workshop for this purpose in the spring of 2013, with the goal of initiating the field test in the summer of 2013.

6. Laboratory Test Overview

The overall goal of the laboratory test is to determine the repeatability and uncertainty of the in-situ pH instruments over week to month periods, under well-characterized conditions and without the influence of bio-fouling. The laboratory test will be conducted at the Hawaii Institute of Marine Biology (HIMB), Kaneohe, HI starting in November 2012. Laboratory tests will be conducted in a single test tank that will accommodate all instruments. The test water will be made from mixtures of 1 μm -filtered seawater and freshwater (de-chlorinated tap water). The laboratory test will last 2-3 months, and will include periods of days at stable temperature, salinity and pH followed by several rapid increases and decreases in pH over a day. Experiments will be conducted at three salinities (nominally 35, 20 and 0 psu), and at three temperatures (approximately 10, 20 and 30 °C) for each salinity. Temperature will be maintained within 1 °C for the duration of each test condition but monitored throughout the test to better than 0.05 °C. Instruments will be tested for 4-5 days at a stable T-S condition and ambient pH, followed by rapid cycles in pH between 6.5 and 8.5 using acid-base additions over periods of hours. The water in the test tank will be mixed using submerged bilge pumps. Temperature, salinity and pH of the tank water will be continuously monitored at several points throughout the tank. The chosen reference standard against which instrument values will be compared will be pH measured on discrete water samples using a spectrophotometric approach with a purified pH indicator dye.

6.1. Laboratory Test Experimental Design

Two thermally insulated, covered, 4.5 m³ “source-water tanks” will be filled with 1 μm filtered seawater, or a mixture of freshwater and filtered seawater. The two tanks will then be isolated so that each can be maintained at a specific temperature. The source-water tanks will be used to supply water into a third smaller “test tank” (capacity - 1 m³), where all instrument performance measurements will take place. One tank with source-water will be used to continuously flush the third test tank (containing the in-situ instruments); and water from the second source tank will be used to create a quick transition to a new temperature condition within the test-tank. Test conditions within the source-water tank will be set and equilibrated for several days prior to delivery into the test tank. The large volume of equilibrated water in the source-water tank will allow for a rapid transition (10-15 minutes) of T-S conditions in the test

tank. Temperature will be maintained within the source water tank to ± 1 °C using an AquaLogic MT-3 circulating heat exchanger. A secondary temperature regulating system may be added to the test tank to try to maintain the temperature to better than 0.5 °C. Water in the tanks will be mixed continuously with several submerged bilge pumps. Evaporation and heat exchange through the water surface will be reduced to a minimum by using a covering on the surface of the water. The test tank will be instrumented with the test instruments, as well as a SeaBird CTD 19 (calibrated with a Guideline Portasal that is calibrated with IAPSO standards) and three factory calibrated RBR temperature recorders (accurate to 0.02 °C) placed near the instruments to continuously measure actual temperature and salinity conditions experienced by the test instruments. These data will be used to help evaluate fine scale variability within the test and to correct for temperature offsets that might exist during pH measurement of discrete reference samples.

The test tank pH will also be monitored continuously with two glass pH electrodes (Metrohm ECOTRODE PLUS 6.0262.100) measured to 0.1 mv, and spaced across the span of the test instruments. These data will be used to create a continuous data record of pH within the tank, and to confirm test conditions during acid/base additions. These pH data will not be used as reference pH data. The pH probes will be calibrated each day by altering the pH of the test water (set at the experimental T-S conditions) and measuring the pH of the water using the dye technique to define the slope response (Easley and Byrne 2012). In this way the electrodes will not experience any change in liquid junction potential from either freshwater or saltwater buffers.

Each week we will conduct testing at a set combination of temperature and salinity (T-S). Nominal temperature conditions will be set for 10, 20 and 30 °C, and nominal salinity conditions will be set for nominally 0, 20 and 35 psu. A week-long test will be performed at each T-S combination. After 4 or 5 days of testing at a stable T-S condition and ambient pH, we will cycle pH over a reasonable range using acid-base additions to the water of the test tank (7.5 to 8.5 for seawater and 6.5 to 8.8 for freshwater). Two, raised - lowered pH cycles will be conducted at each T-S condition over the course of one day. Acid/base additions will be done by first mixing known quantities of acid/base into several liters of the current test solution and then adding this solution into the test tank to facilitate mixing and rapid equilibration.

The sequencing of tests will be to start with a fixed salinity and perform the tests for that salinity at the three different temperatures, starting at 30 °C and decreasing sequentially down to 10 °C. In this way we will be able to use the same source water for all three temperature conditions. Each test is scheduled to last 1 week, except when delays are needed to accommodate work schedules. For each new T-S test condition, the test tank will be flushed and filled with new source water while keeping all test instruments submerged and recording continuously. Each new batch of source water will be filtered through a 1 μ m cartridge prior to use in the tests.

6.2. Reference Sampling

During the stable temperature and salinity period we will collect and analyze reference samples at 4 timepoints each day. In addition, on one day during the stable cycle we will collect a burst sampling of five independent measurements taken 5 minutes apart at one of the timepoints to evaluate the repeatability and uncertainty of the reference measurement with respect to the variability observed within the test tank. Reference samples will be drawn directly

into the spectrophotometer from a supply tube within the test tank. Water from the test tank will also flush a water jacket around the spectrophotometer cell to maintain the water in the cell very near the temperature of the test tank. We will record 10 readings of the reacted dye over 1-2 minutes for each sampling timepoint and calculate a mean and standard deviation of each reference measurement. The temperature of the sample stream will be monitored continuously and the salinity of the sample stream will be measured on duplicate sub-samples with a Guideline Portasal. Once during the stable phase of a given T-S test condition we will conduct a more detailed burst sampling where 6-8 samples are collected over the course of an hour to assess the fine-scale variability (temporal and spatial) of test tank conditions. During the pH cycling phase of the test we will complete 2 reference sampling timepoints during each endpoint (approximately an hour after acid/base addition) of the increase or decrease. We expect each phase (increase or decrease) to occur over roughly 2 hour intervals.

Lastly, duplicate water samples will be collected at the beginning and end of the stable test condition period (day 1 and day 5) to characterize all of the CO₂ parameters. We will take water samples for pCO₂, DIC and TA measurements and preserve and store them in accordance with standard oceanic protocols (Dickson et al., 2007). These water samples will be shipped to Oregon State University (Burke Hales, OSU) and SIO (Andrew Dickson) for analysis. In addition, preserved water samples will be shipped to SIO (Andrew Dickson) and University of South Florida (Robert Byrne, USF) for measurements of pH, thereby providing further indication of the uncertainty of ACT's reference sample measurements. However, because these samples would not be handled identically to the reference samples analyzed real-time and directly from the test tank, they will not be used in any direct assessment against the test instruments without review from the TAC and consent from the manufacturer. Nutrients will also be measured on these samples in Atkinson's lab.

6.3 Sample Handling and Custody Requirements

All collected reference water samples for the entire laboratory test will be handled in the same manner. All reference samples should be processed according to methods defined within these protocols and cited Standard Operating Procedure documents (Dickson et.al. 2007). Each reference sample should be dated and coded according to site, test condition and sample sequence. The actual sample container should be labeled with a number for identification. The reference sample number should be used in all laboratory records and Chain-of-Custody (COC) forms to identify the sample. The COC specifies time, date, sample location, unique sample number, requested analyses, sampler name, required completion time, date and time of sample transaction, and name of receiving party for the samples. Proper labeling of sample bottles is critical. The COC is a mechanism by which samples can be tracked through the various phases of the process: collection, shipping, receiving, logging, sample prep/extraction, analysis and final data QA/QC review. Transfer of reference samples from field personnel to laboratory personnel is also recorded on the COC and records are maintained in the laboratory with the names and signature of persons leaving and receiving the custody. All logs shall be duplicated weekly. The original log shall be retained at the ACT Partner site and a copy shall be sent to the ACT Chief Scientist.

Accumulated samples to be analyzed by outside laboratories shall be shipped for analysis each week to minimize holding time. Samples stored on site for more than one week shall be

routinely inspected by the TC to assure proper preservation and label integrity. All reference samples not immediately analyzed on site by ACT staff will be accompanied by the sample collection sheet and COC forms.

6.4. Analytical Methods for Reference Samples

The reference pH measurements will be the pH of discrete water samples as determined by pH indicator dyes, either, meta-cresol purple or phenol red (freshwater) (Liu et al. 2011, Yao and Byrne 2001 respectively). Water will be withdrawn from the test tank from very near the sensors via a sampling tube, flushed through the spectrometer cell (Hellma 10 cm cell), dye introduced into the cell (10 μ l of purified 10 mM meta-cresol purple from Byrne's lab) and the dye R ratio measured on an Agilent #8453 spectrophotometer (the R ratio is the ratio of absorbance of acid and base dye). The R ratio of the concentrated dye will be adjusted at Byrne's lab before the dye is shipped to HIMB for the lab tests. The spectrophotometer cell will have a thermal jacket that is continuously flushed with test tank water, thereby keeping the cell very near the temperature of the tank. The returning water from the cell-jacket will be measured with an in-line digital thermistor (ERTCO Model 4400). The R value will be measured 10 times over 1-2 minutes to ensure rapid determination of the pH. pH will be calculated from the R ratio, temperature and salinity according to Liu et al. 2011 or Yao and Byrne 2001; both pH total scale and pH free scale will be reported (Liu et al 2011, Eq. 12). Reference sample pH will be adjusted for any temperature offset between in-tank measurements and in-line sample measurements. The anticipated level of accuracy of these measurements is 0.01 pH, but actual laboratory based accuracy and precision levels will be quantified and reported.

6.5. Test Instrument Set-up and Calibration

ACT will test a single instrument from each manufacturer. Instruments will be set-up and calibrated by ACT personnel as instructed by the manufacturer, following a half-day training session with the test instrument. All training sessions will be videotaped to allow ACT staff to review all recommended handling procedures during final set-up for the lab test. Instruments will be calibrated with company-provided buffers, as specified by the manufacturer. Immediately following calibration and/or conditioning, we will conduct readings of independently supplied NIST buffers to help identify any initial offset in pH measurements. After the independent reading of NIST buffers the instrument will be programmed to sample and log measurements at a minimum of every 15 minutes and placed in the test tank at a fixed depth of approximately 0.7 m. The specific sampling frequency can be set by the manufacturer so long as all instruments do sample at a common 15-minute interval. Once the test instrument is added to the tank it will be continuously submerged and operated for the entire lab testing duration. Company representatives may observe all set-up and calibrations steps performed by ACT. If any changes are proposed to the current test protocols, they must be approved by ACT's Chief Scientist following consultation with the Technical Advisory Committee, and with consensus of all participating manufacturers. Clarifications on the proper handling of an individual instrument by the company representative can be accepted directly by the local ACT principal investigator and would not require TAC or other company review.

7. Data Recording, Processing and Storage

This section describes methods to be employed during data recording, processing, and storage to minimize errors and assure high quality analyses in the Performance Verification Statements.

7.1. Documentation and Records

A variety of data will be acquired and recorded either electronically or manually by ACT staff in the current laboratory and planned field components of this Verification. Operational information and results from the reference method will generally be documented in a field/laboratory record book and on the data sheet/chain-of-custody forms (see below). An electronic copy of these raw data will be transferred each week to the ACT Chief Scientist, who will store it permanently along with the rest of the study data.

The results from the test instruments will also be recorded electronically. Test data will only be downloaded and analyzed upon completion of the individual laboratory tests or field deployments. As possible, all original data will be left on the instrument and returned to the manufacturer. Once collected, one copy of these data will reside at the corresponding ACT test facility and a second copy will be archived at ACT Headquarters or with the Chief Scientist until the entire Verification is finished. The table below summarizes the types of data to be recorded and the process for recording data.

Data to be Recorded	Responsible Party	Where Recorded	How Often Recorded	Purpose of Data
Dates, times of sampling events	ACT PI at each test site	Field record books/data sheets	Each reference sample collection and laboratory analysis	Used to organize/check test results; manually incorporate data into spreadsheets - stored in study binder
Test parameters (site conditions)	ACT PI at each test site	Field record books/data sheets	Each reference sample collection	Used to define site characteristics; manually incorporate data into spreadsheets - stored in study binder
Test instrument calibration data	ACT PI at each test site	Laboratory record Book/data sheets	Start/end of test	Document correct performance of test instrument
Test instrument data - digital display - electronic output	ACT PI at each test site	- Data sheets - Instrument data acquisition system (data logger)	After completion of the 26-day field deployments	Used as part of test results; incorporate data into electronic spreadsheets - stored in study binder
Reference analytical results	ACT PI at each test site	Laboratory record Book/data sheets	At the conclusion of each analytical sample batch.	Used to check test results; manually incorporate data into spreadsheets - stored in study binder
Reference calibration data	ACT PI at each test site	Laboratory record books/data	Whenever zero and calibration checks	Document correct performance of

		sheets	are done	reference method
Performance evaluation audit results	ACT HQ	Laboratory record books/data sheets	At times of performance evaluation audits	Test reference method with independent standards/measurements

7.2. Data Review

Data to be reviewed by the ACT Partner test facility will include electronic data, entries in field/laboratory record books, operating data from test facilities, and equipment calibration records. All manually recorded data are to be recorded directly in the field/laboratory record book as soon as they are available. Records are to be written in water-proof ink, written legibly, and have any corrections initialed by the person performing the correction. Any corrections will be crossed out with a line (not blackened or white-out), and the correction made, with initials and date of correction. Records will be spot-checked daily to ensure that the data are being recorded correctly. The checker shall not be the individual who originally entered the data. All data entries will be checked for obvious errors, and a minimum of 10 percent of all records shall be checked in detail. Errors detected in this manner shall be corrected immediately. The person performing the review will add his/her initials and the date to a paper copy of the record being reviewed. The ACT Technical Coordinator (TC) will place this paper copy in the files for this Verification. In addition, data generated by each ACT Partner test site will be provided to the ACT Chief Scientist for review before they are used to calculate, evaluate, or report results.

8.0 Quality Assurance

The ACT quality assurance system includes training, documentation, quality control, and quality assessment. Quality control includes those procedures that ensure that data generated from ACT verifications are of known accuracy and meet data quality goals. Quality assessments provide assurance that quality control is being done effectively. Quality assurance and quality control procedures for this pH Sensor Verification will follow the requirements described in these Protocols, any vendor specified requirements, and the general principles and specific QA/QC from technical documents for measuring pH in aquatic systems (e.g., Dickson et al., 2007).

8.1 Laboratory Quality Control Requirements

Quality control measures undertaken to assure the reliability of the data collected, and described above in the sampling design section, include:

- Duplicate sampling to ensure sample representativeness with respect to sampling and handling procedures. The acceptable range of relative percent difference between a sample and its duplicate is 20% unless specified otherwise in a specific test plan.
- Replicate analysis to ensure sample representativeness with respect to sample processing and analysis. The acceptable range of relative standard deviation among replicate analyzes is 10%.

- Calibration and maintenance procedures, schedules, and standards (certified reference materials) for all equipment used in the test.

8.2 Assessment, Response and Corrective Action

Every effort will be made throughout the Verification to anticipate and resolve potential problems before the quality of performance is compromised. One of the major objectives of these Verification Protocols is to establish mechanisms necessary to ensure that data quality objectives will be met. Internal quality control measures described in the protocols, which is peer reviewed by external experts, implemented by the technical staff and monitored by the ACT Chief Scientist, 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 Chief Scientist. 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 ACT Chief Scientist, who will work with the ACT Quality Assurance (QA) Manager and Technical Advisory Committee 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.

Fundamental principles of the ACT assessment and response process include:

- Assessments shall be performed by a QA Manager, who shall be independent of direct responsibility for performance of the Verification.
- Each assessment must be fully documented.
- Each assessment must be responded to by the appropriate level of the ACT team. ACT quality assessment reports require a written response by the person performing the inspected activity, and acknowledgment of the assessment by the ACT Director.
- Corrective action must be documented and approved on the original assessment report, with detailed narrative in response to the assessor's finding. Initials and date are required for each corrective action response. Acknowledgment of the response will be provided by the ACT Director.

Implementation of corrective actions must be verified by the ACT QA Manager to ensure that corrective actions are adequate and have been completed. This will be done in real-time if corrective actions can be immediately performed and signed off on the assessment report.

8.2.1 Assessments

The standard oversight mechanisms for a Verification Test include: (1) performance evaluation audits (PEAs); (2) technical system audits (TSAs); audits of data quality (ADQs); and data quality assessments (DQAs). The ACT Chief Scientist will be responsible for ensuring that the following audits are conducted as part of this verification.

Performance Evaluation Audits

Performance evaluation (PE) audits are quantitative evaluations used to assess the ability of the ACT measurement system to provide reliable data. The evaluation consists of providing a known reference standard with defined purity and stability to the ACT analytical team for analysis. A PE sample contains known pH. The analytical results obtained by the ACT team

will be compared to the known pH contained in the PE sample(s), as a means of determining if the ACT team demonstrated its ability to properly measure pH within established control limits.

Laboratories from the TAC (Dickson, SIO and Pratt, NIST) will submit PE CRMs and buffers to the ACT team as part of a laboratory-sampling event. The ACT test facility will measure the standards and establish the laboratories methodological level of accuracy and precision. The QA Manager will evaluate the results of the PE samples as soon as they are received from the ACT team. The critical elements for review of PE results include: (1) correct quantitation of the PE sample; (2) accurate and complete reporting of the results; and (3) measurement system operation within established control limits for precision and accuracy. If the accuracy criteria are not met, the laboratory will investigate the cause of the failure and submit a corrective action report to the QA Manager, Chief Scientist, and ACT Director.

Technical System Audit

A Technical System Audit (TSA) is a thorough, systematic, and qualitative audits evaluation of sampling and/or measurement systems associated with a Verification test. The objective of the TSA is to assess and document the conformance of on-site testing procedures with the requirements of the Verification Protocols, published reference methods, and associated SOPs. The TSA may assess test facilities, equipment maintenance and calibration procedures, reporting requirements, sample collection, analytical activities, and QC procedures. Both laboratory and field TSAs may be performed.

The MERC QA Manager will conduct a TSA at least once during each Verification. A TSA checklist based on the Verification Protocol is prepared by the QA Manager prior to the assessment and reviewed by the ACT Chief Scientist. At the close of the TSA, an immediate informal debriefing will be conducted. The results of TSAs will be documented in a formal audit report. The TSA report schedule is as follows:

- The draft TSA report with the completed checklist will be submitted to the ACT Chief Scientist within 10 days of the TSA.
- The ACT Chief Scientist's audit response is due 10 working days from delivery of the TSA report.
- The final TSA, with audit responses, is due to the ACT Director within 10 days of receiving the response.

The final report with the ACT Chief Scientist's responses accepted by the QA Manager and approved by the ACT Director will be signed, scanned, and uploaded to the ACT documents and records archive.

Audit of Data Quality

An Audit of Data Quality (ADQ) is a quantitative evaluation of the Verification test data. The objective of the ADQ is to determine if the test data were collected according to the requirements of the Verification Protocols and associated SOPs and whether the data were accumulated, transferred, reduced, calculated, summarized, and reported correctly. The ADQ assesses data accuracy, completeness, quality, and traceability.

The ADQ is conducted after data have been 100% verified by the ACT Chief Scientist. The ACT QA Manager conducts the ADQ. The ADQ entails tracing data through their

processing steps and duplicating intermediate calculations. A representative set of the data (10%) is traced in detail from raw data and instrument readouts through data transcription or transference through data manipulation through data reduction to summary data, data calculations, and final reported data. The focus is on identifying a clear, logical connection between the steps. Particular attention is paid to the use of QC data in evaluating and reporting the data set.

Problems that could impact data quality are immediately communicated to the ACT Chief Scientist. The results of the ADQ will be documented in a formal audit report with conclusions about the quality of the data from the Verification and their fitness for their intended use:

- The draft ADQ report will be submitted to the ACT Chief Scientist within 10 days of the ADQ.
- The ACT Chief Scientist audit response is due 10 working days from delivery of the ADQ report.
- The final ADQ, with audit responses, is due to ACT Director within 10 days of receiving the response.

Data Quality Assessment

Data quality assessments (DQAs) are scientific and statistical evaluations of validated data to determine if the data are of the right type, quality, and quantity to support their intended use to verify sensor performance. Once data have been examined and assessed, and they are found to be of known and acceptable quality, then the results can be evaluated in the context of the Data Quality Objectives for the test. An assessment also is made as to whether there is a sufficient quantity of data to support test decisions, and whether the original sampling design was appropriate.

Assessment Reporting

Authority to effectively report PEs, TSAs, and ADQs is assigned to ACT QA Manager. These written reports should:

- identify and document problems that affect quality and the achievement of objectives required by the Verification Protocols and any associated SOPs;
- propose recommendations (if requested) for resolving problems that affect quality;
- independently confirm implementation and effectiveness of solutions;
- identify and cite noteworthy practices that may be shared with others to improve the quality of their operations and products;
- provide documented assurance (if requested) that when problems are identified, further work performed is monitored carefully until the problems are suitably resolved.

Quality assessments of project activities are reported to the ACT Chief Scientist and ACT Director. The Chief Scientist is responsible for ensuring that findings from these assessments of project activities are appropriately addressed.

8.2.2 Response

Responses to adverse findings should be addressed within 10 working days after an assessment report is completed. However, it is expected that findings that have a direct impact

on the conduct of the verification test will be corrected immediately following notification of the finding. Responses to each adverse finding shall be documented in the assessment report. The response will indicate the corrective action taken or planned to address the adverse finding. The response should be signed and dated by the staff responsible for implementing the corrective action. The ACT Director reviews and approves the responses to the assessments and thus ensures that responses are thorough, fully address the audit findings and observations, and thoughtfully assess any impact to testing. Any corrective action that cannot be immediately implemented should be verified following completion by the ACT QA Manager. Once all corrective action associated with an assessment report has been taken, the ACT QA Manager will initial the corrective action in the assessment report thus documenting verification of the corrective action. Any impact that an adverse finding had on the quality of BWTS test data should be addressed in the test report.

8.2.3 Corrective Action

Corrective action is implemented in response to any situation that compromises the quality of testing or data generated by ACT. The need for corrective action can be identified by any ACT personnel and implemented with the prior approval of the ACT Chief Scientist, in consultation with the QA Manager. The Chief Scientist is responsible for determining appropriate corrective action to address an issue. The corrective action should minimize the chance that a problem adverse to quality will re-occur. The corrective action will be documented by the Chief Scientist on the assessment report. Implementation of corrective actions must be verified by the QA Manager to ensure that corrective actions are adequate and have been completed. Verification of corrective actions can be by re-assessment or examination of documentation. The assessment report cannot be finalized until each corrective action has been identified and verified.

The corrective action process should include an assessment of the root cause of a problem so that effective changes can be implemented to minimize reoccurrence. Once the root cause determination is verified, appropriate actions can be planned, documented, and implemented by the ACT staff. Any finding that is a deviation in the Verification Protocol must be documented.

9. Summary of Verification Schedule

Note that the below schedule is provisional and actual dates for each milestone may vary.

- Final Verification Protocols and ACT Verification Contract will be sent to Manufacturers by October 5, 2012
- Signed contracts are due back to ACT Headquarters by October 15, 2012
- Testing facilities at HIMB set-up by October 26
- Instruments shipped to HIMB by November 2, 2012
- All dyes and buffers calibrated and shipped to HIMB by November 2, 2012
- ACT staff will conduct an initial training period with each company representatives during November 5-7, 2012.

- Lab test is initiated on November 9, 2012.
- Laboratory tests will be completed by February 2013.
- Instruments will be returned to companies by February 2013
- ACT will convene a workshop to review Lab results and develop the protocols for the field testing component of the Verification in April 2013.
- Finalize Field testing protocols in May 2013
- Conduct field tests July – November 2013
- Final Performance Verification Statements will be released to the public in March 2014.

10. Roles and Responsibilities

The Verification is coordinated and supervised by the ACT Chief Scientist and ACT Partner institution personnel. Staffs from the Partner institutions participate in this test by installing, maintaining, and operating the respective technologies throughout the test; operating the reference equipment, collecting and analyzing the reference water samples, downloading the data from the instrument package, and informing the ACT Chief Scientist staff of any problems encountered. Manufacturer's representatives shall train ACT staff in the use of their respective technologies and, at their discretion, observe the calibration, installation, maintenance, and operation of their instruments throughout the test. QA oversight is provided by the ACT QA Manager. In addition to aiding the development of these protocols, the external Technical Advisory Committee will be consulted during the evaluation in the event problems occur, will assist in the analysis of results, and will review the final Performance Verification Statements prior to their release.

11. References

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