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STANDARD OPERATING PROCEDURE
Procedure for pH Meter Calibration and pH Measurement for Ballast Treatment Systems Utilizing pH as the Active Substance

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RECORD OF AMENDMENTS:

No.	Date	Type	No.	Date	Type
1	06/16/2010	Removed "Basic" from the title, and broadened the applicability of the SOP. Added Orion 3 Star User's Guide and sample containers to "Equipment List". Added text to pH meter calibration procedure, and edited ¶8. Removed all 25°C references in "Procedure". Added "Calibration of ATC Probe" section. Updated background, QAQC and reference sections.	7		
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BACKGROUND

The Great Ships Initiative (GSI) is a regional effort devoted to ending the problem of ship-mediated invasive species in the Great Lakes-St. Lawrence Seaway System and globally. In support of that goal, the GSI has established superlative freshwater ballast treatment evaluation capabilities at three scales—bench, land-based, and on board ship. Each scale is dedicated to addressing specific evaluation objectives. These include:

GSI Bench-Scale Tests

- Range finding for effective doses under a range of ambient conditions;
- Chemical degradation over time under a range of ambient conditions;
- Detection of any residual toxicity under a range of ambient conditions; and
- Confirmation of treatment process.

GSI Land-Based Tests

- Detection of scale-up, mechanical operation issues;
- Effectiveness of a dose with respect to the full range of ambient organisms; and
- Detection of any whole water effluent toxicity.

GSI Shipboard Tests

- Confirmation of biological and operational performance as expected in the ship environment; and
- Confirmation of performance as expected under a broad range of ambient conditions.

The GSI awards its independent status-testing services to developers of ballast treatment systems and processes determined to be promising. GSI status-testing is performed at the scale appropriate to the state of development of the target treatment system, with the goal of facilitating the rapid progression of meritorious ballast treatment systems through the research and development and approval processes to a market-ready condition.

GSI has no involvement, intellectual or financial, in the mechanics, design or market success of the actual treatment systems it tests. To ensure that GSI tests are uncompromised by any real or perceived individual or team bias relative to test outcomes, GSI test activities are subject to rigorous quality assurance/quality control

(QAQC) procedures and documentation. This attention to QAQC assures high quality and credible evaluation of GSI and its findings.

INTRODUCTION

This GSI Standard Operating Procedure (SOP) describes the method used to measure the pH of water samples collected during testing of Ballast Treatment Systems utilizing pH as the active substance. This SOP is applicable to testing at both the bench-scale and GSI Land-Based RDTE Facilty. An accurate measurement of pH is critical to the performance evaluation of such systems. Calibration of pH meters prior to use ensures the accuracy of each pH measurement, therefore, calibration of pH meters is required before each use. The calibration should be performed using commercially available, certified pH buffers. Do not use buffers or other reagents that are past their expiration dates. Change the buffers weekly and record the date that the solutions were renewed on the bottle used for calibration. For storage of the electrodes/probes, always check with the manufacturer's recommendations.
Note: Temperature affects pH measurements, and standard pH buffers have a specified pH at indicated temperatures (e.g., pH 10.00 at 25 °C). It is important to record the temperature of the sample at the time that pH is measured (Eaton *et al*., 2005).

DEFINITIONS

Brackish Water (BW): Synthetic water created from laboratory water (LW) with the addition of commercially prepared salts, such as Instant Ocean®, to obtain a salinity of 16 parts per thousand (as measured by a refractometer).

Duluth-Superior Harbor Water (HW): Natural surface water collected from the Duluth-Superior Harbor of Lake Superior at a depth of approximately 3 m (may be filtered through a glass fiber filter).

High Organic Content Laboratory Water (HOC-LW): Synthetic water created from LW amended with organics and used as a surrogate in place of Duluth-Superior Harbor water.

Laboratory Water (LW): City of Superior, Wisconsin municipal water that has been dechlorinated by passage through an activated carbon filter. Sodium sulfite may be added to remove remaining traces of chlorine. Note: Based on data from previous testing, background levels of chlorine from below the limit of detection (≤ 3 μg/L) to 10 μg/L are expected in dechlorinated LW.

Prospective Ballast Treatment System (BTS): A system containing an active substance and/or component that mechanically, physically, chemically, or biologically serves to remove, render harmless, or avoid the uptake or discharge of potentially invasive organisms within ballast water (IMO, 2005).

Salt Water (SW): Synthetic water created from laboratory water (LW) with the addition of commercially prepared salts, such as Instant Ocean®, to obtain a salinity of 32 parts per thousand (as measured by a refractometer).

EQUIPMENT LIST

- Deionized water
- Electrode filling solution
- Electrode storage solution
- Electronic stir plate and stir bars
- Kimwipes®
- pH buffers (i.e. 4.00, 7.00, 10.00, 12.45)
- pH combination electrode and ATC probe
- pH meter (i.e., Orion 3 Star) and User's Guide
- Sample Containers

PROCEDURE

pH Meter (Orion 3 Star) and pH Combination Electrode Calibration

Note: The pH meter and pH combination electrode must be calibrated each day before use. The ATC probe must be used during calibration of the pH probe and during pH measurement of samples.

1. Adjust the temperature of the pH buffers so that they are the same temperature of the water samples (±3 °C), if required.

2. Follow the calibration instructions for the Orion 3 Star meter and pH combination electrode being used (see " Orion 3 Star Meter User Guide pp.19-20").

3. Press the On/OFF button to turn the meter on. To set the pH meter parameters press the "Setup" button. Press the "Line Select" button and use the down arrow key to change the display to "bUF". Press the "Line Select" key again to accept the selection and move to the next line. The third line should display "USA". If not use the up and down arrow keys until "USA" is displayed. Press the "Line Select" key once more to accept that selection. Press the "Measure" key.

4. To calibrate the pH meter and electrode while in the measurement mode, press the up arrow key until the pH icon in displayed on the right side of the display. Then press the "Calibrate" key to begin the calibration process. The meter will display "CAL.1" on bottom display line.

5. Begin calibration by removing the pH electrode from the storage solution, removing the plug from hole for the internal filling solution, rinsing the electrodes (pH and ATC) with deionized water and blotting dry with a Kimwipe®.

6. Place the electrodes into the bottle containing the pH 4.00 buffer and a stir bar. Stir at a slow speed. When the meter indicates that a stable reading has been obtained for the pH 4.00 buffer (pH icon stops blinking), press the "Calibrate" button on the meter. The meter will display "CAL.2" on bottom display line.

7. Remove the electrodes from the buffer, rinse with deionized water and blot dry.

8. Repeat steps 6 and 7 for the pH 7.00 and 10.00 buffers. After the pH 10.00 buffer has been used for the calibration and the "pH icon" stops flashing, press the "Measurement" key to save and end the calibration. The meter will display the electrode slope. This should be recorded in an equipment- or project-specific notebook. The slope should be between 92 % and 102 %. If the slope is not in this range, the calibration procedure should be repeated.

Analysis of pH Check Buffer (i.e. pH 12.45) and Samples

1. Rinse the electrodes with deionized water and blot dry with a Kimwipe®.

2. Place the electrodes into the pH Check Buffer. Press the "Measure" button. When a stable reading has been obtained, record the pH and temperature of the buffer. Note: the acceptance range for the pH Check Buffer is ±0.2 of the nominal pH value. For example, if the pH Check Buffer has a nominal value of 12.45, the measured pH should be 12.25-12.65. If the measured value falls outside the acceptance range, the pH meter and electrodes must be recalibrated.

3. Determine the pH of the water samples at the temperature at which they are received. Press the "Measure" button, wait for the meter to indicate a stable reading. Record the pH and temperature.

4. Turn the pH meter and stirrer off when all readings have been completed. Rinse the electrodes with deionized water and blot dry. Place the plug back into the interal filling solution hole. Place the pH electrode into storage solution.

Calibration of Automatic Temperature Compensation (ATC) Probe

Note: The ATC probe must be calibrated to provide proper pH correction at various temperatures. The probe should be calibrated before the initial use and checked weekly. If the displayed temperature is >1 °C from the actual temperature, the probe must be recalibrated.

1. In measurement mode, press the up arrow key until that display line shows a temperature (no icon displayed to the right of the temperature). This display option immediately follows the "RmV" option.

2. Press the "Calibrate" key to begin calibration. The meter displays "CAL ATC TEMP".

3. Place the ATC probe in a solution of known temperature. When the reading stabilizes, the arrow icon and the first digit will flash. Enter the temperature by pressing the up or down arrow keys to adjust each digit and the "Digits" key to move to the next digit.

4. When finished setting the temperature, press the "Calibrate" key to save and end the calibration. Record the ATC probe calibration data in an equipment- or project-specific notebook.

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

1. Conduct all quality assurance/quality control procedures according to *GSI/QAQC/QAPP/LB/1 - Quality Assurance Project Plan (QAPP) for Great Ships Initiative Land-Based Tests (2010)* or *GSI/QAQC/QAPP/BS/1 – Quality Assurance Project Plan (QAPP) for Great Ships Initiative Bench Scale Tests (2010)*, depending on the scale of the testing. Analyze data to ensure that all applicable data quality criteria are met.

2. Collect and analyze in duplicate at least 10 % of the samples to document sampling and analytical variability.

3. Follow all procedures outlined in this SOP. Any deviations made during the experiment must be recorded and also approved by the GSI Lead On-Site Investigator (for Land-Based or Bench-Scale Studies) as soon as practicable, and communicated to a GSI QAQC officer.

4. Record data on data collection forms or in specific laboratory notebooks. All instrument data forms must be stored in a project-specific three-ring binder. Ensure hard copies of all raw data collected during treatment technology performance evaluation/certification testing are scanned and stored electronically on the LSRI secured Local Area Network (LAN). The requirement for a backup, electronic copy of raw data is implemented during treatment technology certification testing at the GSI Land-Based RDTE Facility only.

DATA STORAGE AND ARCHIVING

1. Store and archive original, raw data according to *GSI/QAQC/QAPP/LB/1 - Quality Assurance Project Plan (QAPP) for Great Ships Initiative Land-Based Tests (2010)* or *GSI/QAQC/QAPP/BS/1 – Quality Assurance Project Plan (QAPP) for Great Ships Initiative Bench Scale Tests (2010)*, depending on the scale of the testing.

2. Store and archive electronic data (e.g., scanned copies of original, raw data and/or data entered for analysis) by posting the data distribution files to the LSRI LAN in an organized hierarchical folder system such that the entire LSRI-GSI staff are able to recognize and access the data. Distribute data files via email, when needed, to the applicable GSI team members who do not have access to the LSRI LAN.

3. Archive all hard- and electronic-copies of data and records generated for a period of five years.

REFERENCES AND RELATED DOCUMENTS

Eaton, AD, Clesceri, LS, Rice, EW, and AE Greenberg, Eds. (2005). Standard Methods for the Examination of Water and Wastewater, 21st Edition. American Public Health Association, Washington, DC.

GSI/QAQC/QMP/1 – Great Ships Initiative Quality Management Plan (2010).

GSI/QAQC/QAPP/BS/1 - Quality Assurance Project Plan for Great Ships Initiative (GSI) Bench-Scale Tests (2010).

GSI/QAQC/QAPP/LB/1 - Quality Assurance Project Plan for Great Ships Initiative (GSI) Land-Based Tests (2010).

GSI/SOP/G/RA/SC/3- Procedure for Labeling Samples collected at the GSI Land-Based RDTE Facility.

GSI/SOP/G/RA/SC/4 – Procedure for Labeling GSI Bench-Scale Samples.

Great Ships Initiative website: www.greatshipsinitiative.org; Standard Operating Protocols/Procedures: http://www.nemw.org/GSI/protocols.htm.

International Maritime Organization (IMO) (2005). Guidelines for Approval of Ballast Water Management Systems (G8) Adopted by Resolution MEPC.125 (53). London, England.