Great Ships Initiative

Procedure No: GSI/SOP/BS/RA/C/1
Issue Date: July 10, 2009
Number of Pages: 5

STANDARD OPERATING PROCEDURE
Procedure for Analyzing the Concentration of Ozone in Water

Compiled By -

Name: Tom Markee & Kelsey Prihoda

Title: GSI Chemist & GSI Assistant QAQC Officer

Date: July 10, 2009

Approved By -

Name: Nicole Mays

Title: GSI Senior QAQC Officer

Date: July 10, 2009

Cleared For Issue By -

Name: Allegra Cangelosi

Title: GSI Principal Investigator

Date: July 10, 2009

RECORD OF AMENDMENTS:

No.	Date	Type	No.	Date	Type
1			7		
2			8		
3			9		
4			10		
5			11		
6			12		

STANDARD OPERATING PROCEDURE
Procedure for Analyzing the Concentration of Ozone in Water

BACKGROUND

The Great Ships Initiative (GSI) is a collaborative effort to end the problem of ship-mediated invasive species in the Great Lakes-St. Lawrence Seaway System through independent research and demonstration of environmental technology, financial incentives and consistent basin-wide harbor monitoring. To that end, GSI has established research capabilities at three scales—bench, land-based, and shipboard. Each scale is dedicated to addressing specific evaluation objectives, with protocols as consistent with IMO and federal requirements as practicable. Developers of ballast treatment systems apply for GSI research services online, and awards are offered based on an objective review process. GSI incubation/testing will allow meritorious ballast treatment systems to progress as rapidly as possible to an approval-ready and market-ready condition.

GSI bench-scale tests take place year-round at the University of Wisconsin-Superior's Lake Superior Research Institute (LSRI) in Superior, Wisconsin. The LSRI is amply equipped with staff expertise and resources to conduct the tests, and has a long history of successfully undertaking similar tests.

The overarching goals of GSI bench-scale testing are to explore dose-effectiveness, chemical degradation, residual toxicity, and sensitivity to challenge conditions of a proposed ballast treatment method about which little is known. To that end, the tests are "range-finding" missions, to determine the optimal treatment dose/intensity that would maximize effectiveness and minimize residual toxicity. Findings help treatment developers better design an effective system and/or to move to the next stage of treatment evaluation. The tests are also a form of trouble-shooting to encounter possible problems with the proposed treatment in advance of more extensive and larger scale tests.

INTRODUCTION

This GSI Standard Operating Procedure (SOP) describes the procedure used to determine ozone concentrations in water—an important analysis technique for prospective ballast treatments involving ozone. In this procedure water samples are added to a reagent solution containing potassium indigo trisulfonate immediately following collection. If ozone is present in the sample, it decolorizes the indigo. The decrease in absorbance is linear with increasing concentration of ozone. Several chemical species interfere with the ozone determination because they also decolorize the indigo reagent. Species that cause interferences include: hydrogen peroxide, organic peroxides, chlorine, and bromine. Interferences can be reduced by analyzing samples immediately after collection and by making measurements relative to a blank in which the ozone has been selectively destroyed.

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).

High Organic Content Laboratory Water (HOC-LW): Synthetic water created from laboratory water (LW) 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. 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 laboratory water, depending on the source of the water.

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

- Spectrophotometer capable of analysis at 600 nm.
- Cuvettes, 1 cm.
- Kimwipes.
- Wash bottle with deionized water.
- Volumetric flasks (10 mL, 250 mL).
- Volumetric pipet, 25 mL.
- 100-1000 μL pipettor with disposable tips.
- 1000-5000 μL pipettor with disposable tips.
- Analytical balance.
- Spatula.
- Weighing paper.
- Beakers for sample collection.
- Potassium indigo trisulfonate.
- Sodium dihydrogen phosphate.
- Phosphoric acid, concentrated.

REAGENTS

- **Indigo stock solution:** Dissolve 192.5 mg of potassium indigo trisulfonate in deionized water and dilute to volume in a 250 mL volumetric flask. The stock solution is stable for about 4 months when stored in the dark. Discard the solution when a 1:100 dilution falls below an absorbance of 0.16 A/cm at 600 nm.
- **Indigo reagent II:** Prepare by adding 25 mL of the Indigo stock, 2.5 g of sodium dihydrogen phosphate and 1.75 mL of concentrated phosphoric acid to a 250 mL volumetric flask and diluting to volume with deionized water. The solution should be remade when its absorbance decreases to less than 80 % of its initial value, typically within a week.

PROCEDURE

Sample Collection

1. Collect sample water in beakers or sample bottles from the appropriate location(s) depending on the type of test being conducted.

2. Minimize sample agitation to avoid loss of oxidants due to off-gassing from the sample.

3. To minimize residual ozone decay, react sample with the Indigo Reagent II immediately after collection. This is especially true of samples that have substances (i.e. organic compounds and reduced forms of iron and manganese) present with which the oxidants readily react.

4. Collect a minimum of 10 % of samples in duplicate.

Sample Analysis

1. Pipet 1.0 mL of Indigo Reagent II into a 10 mL volumetric flask. Repeat so that a volumetric flask is prepared for each sample and the blank.

1. Prepare the blank by diluting the 1.0 mL of Indigo Reagent II to 10.0 mL with deionized water. If the water sample to be analyzed is colored or has some turbidity, the blank should be prepared from a similar water sample that has not been treated with ozone. In this situation, 2 mL of the untreated water is added to a 10 mL volumetric flask containing 1.0 mL of Indigo reagent II and the blank is then diluted to 10 mL with deionized water.

2. Collect samples in a beaker and using an adjustable pipettor immediately transfer the appropriate volume of sample (usually 2.0 mL) to a 10 mL volumetric flask containing 1.0 mL of Indigo Reagent II. Immediately swirl to mix and dilute to volume with deionized water. Invert the volumetric several times to ensure thorough mixing of the

diluted sample. If the sample causes the Indigo to be completely decolorized, a smaller volume of sample will need to be used.

3. Determine the absorbance of the blank and samples at 600 nm using a one cm cuvette. Be sure to rinse the cuvette with several small portions of the blank or sample before filling and reading the absorbance of the sample. Absorbance values should be determined as soon as possible.

Calculation of Ozone Concentration

1. Determine the concentration of ozone in the sample using the following equation:

$$\text{mg/L } O_3 = \frac{\text{final sample vol. (mL)} \times \Delta A}{f \times b \times V}$$

where: final sample vol. (mL) = volume sample is diluted to in volumetric flask

ΔA = difference in absorbance between blank and sample (blank A – sample A)

f = 0.42 (constant)

b = path length of absorbance cell, cm

V = volume of sample, mL

QUALITY ASSURANCE/QUALITY CONTROL

1. Conduct all quality assurance/quality control procedures according to the GSI/QAPP/1 - Quality Assurance Project Plan (QAPP) for Great Ships Initiative Bench-Scale and Land-Based Biological Tests (2009). 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 known ahead of time must be approved by the GSI Lead Investigator for Bench-Scale Studies. Any deviations made during the experiment must be recorded and also approved by the GSI Lead Investigator for Bench-Scale Studies 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 instrument data output and data collection forms are scanned and stored electronically.

DATA STORAGE AND ARCHIVING

1. Store and archive data according to GSI/QAPP/1 - Quality Assurance Project Plan (QAPP) for Great Ships Initiative Bench-Scale and Land-Based Biological Tests (2009).

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

REFERENCES AND RELATED DOCUMENTS

Cangelosi AA (2006). RDTE Facility for the Great Ships Initiative (GSI) (OAR-SG-2006-20000364). Project Proposal to the National Oceanic and Atmospheric Administration/U.S. Fish and Wildlife Service. Northeast-Midwest Institute, Washington D.C.

Eaton AD, Clesceri LS, Rice EW & Greenberg AE (2005). Indigo colorimetric method for residual ozone analysis. Standard Methods for the Examination of Water and Wastewater: Method 4500-O_3 B, 4-144 to 4-146.

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

Great Ships Initiative website: www.greatshipsinitiative.org.

GSI/QAPP/1 - Quality Assurance Project Plan (QAPP) for Great Ships Initiative Bench-Scale and Land-Based Biological Tests (2009).

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