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ACT VS20-01

PERFORMANCE VERIFICATION STATEMENT
For the SWN-P Total Residual Oxidant (TRO) Sensor: Halogen Systems

TECHNOLOGY TYPE:	Total Residual Oxidant (TRO) analyzers
APPLICATION:	Shipboard ballast water treatment
PARAMETERS EVALUATED:	Accuracy and precision
TYPE OF EVALUATION:	Laboratory performance verifications
DATES OF EVALUATION:	September - October 2019
EVALUATION PERSONNEL:	M.R. First, S.H. Robbins-Wamsley, J. Barnes, K. Davis, M. Getrich, T. Schick, A. Schick, E.N. Buckley, G. Ziegler, and M.N. Tamburri

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1. Background

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 or chlorine dioxide) to ensure that the discharge water meets the specifications.

In-line, Total Residual Oxidant (TRO) instruments are often used as part of a Supervisory Control and Data Acquisition (SCADA) system for BWMS that employ oxidant-based treatments. Within a SCADA system, TRO measurements verify the BWMS meets its treatment specifications, but the measurements may also control dosage or neutralization. The TRO instruments must resolve low concentrations of oxidants to verify compliance with discharge standards well below 1 mg L^{-1}. For example, the U.S. EPA National Pollutant Discharge Elimination System (NPDES) requires a daily maximum TRO discharge concentration of ≤ 0.1 mg L^{-1}, but states or regional authorities may have set lower discharge limits. Therefore, accurate, precise, and reliable measurements of TRO are critical to verify the performance of oxidant-based BWMS and to assure water discharged into the environment does not exceed the regulatory concentrations.

The Alliance for Coastal Technologies (ACT) conducted a verification of the performance of in-line, automated TRO instruments incorporated or designed to be used in BWMS. ACT was established on the premise that independent verification and validation of existing and emerging technologies is essential to facilitate the transitioning of ocean technologies to operational use. The overall goal of ACT's verification program is to document technology performance and potential and to provide technology users with information required for operational use. ACT verifications:

- assist instrument developers and manufacturers to identify strengths and weaknesses of their individual systems,
- provide end-users with independent performance data under relevant conditions, and
- 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.

It is important to note that ACT does not certify technologies or guarantee the levels verified. ACT does not seek to determine regulatory compliance; does not rank technologies or compare their performance; does not label or list technologies as acceptable or unacceptable; and does not seek to determine "best available technology" in any form.

The goal of this Performance Verification was to quantify the performance of instruments designed to monitor TRO in ballast water treatment applications. The verification compared instrument readings to contemporaneous analyses using the standard, DPD[1]-based colorimetric approach for measuring TRO (APHA Standard Method: SM 4500-Cl G). Concentrations of TRO ranged from No Dose to 10 mg L^{-1} reflecting doses relevant to water disinfection. Test water was prepared from deionized water, augmented with dissolved and particulate organic carbon and adjusted to meet target temperatures and salinities reflecting the range of water types processed by BWMS. The verification followed ACT's standardized test procedures, which are designed to provide unbiased comparisons of technologies to a standard, or reference method. Work performed conformed to ACT's quality management systems and is described in the Test Plan **(Appendix A).**

We evaluated the instruments based primarily upon quantitative measurements of accuracy and precision. Laboratory-based testing occurred using a range of relevant water quality conditions, but it was beyond the scope of this specific set of tests to quantify reliability under "real-world" shipboard applications. Therefore, these findings *may not necessarily reflect the instruments' in-service performance*. However, we included some basic measurements of instrument reliability during the laboratory-based testing, which occurred over four [4] weeks. The verification measurements are described below:

- **Accuracy** is a measure of the *closeness* of a measured value to the *true* or *known* value. In this case, since there was no *known* or *true* value, the accuracy of the TRO instruments was determined by comparing measurements from the instrument to the reference method.
- **Precision** is a measure of the repeatability of a measurement. Instrument precision was determined by calculating the standard deviation of 12 consecutive measurements of a single, stable dose level.
- **Reliability** is the ability to maintain functionality of the device and stability of data collections over time. Reliability of instruments during the laboratory tests was determined in two ways. First, comparisons were 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. The physical condition of the instrument (e.g., physical damage, flooding, corrosion, battery failure, etc.) were qualitatively described.

2. Instrument Technology Tested

This report describes the test of the **Halogen Systems SWN-P Total Residual Oxidant Sensor** (hereafter, SWN-P TRO sensor). The instrument uses an amperometric-based approach, and the sensor is designed for direct insertion into a pipe with flowing sample water. For testing, the SWN-P TRO sensor was inserted into a pipe loop with continuously recirculating water. The instrument relayed a signal to a data acquisition unit, connected to a laptop computer. Software

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[1] N,N'-diethyl-p-phenylenediamine

on the laptop computer displayed and logged instrument measurements. The instrument display panel reported the current TRO reading in parts per million (ppm)[2].

3. Evaluation Methods

The test plan was developed in consultation with a Technical Advisory Committee (TAC), and the TAC, as well as instrument vendors, reviewed a draft version of the test plan. All test participants approved the final version of the test plan (**Appendix A**) prior to testing. In general, trials examined either ***Accuracy*** or ***Precision***: ***Accuracy*** trials varied TRO concentration (the "dose"), and over the course of trial day, collected three side-by-side readings from the instrument and from the reference method at each dose level. ***Precision*** trials only used a single dose, but collected 12 consecutive samples paired with instrument readings. Trials examined test water with salinities and temperatures experimentally controlled, except one trial, which used ambient water from the Chesapeake Bay (Table 1. Experimental matrix.). The test plan details the experimental and analytical methods; here and in the following sections, we provide a brief summary of the test methods.

Table 1. Experimental matrix. Tanks were monitored with the same unit throughout all of the trials. Values in parentheses were the values measured in ambient seawater; in other cases, values were target values achieved by manipulating water salinity and temperature.

	Salinity (psu)	Temperature (°C)		
Trial Day	All Tanks	Tank 1	Tank 2	Tank 3
Accuracy Trials				
1 (25-Sep-2019)	15	10	18	25
2 (26-Sep-2019)	30	10	18	25
3 (08-Oct-2019)	0.2	10	18	25
4 (01-Oct-2019)*	15	18		
5 (09-Oct-2019)**	Ambient (16)			Ambient (21)
Precision Trials				
6 (03-Oct-2019)	15		10	

* Alternative oxidant

** Ambient water

3.1. Tank and Pipe Loop

Tests operations occurred within a tank and piping system, which continuously circulated test water through a pipe loop that supplied the TRO instrument and the sample port used for manual sampling. Three tank and piping systems allowed up to three concurrent tests on a single trial

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[2] For the purposes of this validation, ppm and mg L^{-1} are considered equivalent. The conversion between the two units incorporates the density of the sample water. For freshwater, where water density is close to 1 kg L^{-1}, the units are effectively interchangeable. For seawater, however, water density is >1 kg L^{-1}, and the values will differ based upon the unit. However, the difference between units is fairly small (2-3%, where ppm values are lower than mg L^{-1} values).

day, and accuracy trials employed three separate instruments ("units") — each unit dedicated to its own tank and piping system. The tanks — rectangular plastic containers (86 x 53 x 81cm; ~340 L)[3] — were insulated and kept covered throughout to maintain water temperatures and minimize loss through evaporation.

3.2. Test Water

With the exception of a single trial conducted using ambient water, test water was prepared using Type I or Type II deionized (DI) water (hereafter, DI water), which was either produced onsite or shipped in bulk from a supplier. Tanks and piping systems were rinsed with DI water and dried prior to each use. The afternoon before the trial day, we filled each tank with 340 L of DI water.

Test water salinity was modified by the addition of sea salts (conforming to ASTM D1141-98) to achieve to a salinity of **0.2, 15, or 30 psu**. We then added lignosulfonic acid calcium salt (Sigma-Aldrich, Saint Louis, MO; CAS: 8601-52-7) and micromate (micronized humates, Mesa Verde Humates, Lot # 2017) as surrogates for natural dissolved and particulate organic carbon (DOC and POC), respectively. The added materials targeted 6 mg L^{-1} and 4 mg L^{-1} of DOC and POC, respectively, which are concentrations required for certification testing of BWMS (US EPA, 2010)[4]. Water temperature was set and maintained at either 10°C, 18°C, or 25°C using temperature-controlled, refrigerated water circulators (hereafter, "chillers"). The chillers circulated DI water through stainless steel, coiled tube heat exchangers submerged in the test water. At the start of the trial, the tank temperature, salinity, and pH were manually measured to verify values were in the ranges specified in the test plan.

3.3. Tank and Pipe Loop

Tanks were the center of a piping and instrumentation system. We assembled three test tanks and piping systems, allowing concurrent testing of three water types on a single day. All testing occurred at the University of Maryland Center for Environmental Sciences' Chesapeake Biological Laboratory (Solomons, MD). Work occurred in a laboratory environment: the test tanks, pipe loops, instruments, and analytical stations were all in an indoor, temperature-controlled laboratory.

3.4. Dosing

Oxidant was added to the test water as sodium hypochlorite (CAS: 7681-52-9), except for the alternative oxidant trial which used sodium dichloroisocyanurate dihydrate (NaDCC, Batch: MKBW2677V). ***Note:** the manufacturer opted not to participate in the trial with the alternative oxidant.* Small-scale, benchtop tests prior to the trials determined the volumes and concentrations required to achieve the target doses and estimate the rate of TRO consumption. During full-scale

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[3] Imperial units: 34" x 21" x 32"; 90 gal.

[4] **Note:** materials will be added as total mass (DOM and POM), but measurements are based upon carbon mass only (DOC and POC).

testing, we poured a pre-measured volume (ranging from ~10-80 mL) into the center of the tank. The oxidant quickly mixed into the test water, as the pipe recirculation loop and two submerged mixing pumps kept the water well homogenized. We verified mixing efficiency prior to conducting trials by introducing a dye into a tank filled with municipal water. Within seconds, the advection of water from water pumps homogenized the dye. In ***Accuracy*** trials, four doses were added to yield target TRO concentrations within the following ranges:

- < 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)

In the ***Precision*** trial, a single dose was added to yield a target TRO concentration of 3-4 mg L^{-1}. After dosing, we monitored TRO concentrations in the tanks by collecting grab samples from the surface and immediately analyzing the samples using the reference method. Sampling commenced when concentrations were within the target range.

3.5. Sampling

In all trials, samples were collected prior to the first dose ("no dose") and after each dose when the TRO concentration was estimated to be in the target range. The sampling operation involved multiple personnel, including one person stationed at the sample port of each tank and one person stationed at the instrument's display. The manual sample port fed a semi-rigid, plastic tube, which continuously flowed water (directing the flow beneath the water's surface). For rinsing and sampling, analysts removed the tube from its sheath and directed water into sample bottles—250-mL bottles with opaque, glass surfaces cleaned and rinsed with DI water. Samplers rinsed the bottles three times with sample water prior to filling completely, overflowing the bottle's mouth, and then capping the bottle. External surfaces of the bottles were DI rinsed, then dried, and the sample was immediately delivered to an analyst—one dedicated to each tank—who performed the reference method. The process was repeated exactly five minutes after the start of the first sample and repeated again after another five minutes, yielding three samples of each dose level. For the *Precision* trial, the process was repeated until 12 samples were collected at a single dose.

3.6. Instrument Data Collection

At the start of each of the three sampling times, a person stationed at the instrument's display digitally photographed the TRO reading. The photograph provided a time-stamped record of the displayed value and verification of transcription of the value, which occurred during the intervals between or after sample collection. The values were also manually recorded onto a datasheet.

3.7. Ancillary Measurements

Ancillary tank measurements included periodic temperature, conductivity, and salinity readings during the 5-minute intervals between sampling using a YSI ProDSS multi-parameter instrument. Readings were transcribed from the instrument's data logger.

At the start of the trial day, prior to the addition of the first dose, we collected 8.25-L for analysis for water quality characteristics:

- Total suspended solids (TSS)
- Particulate organic carbon (POC)
- Dissolved organic carbon (DOC)
- pH

Note: Particulate carbon (PC) and particulate inorganic carbon (PIC) were analyzed. Since PIC was at or below detection limits, PC served as a proxy for POC during these tests.

3.8. Analysis Using the DPD-based, Reference Method

The reference method used for these trials was 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). We used the instruments and reagents supplied by The Hach Company (Loveland, CO) and followed Hach 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, either 5 or 10 mL of sampled water was transferred into a sample cell, and a pre-measured quantity of dry powder DPD reagent for **Total Chlorine** was added to the vial, which is mixed for 20-seconds, allowed to sit for 3 minutes, then analyzed using a hand-held colorimeter (within 6 minutes). The Pocket Colorimeter II was used to measure low TRO concentrations (<1 mg L^{-1}), so it was used for "no dose" and Dose 1 of the Accuracy Trials. The DR300 Pocket Colorimeter was used to measure concentrations ≥ 1 mg L^{-1}, so it was used for Doses 2, 3 and 4 of Accuracy Trials and the single dose of the Precision Trials.

3.9. Data Analysis

Accuracy was measured as the strength of the relationship between TRO measured by the instrument under evaluation and by the reference method. We used simple linear regression to determine the slope and line-of-best-fit between the measurements. Regression analyses were performed using an iterative curve-fitting algorithm (SigmaPlot V13). Precision was measured as the coefficient of variation (CV, %) among multiple measurements from either the instrument under test or the reference method.

4. Results

4.1. Accuracy

Linear regression analysis compared readings from the TRO instrument to concurrent readings from reference method. Figure 1 shows the readings plotted for Accuracy trials with various temperatures and salinities, and Figure 2 show plots of the trial with ambient water. Regression statistical results are shown in Table 2. Both experimental and ancillary test data are available in **Appendix B** and **C**, respectively.

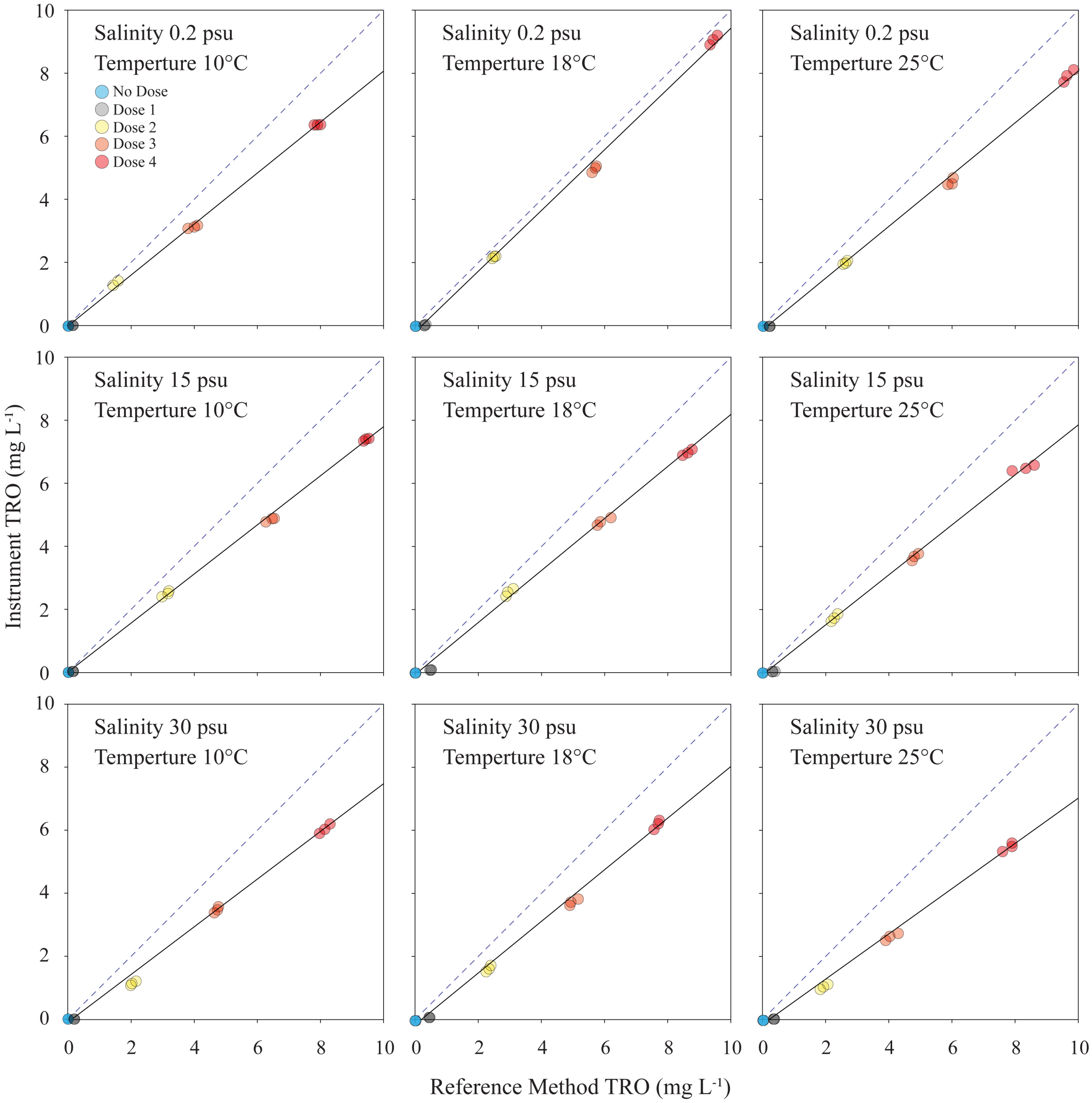

Figure 1. Scatterplots showing results from Accuracy Trials. Readings from the reference method (x-axes) and the instrument (y-axes) are plotted, and the line-of-best fit is the result of Linear Regression Analysis. Dotted lines show a theoretical 1:1 relationship between variables.

Perfect agreement between the instrument and reference method would yield a slope equal to one. In all accuracy trials, slopes were <1, indicating that the instrument readings were lower than from the reference method (Table 2). For this instrument, the slope values ranged from 0.717 to 0.962 (no units). A one-way t-test calculated, in all cases, slopes were significantly different from 1 ($p<0.05$, df = 14).

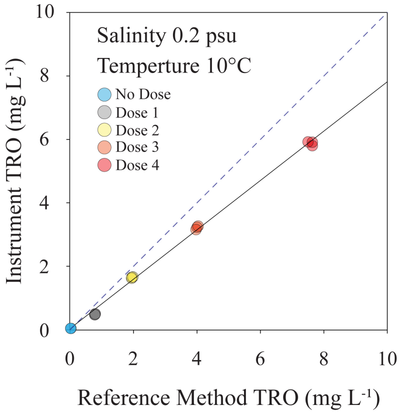

Figure 2. Scatterplot showing results from the Ambient Water trial. Readings from the reference method (x-axis) and the instrument (y-axis) are plotted, and the line-of-best fit is the result of Linear Regression Analysis. The dotted line shows a theoretical 1:1 relationship between variables.

Table 2. Results of the accuracy trials.

Test Water		Regression Coefficient		Line-of-Best-Fit			
Sal. (psu)	Temp (°C)	Adjusted R^2	Stand. Error	y-intercept	Stand. Error	Slope	Stand. Error
Accuracy Trials							
0.2	10	0.999	0.093	-0.021	0.034	0.809	0.008
0.2	18	0.997	0.186	-0.194* ●	0.068	0.962 ●	0.014
0.2	25	0.998	0.128	-0.126*	0.047	0.814	0.010
15	10	0.999	0.092	0.005 ●	0.035	0.779	0.007
15	18	0.997	0.153	-0.059	0.059	0.825	0.012
15	25	0.998	0.115	-0.070	0.042	0.793	0.010
30	10	0.996	0.152	-0.089	0.055	0.756	0.013
30	18	0.997	0.143	-0.161*	0.054	0.818	0.013
30	25	0.997	0.126	-0.152*	0.046	0.717 ●	0.011
Ambient Water							
16	21	0.998	0.108	0.036	0.041	0.778	0.010

*y-intercept p-values<0.05; slope p-values <0.05 in all cases

Extremes of the y-intercept and slope values: ● (lowest) ● (highest)

Results of the linear regression analyses indicate the "offset" of the instrument, or the value measured at 0 mg L^{-1} TRO. In the accuracy trials, offset was measured as the y-intercept of the line-of-best fit. For this instrument, the y-intercept ranged from -0.194 to 0.005 mg L^{-1}. The instrument's baseline correction factor should consider the linear relationship, such that when the reference method records 0 mg L^{-1}, the actual offset considers the slope of the line-of-best fit:

$$y = mx + b$$

When the instrument measures 0 mg L^{-1} (y), the TRO concentration of the reference method (x) is:

$$x = \frac{-b}{m}$$

Based upon this equation, baseline correction values would range from:

$$x = \frac{-(-0.194)}{0.962} = 0.202\ mg\ L^{-1}$$

to

$$x = \frac{-0.005}{0.779} = -0.01\ mg\ L^{-1}$$

Therefore, without a baseline correction, concentrations as high as 0.202 mg L^{-1} (as measured by the reference method) would be measured as 0 mg L^{-1} by the instrument. Conversely, 0 mg L^{-1} measured by the reference method could be measured as high as 0.01 mg L^{-1} by the instrument.

4.2. Precision

The precision of the instrument was determined by calculating the coefficient of variation (CV, %), a relative measure of variation among replicate readings. All readings, the average of all 12 readings, the standard deviation and CV are shown for the instrument and the reference method (Table 3).

Table 3. Results of the precision trial.

Sample Reading	Reference Method	Instrument Reading
1	3.55	3.45
2	3.56	3.45
3	3.48	3.40
4	3.53	3.34
5	3.49	3.34
6	3.50	3.35
7	3.47	3.33
8	3.41	3.28
9	3.38	3.27
10	3.45	3.24
11	3.33	3.22
12	3.27	3.20
Average	3.45	3.32
Standard Deviation	0.09	0.08
CV (%)	2.6%	2.5%

4.3. Reliability

The instrument's reliability was measured as the numbers of readings obtained relative to the total number of readings expected and the number of instrument failure. Each accuracy trial generated 15 samples and concurrent readings on the instrument. Likewise, the precision trial had 15 readings (12 dose readings and three readings prior to dosing). Therefore, for 11 trials, 165 samples and instrument readings were expected. All 165 readings were collected. No issues or problems were observed for the three units evaluated throughout testing.

It must be noted that while estimates of reliability were collected and are reported here, this instrument was only tested under controlled laboratory conditions and not under the true application (onboard active ships) for which it has been designed. Therefore, these results might be considered a best-case scenario for reliability since they do not include all the challenges and possible interferences that may be presented when used for several months at sea and during normal repeated vessel ballasting operations.

5. Quality Management

Work performed for this project was conducted following the quality management system (QMS) developed by the Alliance for Coastal Technologies (ACT). The QMS provided the framework for quality assurance (QA) functions, which covered planning, implementation, and review of data collection activities and the use of data in decision making, and quality control (QC). Results of the technical systems audit and data quality assessments are available in **Appendix D**.

6. Acknowledgements

Support for this effort was provided by the U.S. Department of Transportation Maritime Administration (MARAD). We thank Dr. Carolyn Junemann (MARAD) for the programmatic guidance and support. We are grateful for the technical support and advice from the Technical Advisory Committee, listed here alphabetically: Richard Everett (U.S. Coast Guard), Ray Frederick (U.S. Environmental Protection Agency), James Jensen (University at Buffalo, SUNY), Carolyn Junemann (MARAD), and Gail Roderick (U.S. Coast Guard Research and Development Center).

Appendix A: Test Plan

Available at http://www.act-us.info/evaluations.php

Appendix B. Data tables

Table B1. ***Reference method*** measurements of TRO (mg L^{-1}) in ***Accuracy Trials***. Values shown are the mean ± standard deviation of three repeated readings of a single sample bottle.

Dose	Sample Event	Tank 1 (10°C)	Tank 2 (18°C)	Tank 3 (25°C)
Salinity 0.2 psu				
No Dose	A	0.01 ± 0.01	0.01 ± 0.01	0.02 ± 0.00
	B	0.00 ± 0.01	0.01 ± 0.00	0.02 ± 0.00
	C	0.01 ± 0.00	0.34 ± 0.01	0.23 ± 0.01
Dose 1	A	0.16 ± 0.01	0.28 ± 0.01	0.22 ± 0.01
	B	0.15 ± 0.01	0.30 ± 0.02	0.21 ± 0.01
	C	0.15 ± 0.00	2.55 ± 0.01	2.68 ± 0.03
Dose 2	A	1.59 ± 0.02	2.50 ± 0.01	2.63 ± 0.01
	B*	–	–	–
	C	1.43 ± 0.01	2.44 ± 0.01	2.55 ± 0.02
Dose 3	A	4.10 ± 0.00	5.73 ± 0.06	6.03 ± 0.12
	B	4.00 ± 0.00	5.70 ± 0.1	6.00 ± 0.00
	C	3.80 ± 0.10	5.60 ± 0.00	5.87 ± 0.06
Dose 4	A	8.00 ± 0.00	9.57 ± 0.06	9.85 ± 0.07**
	B	7.90 ± 0.00	9.43 ± 0.06	9.63 ± 0.06
	C	7.80 ± 0.10	9.33 ± 0.06	9.53 ± 0.06
Salinity 15 psu				
No Dose	A	0.01 ± 0.00	0.00 ± 0.00	0.00 ± 0.01
	B	0.01 ± 0.01	0.01 ± 0.02	0.01 ± 0.01
	C	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.00
Dose 1	A	0.17 ± 0.01	0.51 ± 0.02	0.39 ± 0.06
	B	0.15 ± 0.01	0.50 ± 0.03	0.32 ± 0.01
	C	0.15 ± 0.01	0.46 ± 0.01	0.31 ± 0.01
Dose 2	A	3.19 ± 0.31	3.10 ± 0.04	2.38 ± 0.08
	B	3.17 ± 0.03	2.93 ± 0.01	2.26 ± 0.02
	C	2.98 ± 0.03	2.87 ± 0.05	2.17 ± 0.02
Dose 3	A	6.53 ± 0.21	6.20 ± 0.00	4.93 ± 0.12
	B	6.47 ± 0.06	5.87 ± 0.06	4.80 ± 0.10
	C	6.27 ± 0.15	5.77 ± 0.12	4.73 ± 0.12
Dose 4	A	9.43 ± 0.06	8.77 ± 0.12	8.60 ± 0.10
	B	9.53 ± 0.06	8.63 ± 0.12	8.33 ± 0.06
	C	9.37 ± 0.12	8.47 ± 0.31	7.90 ± 0.17
Salinity 30 psu				
No Dose	A	0.00 ± 0.00	0.02 ± 0.01	0.03 ± 0.04
	B	0.00 ± 0.00	0.02 ± 0.01	0.01 ± 0.02
	C	0.00 ± 0.00	0.00 ± 0.00	0.03 ± 0.02
Dose 1	A	0.20 ± 0.01	0.47 ± 0.01	0.38 ± 0.01
	B	0.19 ± 0.01	0.46 ± 0.02	0.36 ± 0.02
	C	0.19 ± 0.01	0.44 ± 0.02	0.35 ± 0.01
Dose 2	A	2.15 ± 0.02	2.40 ± 0.01	2.07 ± 0.02
	B	2.02 ± 0.01	2.34 ± 0.07	1.93 ± 0.00
	C	1.99 ± 0.04	2.25 ± 0.01	1.83 ± 0.03
Dose 3	A	4.77 ± 0.15	5.17 ± 0.06	4.30 ± 0.10
	B	4.73 ± 0.23	4.93 ± 0.06	4.03 ± 0.06
	C	4.63 ± 0.06	4.90 ± 0.00	3.90 ± 0.17
Dose 4	A	8.30 ± 0.00	7.73 ± 0.21	7.90 ± 0.17
	B	8.13 ± 0.21	7.70 ± 0.10	7.90 ± 0.00
	C	7.97 ± 0.12	7.57 ± 0.12	7.60 ± 0.00

* Readings were made more than 15 min. following collection and were not reported.

**One of three readings exceeded the limit of detection (10 mg L^{-1}) and was not reported.

Table B2. ***Reference method*** measurements of TRO (mg L^{-1}) in ***Accuracy Trials*** with an alternative oxidant and ambient water. Values shown are the mean ± standard deviation of three repeated readings of a single sample bottle.

Dose	Sample Event	Alternative Oxidant	Ambient Water
No Dose	A	0.02 ± 0.00	0.02 ± 0.01
	B	0.01 ± 0.00	0.02 ± 0.01
	C	0.01 ± 0.00	0.02 ± 0.01
Dose 1	A	0.95 ± 0.03	0.79 ± 0.02
	B	0.92 ± 0.01	0.78 ± 0.01
	C	0.89 ± 0.01	0.77 ± 0.01
Dose 2	A	3.34 ± 0.03	1.98 ± 0.03
	B	3.32 ± 0.04	1.94 ± 0.02
	C	3.22 ± 0.08	1.94 ± 0.01
Dose 3	A	5.40 ± 0.10	4.03 ± 0.06
	B	5.27 ± 0.06	4.00 ± 0.00
	C	5.23 ± 0.06	3.97 ± 0.06
Dose 4	A	7.80 ± 0.26	7.63 ± 0.21
	B	7.67 ± 0.06	7.50 ± 0.20
	C	7.50 ± 0.26	7.63 ± 0.12

Table B3. ***Reference method*** measurements of TRO (mg L^{-1}) in the ***Precision Trial.*** Twelve sample events (AL) occurred at approximately 5-minute intervals; sample times are shown.

Dose	Sample Event	Sample Time	Precision Trial
No Dose	A	08:25	0.01 ± 0.00
	B	08:30	0.00 ± 0.01
	C	08:35	0.00 ± 0.01
Dose 1	A	09:30	3.55 ± 0.12
	B	09:35	3.56 ± 0.06
	C	09:40	3.48 ± 0.15
	D	09:45	3.53 ± 0.08
	E	09:50	3.49 ± 0.11
	F	09:56	3.50 ± 0.07
	G	10:01	3.47 ± 0.12
	H	10:06	3.41 ± 0.05
	I	10:11	3.38 ± 0.07
	J	10:16	3.45 ± 0.03
	K	10:22	3.33 ± 0.07
	L	10:27	3.27 ± 0.10

Table B4. ***Instrument*** measurements of TRO (mg L^{-1}) in ***Accuracy Trials***. Values shown were reported at the time of sample collection.

Dose	Sample Event	Tank 1 (10°C)	Tank 2 (18°C)	Tank 3 (25°C)
Salinity 0.2 psu				
No Dose	A	0.00	0.00	0.00
	B	0.00	0.00	0.00
	C	0.00	0.00	0.00
Dose 1	A	0.02	0.06	0.00
	B	0.02	0.04	0.00
	C	0.02	0.02	0.00
Dose 2	A	1.43	2.22	2.08
	B	1.36	2.21	2.00
	C	1.29	2.15	1.97
Dose 3	A	3.19	5.07	4.70
	B	3.14	5.01	4.51
	C	3.09	4.87	4.49
Dose 4	A	6.38	9.21	8.12
	B	6.37	9.07	7.93
	C	6.37	8.91	7.73
Salinity 15 psu				
No Dose	A	0.04	0.03	0.03
	B	0.04	0.03	0.03
	C	0.04	0.03	0.03
Dose 1	A	0.07	0.13	0.08
	B	0.07	0.12	0.08
	C	0.07	0.12	0.07
Dose 2	A	2.62	2.70	1.90
	B	2.54	2.59	1.77
	C	2.44	2.46	1.67
Dose 3	A	4.92	4.95	3.81
	B	4.91	4.82	3.72
	C	4.81	4.71	3.59
Dose 4	A	7.43	7.11	6.61
	B	7.45	7.00	6.51
	C	7.37	6.92	6.43
Salinity 30 psu				
No Dose	A	0.07	0.03	0.04
	B	0.07	0.03	0.04
	C	0.07	0.03	0.04
Dose 1	A	0.07	0.13	0.08
	B	0.07	0.13	0.08
	C	0.07	0.13	0.08
Dose 2	A	1.27	1.78	1.18
	B	1.20	1.67	1.10
	C	1.14	1.58	1.02
Dose 3	A	3.63	3.88	2.79
	B	3.53	3.78	2.70
	C	3.44	3.68	2.57
Dose 4	A	6.25	6.37	5.65
	B	6.08	6.26	5.54
	C	5.95	6.08	5.38

Table B5. ***Instrument*** measurements of TRO (mg L^{-1}) in ***Accuracy Trials*** ambient water. Values shown are the mean ± standard deviation of three repeated readings of a single sample bottle.

Dose	Sample Event	Ambient Water
No Dose	A	0.06
	B	0.06
	C	0.06
Dose 1	A	0.52
	B	0.50
	C	0.49
Dose 2	A	1.68
	B	1.67
	C	1.64
Dose 3	A	3.28
	B	3.24
	C	3.17
Dose 4	A	5.92
	B	5.93
	C	5.81

Table B6. ***Instrument*** measurements of TRO (mg L^{-1}) in the ***Precision Trial.*** Twelve sample events (A-L) occurred at approximately 5-minute intervals; sample times are shown.

Dose	Sample Event	Sample Time	Precision Trial
No Dose	A	08:25	0.07
	B	08:30	0.07
	C	08:35	0.06
Dose 1	A	09:30	3.45
	B	09:35	3.45
	C	09:40	3.40
	D	09:45	3.34
	E	09:50	3.34
	F	09:56	3.35
	G	10:01	3.33
	H	10:06	3.28
	I	10:11	3.27
	J	10:16	3.24
	K	10:22	3.22
	L	10:27	3.20

Appendix C. Ancillary Data

Table C1. Tank water characteristics in ***Accuracy Trials***. Temperature and salinity were measured initially and following doses 1, 2, and 3 using a ProDSS submersible probe; values shown are mean and standard deviation of four readings.

Salinity	Tank 1 (10°C)	Tank 2 (18°C)	Tank 3 (25°C)
Temperature (°C)			
0.2 psu	10.3 ± 0.2	18.6 ± 0.0	24.8 ± 0.0
15 psu	10.6 ± 0.2	18.8 ± 0.1	25.0 ± 0.6
30 psu	10.6 ± 0.1	18.9 ± 0.1	25.4 ± 0.1
Salinity (psu)			
0.2 psu	0.24 ±0.01	0.25 ± 0.01	0.25 ± 0.01
15 psu	14.9 ± 0.02	15.02 ± 0.02	14.90 ± 0.02
30 psu	30.0 ± 0.12	29.37 ± 0.02	29.15 ± 0.03
Dissolved Organic Carbon (mg C L^{-1})			
0.2 psu	5.97 ± 0.09	6.11 ± 0.25	5.89 ± 0.07
15 psu	12.8 ± 0.81	11.8 ± 1.13	11.7 ± 0.11
30 psu	18.3 ± 0.34	19.0 ± 0.21	17.6 ± 0.48
Total Suspended Solids (mg L^{-1})			
0.2 psu	5.33 ± 0.12	6.00 ± 0.26	4.90 ± 0.10
15 psu	10.7 ± 0.25	11.4 ± 0.3	12.2 ± 0.20
30 psu	17.1 ± 0.76	19.1 ± 0.82	15.0 ± 0.92
Particulate Carbon (mg C L^{-1})			
0.2 psu	1.95 ± 0.11	2.17 ± 0.03	1.96 ± 0.04
15 psu	2.85 ± 0.07	3.45 ± 0.23	3.53 ± 0.12
30 psu	2.99 ± 0.06	3.45 ± 0.18	3.43 ± 0.17
Particulate Inorganic Carbon (mg C L^{-1})			
0.2 psu	0.03 ± 0.01	0.03 ± 0.01	0.04 ± 0.03
15 psu	0.04 ± 0.01	–	–
30 psu	0.09 ± 0.02	0.08 ± 0.01	0.06 ± 0.01
pH (No Units)			
0.2 psu	7.55 ± 0.01	7.79 ± 0.02	7.79 ± 0.03
15 psu	7.69 ± 0.03	7.82 ± 0.01	7.79 ± 0.00
30 psu	8.27 ± 0.02	8.29 ± 0.02	8.28 ± 0.01

Table C2. Tank water characteristics in ***Accuracy Trials*** (Ambient Water and Alternative Oxidant) and the ***Precision Trial***. Temperature and salinity were measured initially and following doses 1, 2, and 3 using a ProDSS submersible probe; values shown are mean and standard deviation of four readings.

Salinity	Tank Water
Temperature (°C)	
Ambient Water	21.2 ± 0.30
Alternative Oxidant	18.7 ± 0.06
Precision Trial	10.8 ± 0.06
Salinity (psu)	
Ambient Water	15.7 ± 0.01
Alternative Oxidant	14.8 ± 0.01
Precision Trial	15.0 ± 0.01
Dissolved Organic Carbon (mg C L^{-1})	
Ambient Water	2.80 ± 0.03
Alternative Oxidant	11.8 ± 0.09
Precision Trial	6.86 ± 0.18
Total Suspended Solids (mg L^{-1})	
Ambient Water	4.30 ± 0.17
Alternative Oxidant	10.8 ± 0.21
Precision Trial	2.30 ± 0.26
Particulate Carbon (mg C L^{-1})	
Ambient Water	0.73 ± 0.01
Alternative Oxidant	3.24 ± 0.24
Precision Trial	0.26 ± 0.00
Particulate Inorganic Carbon (mg C L^{-1})	
Ambient Water	0.00 ± 0.00
Alternative Oxidant	0.03 ± 0.02
Precision Trial	0.00 ± 0.00
pH (No Units)	
Ambient Water	7.76 ± 0.01
Alternative Oxidant	7.66 ± 0.01
Precision Trial	7.69 ± 0.01

Appendix D. Technical Systems Audit Report

Available upon request.

Appendix E. Manufacturer’s Response Letter

HaLOGEN
systems

Halogen’s comments on the ACT report

Halogen Systems was eager to participate in The Alliance for Coastal Technologies (ACT) testing of TRO sensor. Unfortunately for us, the timing was problematic. We were in the middle of firmware modifications and we could not deliver a production sensor in time. In the end we opted to supply an interim, unfinished version that did not perform up to our specifications.

This interim version is <u>not representative of any released product</u> from Halogen. Results should be considered qualitative at best.

Halogen struggled to develop a process that produces similar behavior among different sensors. In the intervening months since the ACT test, Halogen achieved this goal by implementing a new process that produces and uniform electrochemical surface on the all the sensors. This dramatically lowered the standard deviation between sensors (an improvement of more than 50%).

It is never easy to compare different analytical methods since they will never agree 100% of the time. For example, while DPD is loses about 25 to 30% of recovery in seawater (lower sensitivity), (Ji-Hyun Lee), the Halogen (HSI) sensor has higher sensitivity in seawater than in freshwater. The HSI Sensor is designed to mimic the response of a DPD system under the real-world conditions of ballast water operation. This correlation between DPD and the HSI Sensor signal could not be completed by the time the test started. There was some overfitting in the seawater range that led to poor accuracy in seawater and better accuracy in the freshwater range. This is clearly an artifact of a poor compensation algorithm, since one would expect the opposite with uncompensated bare electrode amperometry. Since the ACT Study, Halogen has rapidly introduced improvements in the hardware and firmware and made great strides in closing the gap between its sensor and DPD measurements through:

- An improved mathematical model that correlates with DPD Total levels across a wide range of conditions.
- A new process for sensor manufacturing that produces very similar behavior between individual sensors and batches.
- Increasing sensor signal sensitivity at low concentrations.
- Improving linearity across all parameters
- Improved accuracy at all tested temperatures, salinities and pH levels
- Improvement in conductivity accuracy
- Improvement in pH measurement using new pH cartridge design

Halogen is in the process of evaluating its production sensor to ISO15839 “Water quality—On-line sensors/analyzing equipment for water—Specifications and performance tests.” This report will be made available by request. If you would like a copy of this report, please submit your name, company name and email to: info@halogensys.com.

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Background

The HSI Sensor is a multiparameter sensor that uses a three electrode amperometric measurement method to measure chlorine with bare electrodes. It also measures conductivity (salinity), pH, temperature and ORP (Oxidation Reduction Potential) sequentially. It uses the conductivity, temperature and pH readings to compensate for the changes in signal that occur at lower conductivity water.

Halogen offers the only the only amperometric sensor that is flow independent and self-cleaning, hence capable of installation directly into a ballast pipe. Flow velocities of 0 to 4 meters per second do not significantly affect the accuracy. This installation method allows TRO and salinity measurements in as little as 30 seconds after chemical injection. There are some advantages in the elimination of sampling lines and resultant extended sampling times for remote instruments. It has been reported that long sampling lines often contain biofouling since the water in them is stagnant for up to two weeks between ballasting cycles. This creates a TRO demand that reduces TRO in the sampling lines. When these conditions exist, it results in a lower instrument reading level than what is actually discharged.

By using Halogen's integrated salinity measurement many BWMS makers can eliminate a discrete salinity sensor and its associated cost. The HSI sensor operates without requiring reagents, membranes or electrolytes. Since no filters are present, filter cleaning is not required. Sensor troubleshooting is straightforward is usually be handled onboard. There is no waste stream disposal or plumbing required for it. There is an industry need for more TRO options and Halogen is actively and constantly improving its sensor technology.

References

Ji-Hyun Lee, Jun-Ho Park, Young-Keum In, Sang-Ho Moon, Young-Soo Kime, Ki-Tae Rhie. "Optimization of Analysis Method for Total Residual Oxidant in Ballast Water Management System." *5th Global R&D Forum and Exhibition on Ballast Water Management* . Busan, Republic of Korea, 2013. 167-170.