Great Ships Initiative

Procedure No: GSI/SOP/BS/RA/C/6
Issue Date: July 16, 2009
Number of Pages: 8

STANDARD OPERATING PROCEDURE
Procedure for Analyzing Total Residual Chlorine (TRC) Concentrations in Water

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RECORD OF AMENDMENTS:

No.	Date	Type	No.	Date	Type
1	06/10/2010	Added "(TRC)" to SOP title. Edited definitions to provide consistency between GSI Chemistry SOPs. Removed text regarding the use of commercial bleach to create standards (¶1d and ¶2-¶5). Added ¶2. Added information regarding storage and archiving of electronic data to "QA/QC" and "Data Storage and Archiving" sections. Updated references.	7		
2	07/01/2010	Added text to ¶4 regarding reagent reaction time during analysis of standards.	8		
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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 analyze the total residual chlorine concentration (TRC) in water samples that have been collected from a prospective ballast treatment system (BTS) using chlorine as the active substance. Chlorine is a reactive compound and its concentration may change rapidly when added to water, especially water having a high organic carbon concentration. A chlorine electrode allows total residual chlorine to be measured quickly and accurately. All forms of chlorine are measured: free chlorine, hypochlorites, and chlorine bound to nitrogenous compounds. It is important to analyze chlorine samples as soon as possible after collection to minimize loss of chlorine. Samples not analyzed immediately after collection are subject to loss due to reaction with oxidizable species in the sample.

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 ($\leq$ 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 (>10 megohms resistance).
- Sodium Hydroxide.

- Potassium Iodate.
- Sodium Acetate.
- Glacial (concentrated) Acetic Acid.
- Potassium Iodide.
- pH 4 Buffer Reagent.
- Iodide Reagent.
- Orion 97-70 Chlorine Electrode and Appropriate Meter (e.g., Orion 290A).
- Magnetic Stir Plate and Teflon Stir Bars.
- 1-20, 10-100 and 100-1000 μL Pipettes and Disposable Tips.
- 30 and 150 mL Beakers.
- 100 and 500 mL Volumetric Flasks.
- Sampling Containers.
- Wash Bottle with Deionized Water.
- 1 L Small Mouth Container to Deaerate DI H_2O in Sonicator Bath.
- 100 mL Grad Cylinder, Plastic.
- Volumetric pipets (i.e. 5, 10, 15 mL).

PROCEDURE

1. Prepare reagents:

    a. Iodide Reagent - Dissolve 10 g of potassium iodide in deionized water (DI). Add 0.1 g of sodium hydroxide and dilute the solution to 100 mL with DI water. Note: Discard if the reagent begins to turn brown.
    b. Buffer Reagent, pH 4 - Dissolve 122 g of sodium acetate trihydrate in 229 mL of glacial acetic acid and dilute to 500 mL with DI water. Adjust the pH of the solution to 4.0 by adding either acetic acid or sodium hydroxide.
    c. Potassium Iodate Stock - Dissolve 0.501 g of potassium iodate (KIO_3) in deionized water and dilute to 500 mL in a volumetric flask. Note: This solution has a concentration equivalent to 1000 mg/L as chlorine. The solution should be remade every 3 months.

2. For very low level chlorine concentration measurements (i.e., < 10 μg/L), prepare 1 L of deaerated DI by bubbling nitrogen gas through the water for approximately 15 minutes or by a combination of vacuum and sonication of the water for 10-15 minutes. If the measured chlorine concentrations are not expected to be this low, DI can be used for preparation of chlorine standards.

3. Add 100 mL of DI water to a 150 mL beaker. Add 1.0 mL of iodide reagent and 1.0 mL of buffer reagent to the water. Stir at a slow speed and place the electrode into the solution. After a stable reading has been obtained for this solution, record the value. This is the blank.

4. Use the potassium iodate stock (1000 mg/L as chlorine) to prepare the chlorine standards

listed in Table 1. Iodate oxidizes iodide to iodine very slowly in dilute solutions. For this reason, analyze each of the standards by adding 1.0 mL of pH 4.0 buffer and 1.0 mL of iodide reagent to a 150 mL beaker followed by the required volume of iodate stock (Table 1). Swirl the beaker to mix and allow the solution to react for two minutes. Add a magnetic stir bar to the beaker, dilute to 100 mL with DI water and place on a stirrer and stir at a slow speed. Lower the chlorine electrode into the solution and wait for a stable millivolt (mV) reading. Record the reading.

Table 1. Chlorine Standards.

Volume of Iodate Stock (mL)	Chlorine Concentration (mg/L)
0.010	0.10
0.050	0.50
0.100	1.00
0.500	5.00
1.00	10.0

5. Collect water samples to be analyzed and analyze as soon as possible after collection using the following procedure:

   a. Place 100 mL of sample into a 150-mL beaker.
   b. Add 1.0 mL each of pH 4 buffer and iodide reagent.
   c. Add a stir bar to the beaker, place beaker on magnetic stirrer, stir at a slow speed, and place the chlorine electrode into the solution.
   d. Record the mV reading after it has stabilized.

Note: If the volume of sample is limited, a volume as low as 20 mL can be used for the analysis. If the sample volume is reduced, be sure to reduce the amount of reagents used in proportion to the reduction in sample volume (i.e., 20 mL sample uses 0.2 mL of each reagent).

6. Analyze Data:

   a. Enter the mV readings for the chlorine standards into a Microsoft Excel spreadsheet (see Appendix 1 for example Chlorine Analysis Worksheet).
   b. Graph the response vs. concentration by plotting the mV readings on the y-axis and the log of the chlorine concentration on the x-axis.
   c. Conduct a linear regression analysis of the data. Use the following equation for a straight line, $y = mx + b$, to determine the log of the concentrations of the standards. Ensure the equation of the line is displayed on the graph and obtain the slope and y-intercept values for the line. After obtaining the log of the concentrations, the spreadsheet will calculate the antilogs of those values. These are the calculated chlorine concentrations of the standards in mg/L.

d. Enter the sample IDs and corresponding mV values for each of the samples into the Microsoft Excel spreadsheet (see Appendix). The spreadsheet is designed to then calculate the total residual chlorine concentration of the samples.

QUALITY ASSURANCE/QUALITY CONTROL

1. Conduct all QAQC procedures according to *GSI/QAQC/QAPP/LB/1 - Quality Assurance Project Plan for Great Ships Initiative (GSI) Land-Based Tests (2010) or GSI/QAQC/QAPP/BS/1 - Quality Assurance Project Plan for Great Ships Initiative (GSI) Bench-Scale Tests (2010).* 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. When appropriate, 10% of samples should be spiked with a known concentration of chlorine to determine spike recoveries. Samples containing compounds that will rapidly react with chlorine will not give accurate spike recoveries. A chlorine containing reference standard can be used to check the accuracy of the TRC analysis.

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

4. Record data on data collection forms or in specific laboratory notebooks. All instrument data output and data forms must be stored in a project-specific three-ring binder. Ensure hard copies of all raw data (e.g., data output and data collection forms) 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 only during treatment technology certification testing at the GSI Land-Based RDTE Facility.

DATA STORAGE AND ARCHIVING

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

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 for a period of five years.

REFERENCES AND RELATED DOCUMENTS

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.

Thermo Orion. Thermo Orion Model 97-70 Residual Chlorine Electrode Instruction Manual. Beverly, MA.

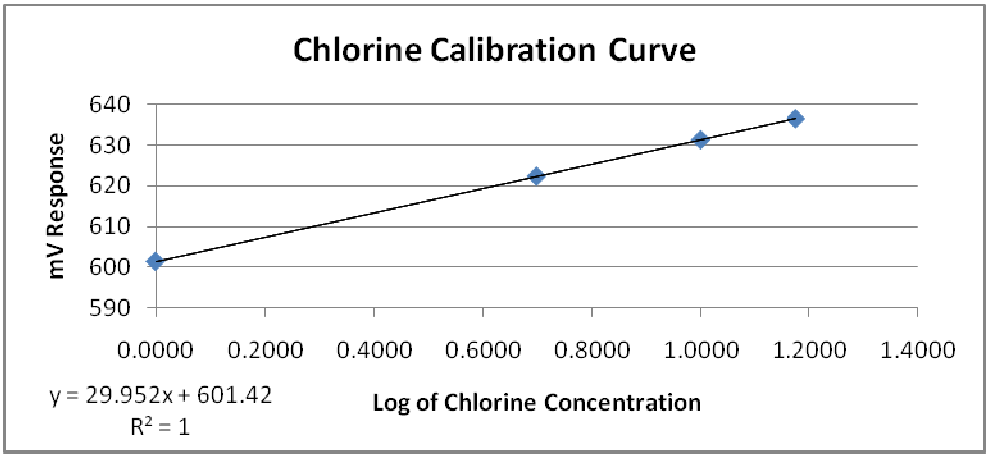
APPENDIX 1

EXAMPLE CHLORINE CONCENTRATION WORKSHEET

Chlorine Analysis Data Sheet

Name: Date:
Project:

Standard (mg/L)	Log of Conc.	mV	Log of Conc. (Calculated)	Calc. conc. (mg/L)
1.0	0.0000	601.4	-0.0007	1.00
5.0	0.6990	622.4	0.7005	5.02
10.0	1.0000	631.4	1.0009	10.02
15.0	1.1761	636.6	1.1745	14.95



Slope = 29.952
y-intercept = 601.42

Sample ID		mV	Log of Conc. (Calculated)	Calc. conc. (mg/L)	Spk Rec (%)	Dup Agree (%)
L-0 mg/L 5D-S 0 Hr		535.9	-2.1875	0.006		
L-0 mg/L 5D-S 0 Hr Spk		613	0.3866	2.44	99.8	
L-6 mg/L 5D-S 0 Hr		622.4	0.7005	5.02		
L-6 mg/L 5D-S Dup 0 Hr		622.0	0.6871	4.87		97.0
SL-0 mg/L 5D-S 0 Hr		537	-2.1508	0.007		
FH50-6 mg/L 5D-S 0 Hr		563.8	-1.2560	0.055		