

Verification of Total Residual Oxidant Analyzers Designed for Shipboard Monitoring of Ballast Water Treatment

Final Protocol
August 25, 2019



A test protocol developed by the **Alliance for Coastal Technologies (ACT)** for the evaluation of Total Residual Oxidant (TRO) detectors used in association with ballast water treatment.

Table of Contents

Contents

Test Synopsis	1
Alliance for Coastal Technologies (ACT)	2
1. Introduction	3
2. Goals and Objectives	4
3. Verification Measurements	4
3.1. Test Method: Continuous, In-Line TRO Measurements.....	5
3.2. Reference Standard: Periodic, manual measurements using the DPD-based method (Standard Method 4500-CL G)	5
3.3. Ancillary Measurements: Temperature, conductivity, salinity, pH, DOC, POC, TSS	6
4. Laboratory Methods	6
4.1. Test Water Preparation.....	6
4.2. Tank and Pipe Loop	7
4.3. TRO Dose Escalation.....	7
4.4. Synchronous recording from instruments and sampling for the reference method	8
5. Experiments.....	8
5.1. Accuracy.....	8
5.2. Precision.....	8
5.3. Natural water tests.....	9
5.4. Alternative oxidant.....	9
6. Data Recording and Archiving.....	9
7. Data Analysis.....	10
8. Roles and Responsibilities.....	10
9. Schedule	11
10. References	11
Appendix A: Quality Management.....	13
A1. Quality Control Requirements for Field Samples and Laboratory Analyses.....	13
A2. Quality Assessment	14
A3. Technical Audits.....	15
A3.1 Technical System Audit.....	15
A3.2 Audit of Data Quality	15
A4. Data Quality Assessment.....	16
A4.1 Data Verification	16
A4.2 Data Validation.....	17
A4.3 Data Usability	17
A5. Corrective Action	17
A6. Audit Reporting.....	18
Appendix B. Trial and Sample Matrix.....	19
Appendix C. Standard Operating Procedures	20

Test Synopsis

- The Total Residual Oxidant (TRO) instruments to be tested are designed for shipboard use associated with ballast water management systems. However, this verification will focus on laboratory assessments of instrument accuracy and precision, under various relevant water quality conditions.
- The Reference Standard (i.e., known or “true” TRO values) for this verification will be the manual, US Environmental Protection Agency (EPA) certified, DPD-based analysis using the standard method (SM 4500-Cl G). Like most measures of TRO, SM 4500-Cl G is based on measure of total residual chlorine (TRC). Therefore, TRO and TRC will be considered equivalent for this Verification. Instrument readings and reference sampling will take place simultaneously at approximately 2.5-minute intervals for each dose level and water quality condition.
- Test water (~340 L per tank) will flow through a recirculation loop, with sample ports for multiple TRO instruments. The instruments will analyze TRO concentrations. For each dose and water quality condition, three consecutive readings (spaced at approximately 2.5-minute intervals) will be collected from each of the instruments’ display.
- Test water will be prepared from deionized water and standard ASTM D1141 ocean water salt mixture—will be adjusted to meet target **temperatures (7-10, 15-18, or 24-28°C)** and **salinities (0.2, 15, 30 psu)**. Test water will also be amended with dissolved and particulate organic carbon (target concentrations of 6 and 4 mg L⁻¹, DOC and POC, respectively).
- Accuracy will be measured as the percent difference between the values of the reference standard and the TRO instrument with test water along a range of temperatures and salinities.
- Each trial day, one salinity and three temperatures will be tested simultaneously (Appendix B). Over the course of the daylong trial, oxidant (in the form of sodium hypochlorite) will be added to achieve TRO concentrations of ranging from initial starting concentration (i.e., **no oxidant added** to approximately **10 mg L⁻¹ TRO**). Sodium hypochlorite will be added in **four** batches, targeting the following five concentration ranges:
 - No oxidant added (initial conditions) - NOA
 - < 1 mg L⁻¹ (Dose 1)
 - 2 - 3 mg L⁻¹ (Dose 2)
 - 4 - 6 mg L⁻¹ (Dose 3)
 - 8 - 10 mg L⁻¹ (Dose 4)

It should be noted that these are *simply target TRO levels to capture a realistic range*. The actual measures of accuracy (and precision) will be calculated based on contemporaneous measurements from the instrument to the reference standard.

- Precision will be quantified using a series of 10 repeated measures at one stable TRO level. On a separate day, using water conducive to minimizing TRO consumption: One tank will be filled with test water with brackish **salinity (15 psu)**, low **temperature (7-10°C)**, with no DOC or POC added. Only **one medium dose** of sodium hypochlorite will be tested. Instrument readings and simultaneous reference standard samples will be collected as described above.
- Two additional trials will examine accuracy in two alternate test conditions:
 1. An **alternate oxidant** (e.g., sodium dichloroisocyanurate dihydrate or NaDCC) will be used instead of sodium hypochlorite. NaDCC granules will be dissolved in DI water to form a stock solution before dosing into the test water. Only one temperature (15-18°C) and one salinity (15 psu) will be examined (Appendix B); however, the four dosing concentrations, plus, instrument readings and reference standard sampling will be conducted as described above.
 2. **Ambient, unfiltered water** from the Patuxent River, a tributary of Chesapeake Bay, near Solomon's Island, will be used as the test water. Thus, only one temperature (ambient) and one salinity (ambient) will be examined; however, dosing of sodium hypochlorite, plus, instrument readings and reference standard sampling will be conducted as described above. will be added as described above.
- All testing will follow the Alliance for Coastal Technologies (ACT) approach, which includes quality assurance/quality control procedures. A concurrent, technical systems audit will occur during a portion of the test. Results of individual instruments compared to the reference method will be posted on the ACT website (www.act-us.info), following completion and review of results.

Alliance for Coastal Technologies (ACT)

ACT was established on the understanding that instrument validation is necessary so that effective, existing technologies are recognized and promising new technologies can be made available to support both successful coastal science and resource management. The specific functions of ACT are to serve as: (1) an unbiased, third-party testbed for evaluating existing, new, and developing coastal sensors and sensor platforms, (2) a comprehensive data and information clearinghouse on coastal technologies, and (3) a forum for capacity and consensus building. It is important to note that ACT does not certify technologies or guarantee that a technology will always, or under circumstances other than those used in testing, operate at the levels verified. ACT *does not*:

- Seek to determine regulatory compliance;
- Rank technologies or compare their performance;
- Label or list technologies as acceptable or unacceptable; and

- Seek to determine “best available technology” in any form.

ACT will avoid all potential pathways to picking “winners and losers”. Therefore, although performance verification will apply to all instruments evaluated under common testing protocols, no direct comparisons will be made between instruments from different manufacturers. Instrument-specific *Verification Statements* will be released to the public for each instrument type as a final report.

1. Introduction

In an effort to mitigate the risk of transporting aquatic nuisance species, the United States Coast Guard (USCG) has finalized a rule limiting the concentrations of organisms in ships’ ballast water discharged into U.S. Ports (U.S. Coast Guard 2012). The specified concentrations reflect those in the International Maritime Organization’s (IMO) convention (IMO 2004). In order to meet these limits, most ships will use a ballast water management system (BWMS). Many of these systems employ oxidant-based treatment technologies (e.g., sodium hypochlorite, chlorine dioxide, and ozone) to ensure that the discharge water meets the specifications.

In-line, Total Residual Oxidant (TRO) instruments are often used as part of the control systems for BWMS that employ oxidant-based treatments. The TRO instruments are used to monitor dosage (to ensure it meets treatment design requirement) and discharge concentrations (to activate a neutralization step and/or ensure environmental safety). The U.S. EPA National Pollutant Discharge Elimination System (NPDES) requires a daily maximum TRO discharge concentration of $\leq 0.1 \text{ mg L}^{-1}$, with some individual states having slightly lower discharge requirements and some other countries having slightly higher requirements. Accurate, precise and reliable measurements of TRO are therefore critical to verify the performance of oxidant-based BWMS and to assure water discharged into the environment does not exceed the regulatory or target concentrations.

As BWMS incorporate in-line TRO instruments for monitoring and control, it is important to understand the performance of these critical system control and compliance monitoring instruments, relative to a certified standard measurement of TRO. It is also important to understand the limitations of TRO instruments, considering that the source water characteristics will vary greatly.

This verification will focus on the performance of TRO instruments along a spectrum of TRO concentrations in test water with varying temperatures and salinities. The evaluation — conducted by the Alliance of Coastal Technologies (ACT) — will proceed following a standardized approach, designed to provide unbiased comparisons of technologies to a standard, or reference method. Work performed will conform to the Quality Management principles outlined in **Appendix A**. This evaluation will determine instrument accuracy and precision by

comparing instrument readings to contemporaneous analysis using the standard, DPD-based colorimetric approach for measuring TRO (APHA Standard Method: SM 4500-Cl G). While limited in scope, general observations on instrument reliability will also be recorded.

2. Goals and Objectives

The overall goal of this verification is to quantify the performance of commercially-available instruments designed to monitor TRO in shipboard ballast water treatment applications. This effort will help instrument developers/manufacturers identify strengths and weaknesses of their individual systems, provide end-users with independent performance data under relevant conditions, and to provide the fundamental information needed by regulatory and compliance monitoring agencies on data quality for this critical suite of system control and environmental safety instruments. While instrument accuracy and precision will be quantified under a range of relevant water quality conditions, it is beyond the scope of this specific set of tests to quantify reliability under “real-world” shipboard applications, thus *will not necessarily reflect the instruments’ in-service performance*. However, some basic measure of instrument reliability will be included in the laboratory testing (see below).

Individual ACT Verification Reports will be produced for each instrument tested. These reports will be reviewed by the project Technical Advisor Committee (TAC) and by the individual instrument manufacturers prior to public release on the ACT website along with the final TRO Test Protocols.

3. Verification Measurements

- **Accuracy** – a measure of the closeness of a measured value to the true or known value under multiple water quality conditions. In this case, since there is no known or true value, these verifications, the accuracies of the compliance monitoring device will be determined by making repeated (three readings at each target concentration) comparisons between device measurements and a reference standard.
- **Precision** – a measure of the repeatability of a measurement. Instrument precision will be determined by calculating the standard deviation of 10 consecutive measurements of a reference solution under stable conditions.
- **Reliability** – Reliability is the ability to maintain integrity or stability of the device and data collections over time. Reliability of instruments during the laboratory tests will be determined in two ways. First, comparisons should be made of the percent of data recovered as a proportion of the data that the device was intended to have collected over a set period of time. Second, the percentage of time, and total number of times, the device operated/functioned as designed without interruption or non-scheduled maintenance, calibration or repair will be estimated. Comments on the physical condition of the

instrument (e.g., physical damage, flooding, corrosion, battery failure, etc.) will also be recorded.

The verification of the instruments will be performed in a laboratory environment. Experiments are designed to challenge the instruments by analyzing ranges of oxidant concentrations in test water with varying temperatures and salinities. Instrument readings will be compared to the reference method, the manual, DPD-based approach (APHA Standard Method: SM 4500-Cl G). The basic measurement approach for any TRO dose follows: one analyst will transcribe the instruments' displays while a second analyst will collect a water sample for the reference method. Using the standard methods, the second analyst will add the DPD reagent and measure the color intensity with a colorimeter.

3.1. Test Method: Continuous, In-Line TRO Measurements

The instruments evaluated in this study will be either amperometric-based sensors or DPD-based analyzers with automated sample preparation and processing. All instruments are designed to process and analyze a whole water sample with minimal direct human involvement. The specific protocols for operating the test instruments will be provided by the instrument manufacturers. A recirculation pipe loop will circulate water continuously, keeping the test water well mixed. TRO instruments will be installed on a manifold on the pipe loop. Instruments evaluated will have all ancillary equipment (e.g., air compressors, AC/DC power adaptors, tubing, etc.) and reagents needed to conduct measurements. Instruments will have a local display unit, as analysts will manually record readings concurrent with sampling for the reference method. Concurrent readings will also be digitally recorded using photography. Data logged and stored will be used as a quality control to assure correct transcription of the manually recorded values.

3.2. Reference Standard: Periodic, manual measurements using the DPD-based method (Standard Method 4500-CL G)

The Reference Standard is the EPA-certified Standard Method for measuring **Total Chlorine** (equivalent to total oxidizing capacity of the sample expressed as TRO) using the DPD method (Standard Method 4500-CL G, 2017). The Hach Company (Loveland, CO, DOC316.53.01027) implements this method using a standard set of reagents and instruments following three protocols for low, medium and high total chlorine or oxidant (TRO) concentrations. The Hach methods include Method 8167 for low TRO concentrations (0.2 to 2.0 mg L⁻¹), Method 10250 for medium TRO concentrations (2.0 to 4.0 mg L⁻¹), and Method 10070 for high TRO concentrations (4.0 to 10 mg L⁻¹). The full protocols are available at <https://www.hach.com>. Briefly, a specified amount of sampled water is transferred into a sample cell and processed. A pre-measured quantity of dry powder DPD reagent for Total Chlorine is added to the vial, which is mixed for 20-seconds, allowed to sit for 3-6 minutes, then analyzed using a hand-held colorimeter. Hach Company hand-held colorimeters will include the Pocket Colorimeter II for low range TRO concentrations, and the DR300 Pocket Colorimeter for medium and high TRO

concentrations. Calibration checks using gel standards will be performed daily on all instruments.

3.3. Ancillary Measurements: Temperature, conductivity, salinity, pH, DOC, POC, TSS

Ancillary measurements will track the water characteristics over the course of the experiments. In each tank, temperature, conductivity, and salinity will be measured using a YSI EXO-02 multi parameter instrument. Measurements will be logged throughout each test. We will also spot-check and record temperature, conductivity and salinity throughout test using a hand held YSI Pro DSS. At each oxidant dose, pH will be measured using an Orion Star A214 benchtop pH meter via grab samples from each tank. Dissolved and particulate organic carbon (DOC and POC, respectively) and total suspended solids (TSS) concentrations will be measured using grab samples from each tank at the start and end of the trial day. Sampling and analyses will follow standard protocols used by ACT and affiliated organizations (see Appendix C).

4. Laboratory Methods

4.1. Test Water Preparation

Laboratory tests will use a range of concentrations of oxidant in three different salinities and at three different temperatures. Three water tanks will be prepared in parallel with identical parameters except for temperature. Tank water will be augmented with the addition of dissolved organic matter (DOM, final concentration: 6 mg L⁻¹), and particulate organic carbon (POM, final concentration: 4 mg L⁻¹), which are used to achieve ‘challenge water’ conditions employed in ballast water management system (BWMS) certification testing (US EPA, 2010). Note, materials will be added as total mass (DOM and POM), but measurements are based upon carbon mass only (DOC and POC). Each tank will be modified by the addition of sea salts (conforming to ASTM D1141-98) to achieve to a salinity of **0.2, 15, or 30 psu**. All tanks will receive equal doses of oxidant at **30-45 minute** intervals to capture a TRO range from **no oxidant added to 10 mg L⁻¹** (most commonly used for currently commercially-available BWMS). Water temperature targets ranges are **7-10, 15-18, or 24-28°C**. For each trial day, the salinity for the three tanks will be in the same range, but each tank will have a different water temperature. Test tank temperatures will be adjusted and stabilized through the use of water circulators that can chill or heat. To minimize temperature fluctuations, the test tanks will be covered and insulated.

4.2. Tank and Pipe Loop

The water tanks are rectangular plastic containers (86 x 53 x 81cm; ~340 L)¹. Each tank will be fitted with a recirculation pump (Fig. 1). The recirculation pump will move tank water through a manifold which separates the water flow into multiple parallel sample lines, each line dedicated to a single TRO meter. Meters which rely on DPD technology will sample from dedicated lines and discharge any waste or rinse water into a separate waste collection container. One parallel line will be dedicated to sample collection for standard TRO analysis. All parallel lines will return unused water back to water tank for continuous mixing and recirculation.

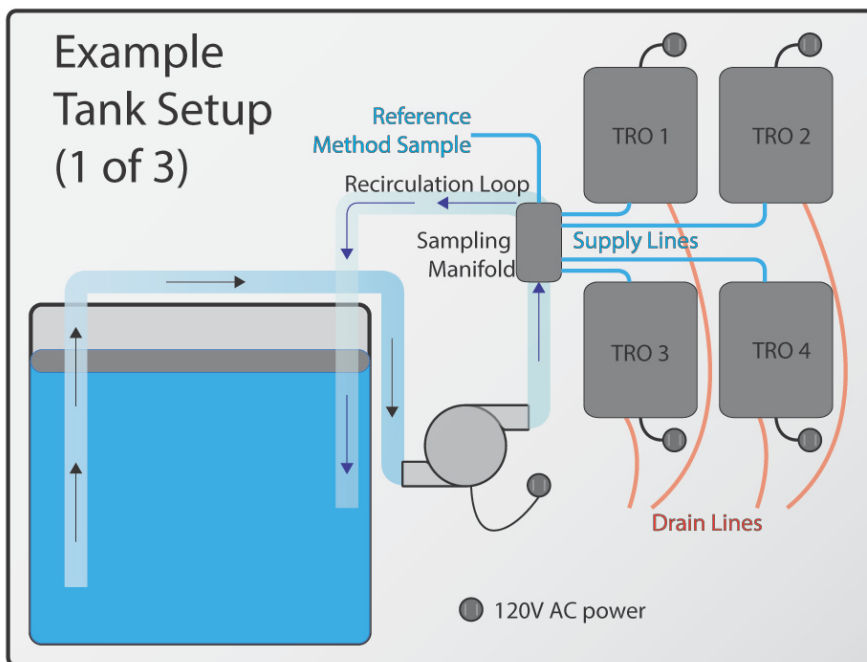


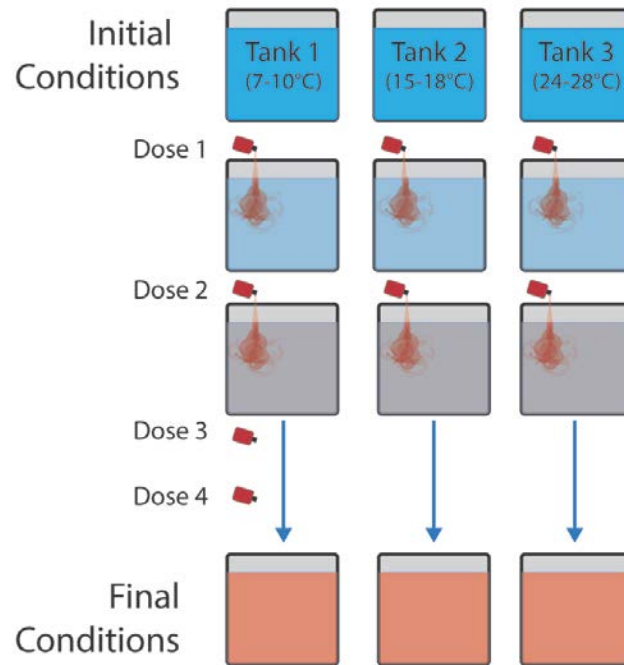
Figure 1. Test water tank recirculation loop. This shows one of three test tank setups that will be operating concurrently.

4.3. TRO Dose Escalation

Analysis will begin at baseline, prior to the addition of sodium hypochlorite (no oxidant added). Once analysis begins, aliquots of sodium hypochlorite will be added simultaneously and equally in to each tank, step-wise every until a final target TRO concentration of **10 mg L⁻¹** is achieved (Fig. 2).

¹Imperial units: 34" x 21" x 32"; 90 gal.

Figure 2. Dosing plan. The experiment will start with analysis of the test water in the initial condition – no oxidant added. Periodically, chlorine (in the form of sodium hypochlorite) will be added to achieve target doses and finally reach the maximum target concentration (10 mg L^{-1}).



4.4. Synchronous recording from instruments and sampling for the reference method

Regardless of whether an electronic data logging system is available, all readings will be manually recorded (and photographed) for each meter concurrent to taking the water sample for the reference analyses. As multiple actions are completed nearly simultaneously, two analysts are needed for each tank. An example timeline for each TRO level is below, with actions assigned to either analyst. Actual times may vary, depending on the pre-test practice runs.

5. Experiments

5.1. Accuracy

Accuracy will be measured by comparing the contemporaneous measurements from the instrument to the reference method. Trial for accuracy will be performed using the test water described above, with varied temperatures and salinities and with added DOM and POM. Trials will be conducted over three days, with a single salinity and three water temperatures tested in each of the three tanks per day (Appendix B).

5.2. Precision

Precision will be performed using low temperature (7-10°C) water, with salinity set to 15 psu. DOM and POM *will not* be added, to minimize the consumption of TRO. Precision will be

measured as the coefficient of variation among 10 repeated readings (collected consecutively every 2.5 minutes) at a single measured dose.

5.3. Natural water tests

A single trial will be performed using ambient seawater from the University of Maryland Center for Environmental Science's seawater supply (typically 8-12 psu, likely 24-26°C). The seawater will contain typical constituents of estuarine water (microorganisms, zooplankton, dissolved and particulate organic matter, etc.). Accuracy will be measured along the range of doses used for other accuracy trials. A single tank will be used.

5.4. Alternative oxidant

A single tank will also be used to measure accuracy, using an alternative oxidant with 15-18°C, 15 psu water. Instead of sodium hypochlorite, NaDCC will be used for the four doses. This trial will be comparable to the trial with the same temperature and salinity using sodium hypochlorite as the oxidant.

6. Data Recording and Archiving

The procedures outlined here are similar to those used in other test protocols published by the Alliance for Coastal Technologies (ACT; www.act-us.info). An example protocol describes the data recording procedures for water quality analyses (MERC, 2013). Data logs for TRO readings are recorded throughout the day of analyses and will be archived daily. The datasheets are signed upon completion and stored until the data are manually logged into a digital file. The Quality Officer (QO) verifies that each datasheet has been completed and correctly logged into a digital format. Data reported by the instrument will be manually transcribed on formatted data sheets, which will be tailored to each instrument's data output. Additionally, data from other analyses will be recorded in standard formats such as data collection forms, bound and paginated laboratory and field notebooks, spreadsheets, and electronic data files.

Hand-written data logs and records are submitted to a team member familiar with the parameter for review, and the originator and the reviewer both sign, date, and initial the form. The originator creates a digital copy of the document, and both the digital document and the hand-written form are turned into the data manager (DM) at the end of the day. The DM files the hard copies in a binder specific to the trial and uploads the digital scans to a secured website that is backed up daily to an offsite location. All the documents (both hand-written and digital) must include the test cycle number, the sample date, and other relevant metadata. Data on hand-written forms are also transcribed into electronic data files. Each of the fields is included in a raw data table in a spreadsheet compatible with Microsoft Excel. Data on data sheets are manually entered into the spreadsheet and the entry is verified by a second analyst. Datasheets will have signature lines for the analyst recording the data, entering the data, and reviewing the

data entry; all analysts will sign the data sheet analysis collecting the data upon the completion and verification of their task. Data sheets are assigned a unique identification code so that the data in electronic data tables can be quickly traced back to the original data sheet. Chain-of-custody forms will be used as needed.

7. Data Analysis

Accuracy is measured relative to the standard, reference method using a standard approach (e.g., percent difference). Precision is measured as the variation among replicate readings and subsamples. Additional analyses may also be performed, e.g., linear regression to compare readings from the test method to the reference method.

8. Roles and Responsibilities

The Chief Scientist has the overall responsibility for ensuring that the technical goals and schedule established for the verification are met. The Chief Scientist will:

- Prepare the Test Protocols in consultation with TAC and staff.
- Coordinate testing, measurement parameters, and schedules.
- Ensure that all quality procedures specified in the Test Protocols are followed.
- Respond to any issues that may arise during the tests.
- Serve as the primary point of contact for participants and testing staff.
- Ensure that confidentiality of proprietary participant technology and information is maintained.

The QA Manager will:

- Review the Challenge Test Protocols.
- Conduct technical audit and data quality assessments.
- Notify the Chief Scientist if a stop work order should be issued if audits indicate that data quality is being compromised or if proper safety practices are not followed
- Verify implementation of any necessary corrective action.
- Prepare audit reports.

Testing Team:

- Assist in developing the Test Protocols.
- Select a secure location for the tests.
- Support participants in the setting up test instrument.
- Operate test instrument as described in user manual.
- Perform sample collections as detailed in the Test Protocols.

- Provide all test data to the Chief Scientist electronically, in a mutually agreed upon format.

Verification participants will:

- Commit to a specific set of location and dates for testing according to the Test Protocols.
- Assist with setup, calibration, and takedown of test instruments at the location and dates agreed to.
- Provide a complete user manual and all materials, supplies and equipment needed to setup, calibrate, deploy, operate, maintain and recover test instruments data.

The Technical Advisory Committee will:

- Review and comment on Test Protocols.
- Provide specific advice during testing, as needed.
- Review and comment on individual final reports
- TAC members include (alphabetically)
 - Richard Everett, U.S. Coast Guard
 - Ray Frederick, U.S. Environmental Protection Agency
 - James Jensen, University at Buffalo, SUNY
 - Carolyn Junemann, U.S. Department of Transportation Maritime Administration
 - Gail Roderick, U.S. Coast Guard Research and Development Center

9. Schedule

[TBD]

10. References

4500-Cl Chloride (2017) Standard Methods For the Examination of Water and Wastewater, 23rd.
<https://doi.org/10.2105/SMWW.2882.079>

ASTM D1141-98 (Re-approved 2013) Formula A, Table X1.1. Original Standard: ASTM D 1141-52, Formula A, Table 1, Section. *Standard Practice for the Preparation of Substitute Ocean Water*.

American National Standards Institute and American Society for Quality Control (ANSI/ASQC), 2004. *Quality Systems for Environmental Data Collection and Environmental Technology Programs: Requirements with Guidance for Use*. E4-2004. Milwaukee, WI.

International Maritime Organization; IMO (2004) International convention for the control and management of ships' ballast water and sediments.
<http://www.imo.org/OurWork/Environment/BallastWaterManagement/Pages/BWMConventionandGuidelines.aspx>

US Coast Guard (2012) Standards for living organisms in ships' ballast water discharged in U.S. waters. Federal Register 77:17254–17320

US Environmental Protection Agency (2013) Vessel General Permit for Discharges Incidental to the Normal Operation of Vessels (VGP). Washington, DC,
http://water.epa.gov/polwaste/npdes/vessels/upload/vgp_permit2013.pdf

Hach Co. (2018) Chlorine, Free and Total, High Range, DPD Method 10069 (free)/10070 (total), Powder Pillows, DR300 and Pocket Colorimeter II. DOC316.53.01490. Date: 03/2018, Edition 2.

Hach Co. (2018) Chlorine, Free and Total, Mid-Range, DPD Method 10245 (free)/10250 (total), Powder Pillows, DR300 and Pocket Colorimeter II. DOC316.53.01451. Date: 12/2018, Edition 2

Hach Co. (2018) Chlorine, Free and Total, Low-Range, DPD Method 8021 (free)/8167 (total), Powder Pillows, DR300 and Pocket Colorimeter II. DOC316.53.01450. Date: 12/2018, Edition 4

Appendix A: Quality Management

Work performed for this project will be conducted following the quality management system (QMS) developed by the Alliance for Coastal Technologies (ACT). The QMS is a comprehensive set of policies, processes, and procedures that ensure that the quality of data, products, and services consistently meet or exceed meeting the clients stated quality requirements and comply with all applicable quality standards. The QMS also ensures that data collection and processing activities are carried out in a consistent manner, to produce data of known and documented quality that can be used with a high degree of certainty by the intended user to support specific decisions or actions regarding technology performance. The QMS provides the framework for quality assurance (QA) functions, which cover planning, implementation, and review of data collection activities and the use of data in decision making, and quality control (QC), which is a technical function that includes all the scientific precautions that are needed to acquire data of known and adequate quality. ACT's QMS meets the requirements of ISO/IEC 17025:2017(E), *General requirements for the competence of testing and calibration laboratories*; the American National Standards Institute (ANSI)/American Society for Quality (ASQ) E4-2004 *Quality Systems for Environmental Data and Technology Programs*; and U.S. Environmental Protection Agency, quality standards for environmental data collection, production, and use. Preventive actions will be made throughout this evaluation to anticipate and resolve potential problems before the quality of performance is compromised. The QA/QC procedures for this evaluation will follow the requirements described in this protocol, any vendor specified requirements, and the general principles and specific QA/QC from technical documents. 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 Principle Investigator (PI), who will work with the Quality Assurance (QA) Manager and Technical Advisory Committee (TAC) 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.

Additional information on the sections below can be found in:

ACT/SOP/QS/TSA 1.0 – Technical Systems Audit;
ACT/SOP/QS/CA 1.0 – Corrective Actions
ACT/SOP/QS/ QCFL1.0 - Quality Control for Field Samples and Laboratory Analyses;
ACT/SOP/QS/TETP 1.0 – Technology Evaluation Test Protocols;
ACT/QS/QMP 2.0 – Quality Management Plan; and
ACT/QS/QAPP 1.0 – Quality Assurance Project Plan.
(all documents available upon request)

A1. Quality Control Requirements for Field Samples and Laboratory Analyses

The three major categories of QC checks are accuracy, precision, and contamination. Accuracy is assessed by measuring percent recovery of a known quantity of analyte (e.g. via a matrix spike or laboratory control spike) and comparing it against prescribed acceptability limits. Precision is assessed by calculating the relative difference between analytical results for replicate samples and comparing the relative percent difference (RPD) against prescribed acceptability limits. Contamination is assessed using blank samples to identify sources of contamination. QC sample data provide an estimate of the total uncertainty in the data set.

Field QC represents the total integrated program for assuring the reliability of measurement data. It consists of the daily field logs, sample handling and custody procedures, and QC samples. For this verification, “field” is considered the water tanks set up in the laboratory. QC samples collected from the test tanks include concurrent replicate samples and field blanks. Replicate samples assess variability attributable to collection and handling of the samples. Concurrent replicates also provide basic QC data for the variability inherent in the aqueous system across a short distance in space and time. Field blanks are used to evaluate whether contamination is introduced during sampling.

Laboratory or analytical QC refers to all those processes and procedures designed to ensure that the results of laboratory analysis are consistent, comparable, accurate and within specified limits of precision. The minimum analytical quality controls needed to perform the method are initial demonstration of laboratory capability and method calibration (Standard Methods). The initial demonstration of capability (IDC) is done by analyzing for mid-range concentration laboratory-fortified blanks (LFB) and calculating the percent recovery for each. An IDC is performed initially by each analyst. Method calibration will follow the protocols described in Hach Method 8167. Recommended additional analytical QC measures for each analytical batch (for up to 20 samples) include:

- Method blank, (MB) is a volume of reagent water in which no target analytes or interferences are present at concentrations that impact the analytical results. The MB evaluates contamination from the sample preparation and measurement process only.
- Laboratory-fortified blank (LFB), also called a laboratory control sample (LCS) is a blank water sample, free from the analytes of interest, spiked with verified known amounts of analytes from the same source as the calibration standards. The LFB is processed through the entire analytical method.
- Replicate analysis of random samples.

Quality control measures are implemented by technical staff and monitored by the PI. The responsibility for interpreting the results of QC checks with the QA Manager. Resolution any potential problems resides with the PI, in conjunction with the QA Manager.

A2. Quality Assessment

Quality assessments include technical audits and data quality assessments. Fundamental principles of the assessment process include:

- Assessments are performed by the QA Manager, who is independent of direct responsibility for performance of the Verification.
- Each assessment is fully documented.

- Each assessment must be responded to by the appropriate level of the testing team. Quality assessment reports require a written response by the person performing the inspected activity, and acknowledgment of the assessment by the PI.
- 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 PI.

A3. Technical Audits

Technical audits are systematic and objective examinations of the verification test implementation to determine whether data collection activities and related results comply with the test protocol, are implemented effectively, and are suitable to achieve its data quality goals. Audits for the TRO performance verification will include technical system audits (TSA) and audits of data quality (ADQ). The PI is responsible for ensuring that audits are conducted as part of this verification.

A3.1 Technical System Audit

A TSA is a thorough, systematic, and qualitative evaluation of the sampling and 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 test protocol, published reference methods, and associated procedures. The TSA assesses test facilities, equipment maintenance and calibration procedures, reporting requirements, sample collection, analytical activities, and QC procedures. Both laboratory and field TSAs are performed.

The QA Manager will conduct a TSA of the laboratory component and at least one field test during the verification. The TSA is performed following the Environmental Protection Agency (EPA) document *Guidance on Technical Audits and Related Assessments for Environmental Data Operations* (EPA QA/G-7, January; 2000). A TSA checklist based on the test protocol is prepared by the QA Manager prior to the TSA and is reviewed by the PI. At the close of the TSA, an immediate informal debriefing will be conducted. Non-conformances are addressed through corrective action. The QA Manager will document the results of TSAs and any corrective actions in a formal audit report. The TSA report will be prepared within approximately 30 days of completion of the audit.

A3.2 Audit of Data Quality

An 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 test protocol and associated procedures and to verify 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 by the QA Manager after data have been 100% verified by the technical staff. 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.

Problems that could impact data quality are immediately communicated to the PI. The results of the ADQ are documented in a formal audit report with conclusions about the quality of the data from the verification and their fitness for their intended use.

A4. Data Quality Assessment

The QA Manager reviews all data so that only sound data that are of known and documented quality and meet technology testing quality objectives are used in making decisions about technology performance. A data quality assessment (DQA) is conducted in two phases. The first phase, data verification and validation, consists of reviewing and determining the validity of the analytical data. The second phase, usability assessment, consists of interpreting the data to determine its applicability for its intended use. ADQA report documents the results of a quality assurance review of data. The report addresses three data quality factors:

- Sample representativeness;
- Data accuracy; and
- Usability of the data for decision-making.

The report generally includes:

- A summary description of the data review process;
- A summary of the data verification and data validation results that highlights significant findings and a discussion of their impact on data usability;
- A discussion of the statistical tests for sample representativeness and data accuracy; and
- A recommendation or decision on the usability of the data set for the project's decision-making.

A4.1 Data Verification

Data verification is the process of evaluating the completeness, correctness, and consistency of the test data sets against the requirements specified in the test protocol. Data verification is conducted by the QA Manager. The process includes verifying that:

- The raw data records are complete, understandable, well-labeled, and traceable;
- All data identified in the test protocol has been collected;

- Instrument calibration and QC criteria were achieved;
- Data calculations are accurate.

Corrective action procedures are implemented if data verification identifies any non-compliance issues.

A4.2 Data Validation

Data validation evaluates data quality in terms of accomplishment of measurement quality objectives, such as precision, bias, representativeness, completeness, comparability, and sensitivity. Data validation:

- Establishes that required sampling methods were used and that any deviations were noted;
- Ensures that the sampling procedures and field measurements met performance criteria and that any deviations were noted;
- Establishes that required analytical methods were used and that any deviations were noted;
- Verifies that QC measures were obtained and criteria were achieved; and that any deviations were noted.

Data validation is performed by the QA Manager. Any limitations on the data and recommendations for limitations on data usability are documented.

A4.3 Data Usability

Data usability assessments determine the adequacy of the verified and validated data as related to the data quality objectives defined in the test protocol. All types of data and associated information (e.g., sampling design, sampling technique, analytical methodologies) are evaluated to determine if the data appear to be appropriate and sufficient to support decisions on technology performance.

A data usability assessment has an analytical and a field component. An analytical data usability assessment is used to evaluate whether analytical data points are scientifically valid and of a sufficient level of precision, accuracy, and sensitivity. The field data usability assessment evaluates whether the sampling procedure (e.g., sampling method, sample preservation and hold times) ensures that the sample that is collected for analysis is representative.

A5. Corrective Action

Corrective action is implemented in response to any situation that compromises the quality of testing or data generated in the execution of this project. The need for corrective action can be identified by any project personnel and implemented with the prior approval of the PI, in consultation with the QA Manager. The PI is responsible for determining appropriate corrective action to address an issue. Any findings that have a direct impact on the conduct of the

verification test will be corrected immediately following notification of the finding. Implementation of corrective actions must be verified by the 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. All corrective actions are documented. Any impact that an adverse finding had on the quality of the verification test data is addressed in the corrective action report. The report includes:

- Identification of nonconformity;
- Description of extent of the nonconformity with respect to achievement of the project's objectives;
- Findings and conclusions;
- Determination of cause to prevent reoccurrence;
- Corrective action taken and implemented; and
- Follow-up by the QA Manager to document the effectiveness of solutions.

A6. Audit Reporting

The QA Manager is responsible for all audit reports. These written reports focus on whether the test activities and related analytical results:

- Comply with the Test Protocol and related SOPs,
- Are implemented effectively, and
- Are suitable to achieve data quality goals.

An audit report usually consists of:

- An introduction describing the date, location, purpose, and scope of the audit;
- A detailed account of the findings and their basis;
- Conclusions, including a discussion of any findings requiring corrective action; and
- Recommendations (if requested) for resolving problems that affect quality.

Findings are audit results that can generally be divided into three categories:

- Noteworthy practices or conditions;
- Observations, which are neither positive nor negative; and
- Nonconformances, which are deviations from standards and documented practices (e.g., Test Protocol, SOPs, reference methods).

Nonconformances can be divided into two subcategories:

- Deficiencies, which adversely impact the quality of results, and
- Weaknesses, which do not necessarily (but could) result in unacceptable data.

Appendix B. Trial and Sample Matrix

Table B1. Trial list separated by workday. Days 1-3 will focus on accuracy across a temperature and salinity gradient. Day 4 will examine precision at one temperature, one salinity, and one dose. Day 5 will examine using an alternative oxidant, plus, the use of ambient (Chesapeake Bay) water.

Trial Day	Tank ID	Purpose	Trial Date	Temperature	Salinity	Target Doses (mg L⁻¹)
Day 1	A	Accuracy	TBD	7-10°C	0.2 psu	Steps: *NOA plus 4 doses
Day 1	B	Accuracy	TBD	15-18°C	0.2 psu	Steps: NOA plus 4 doses
Day 1	C	Accuracy	TBD	24-28°C	0.2 psu	Steps: NOA plus 4 doses
Day 2	A	Accuracy	TBD	7-10°C	15 psu	Steps: NOA plus 4 doses
Day 2	B	Accuracy	TBD	15-18°C	15 psu	Steps: NOA plus 4 doses
Day 2	C	Accuracy	TBD	24-28°C	15 psu	Steps: NOA plus 4 doses
Day 3	A	Accuracy	TBD	7-10°C	30 psu	Steps: NOA plus 4 doses
Day 3	B	Accuracy	TBD	15-18°C	30 psu	Steps: 0 plus 4 doses
Day 3	C	Accuracy	TBD	24-28°C	30 psu	Steps: NOA plus 4 doses
Day 4	A	Precision	TBD	7-10°C	15 psu	Single medium dose
Day 5	A	Ambient	TBD	Ambient	8-12 psu	Steps: NOA plus 4 doses
Day 5	B	Alt. oxidant	TBD	15-18°C	15 psu	Steps: NOA plus 4 doses

TBD = to be determined.

*NOA = No oxidant added

Appendix C. Relevant Standard Operating Procedures

Available Upon Request

ACT.MERC SOP# TRO 2.3 *Total Residual Oxidant Determination Using the Chlorine Hach Pocket Colorimeter II Standard Operating Procedure (Rev. 7.0) for the low chlorine concentration 0.02 to 2.0 mg L⁻¹.*

ACT.MERC SOP# TRO DR300 *Total Residual Oxidant Determination Using a Hach DR300 Standard Operating Procedure (Rev. 1.0) for the the Mid-range chlorine (0.05 to 4.0 mg/L Cl₂) and high-range chlorine (4 to 10.0 mg L⁻¹ Cl₂).*

ACT/SOP/QCFL 1.0 - *Quality Control for Field Samples and Laboratory Analyses* (2018)

ACT/SOP/TSA 1.0 - *Technical Systems Audit* (2015)

MERC/SOP/WQI 4.0 – *Water Quality Instrumentation.*

MERC/SOP/WQA 2.2 – *Water Quality Analysis.*

NASL/SOP – *Determination of Dissolved Organic Carbon (NPOC), Total Organic Carbon, and Dissolved Inorganic Carbon in Fresh/Estuarine/Coastal Waters Using High Temperature 28 Combustion and Infrared Detection.*

NASL/SOP – *Determination of Carbon and Nitrogen in Particulates and Sediments of Fresh/Estuarine/Coastal Waters, Plant and Animal Tissue and Soils Using Elemental Analysis.*

NASL/SOP – *Determination of Total Suspended Solids and Total Volatile Solids in Fresh/Estuarine/Coastal Waters.*