

## STANDARD OPERATING PROCEDURE Procedure for Analyzing Total Suspended Solids (TSS)

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### RECORD OF AMENDMENTS:

No.	Date	Type	No.	Date	Type
1	07/09/2010	Updated background and definitions. Added analytical balance capable of weighing to 0.01 mg to Equipment List. Added Appendix 1, and referenced in the procedure. Added requirement to record date and time filters are placed into/out of the oven. Updated QA/QC, Data Storage and Archiving, and References sections.	7		
2	02/21/2011	Separated equipment from supplies in "Equipment List". Added "General" and "Aluminum Weigh...Preparation". Corrected error in TSS calculation. Added text to "QA/QC" ¶3. Changed archive length of time.	8		
3	05/23/2011	Added text to "Introduction" to reference sample collection SOPs. Added § "Sample Handling". Removed Appendix 1 and added new Appendix 1 and Appendix 2. Added ¶2.i. to § "Preparation".	9		
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## **STANDARD OPERATING PROCEDURE**

### **Procedure for Analyzing Total Suspended Solids**

#### **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 treatment dose against diverse freshwater taxa and water quality conditions;
- Generation of freshwater relevant chemical degradation curves; and
- Estimation of residual toxicity given diverse freshwater taxa and water quality conditions.

##### *GSI Land-Based Tests*

- Pre-certification testing, i.e., operational and biological performance (including residual toxicity) status-testing given scale-up and a range of challenge conditions; and
- Certification/verification testing, i.e., formal assessment of performance against international and other discharge standards.

##### *GSI Shipboard Tests*

- Confirmation of biological and operational treatment performance as expected in the ship environment;
- U.S. Coast Guard Shipboard Technology Evaluation Program (STEP) testing;
- Shipboard type approval testing;
- Ship discharge monitoring; and
- Methods development.

GSI awards its independent status-testing services to candidate systems only if technical and programmatic criteria are met. Decisions are based on third party technical assessments as well as GSI Advisory Committee programmatic input. Testing services are currently offered at no cost to the developer with the exception of transportation and system installation/removal costs. Instead, tests are supported by general project funds which derive from federal and state agency grants, Great Lakes port contributions, and in-kind contributions by local governments and universities.

GSI has no involvement, intellectual or financial, in the mechanics, design or market success of the actual treatment systems it tests. To ensure GSI remains completely independent and is uncompromised by any real or perceived individual or project bias, GSI subjects itself to rigorous quality management policies and procedures. In addition, GSI test activities are subject to rigorous QAQC procedures and documentation. This attention to quality management and QAQC assures the high quality and credible evaluation of both GSI and its findings.

## INTRODUCTION

This GSI Standard Operating Procedure (SOP) describes the method used to analyze total suspended solids (TSS) in water samples. This procedure applies to analysis of TSS for bench-scale research and development trials and land-based evaluation/certification of ballast water treatment systems. During bench-scale research, samples are collected in either glass or plastic (i.e., high-density polyethylene, HDPE) bottles following *GSI/SOP/BS/RA/CD/1 – Procedure for Examining the Aquatic Degradation of Active Substance(s) in a Ballast Treatment System* or *GSI/SOP/BS/RA/CD/2 – Procedure for Examining the Degradation of Active Substance(s) in a Ballast Treatment System using Large-Volume Influent and Effluent Tanks*. During land-based testing, samples are collected using glass or HDPE sample bottles following *GSI/SOP/LB/RA/SC/8 – Procedure for Collecting Water Chemistry Samples and Data at the GSI Land-Based RDTE Facility*.

TSS are organic (e.g., algae) and inorganic (e.g., soil particles) material suspended in the water column. As TSS increase, the turbidity of the water and the absorption of light are also increased. Analyses of TSS are determined on a well-mixed sample that is filtered through a pre-weighed standard glass-fiber filter. The retained residue on the filter is dried to a constant weight at 103-105 °C. The increase in the weight of the filter is due to the TSS present in the filtered 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).

**High Organic Content Laboratory Water (HOC-LW):** Synthetic water created from laboratory water (LW) that is 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 ( $\leq 3 \mu\text{g/L}$ ) to  $10 \mu\text{g/L}$  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

- Analytical Balance Capable of Weighing to 0.01 mg
- Desiccator with Indicating Desiccant
- Drying Oven, for Operation at 103-105 °C
- Membrane Filter Funnel
- Vacuum Pump
- Vacuum Tubing

## SUPPLIES

- Glass-fiber Filter Disk, 47 mm (i.e., Whatman 934AH, Gelman Type A/E).
- Deionized Water.
- 1 L Filtration Flask.
- Forceps.
- Graduated Cylinders, 500 and 1000 mL.
- Aluminum Weighing Pan, 42 mL.
- Datasheet.

## PROCEDURE

### General

1. Conduct procedure in a vented work area, taking appropriate health and safety measures.

### Sample Handling

1. Cool samples immediately after collection by placing them in a refrigerator or in a cooler with ice packs.
2. If samples are not analyzed immediately after collection, hold samples in a refrigerator until analysis.
3. Analyze samples within seven days of collection according to the procedure below.

### Aluminum Weigh Pan and Glass-Fiber Filter Preparation (Prior to Sample Filtration)

1. Prepare the aluminum weigh pans using the following procedure:
  - a. Label each aluminum weigh pan on the pan tab using the last digit of the current year, a dash, and then increasing numerically.
  - b. Record the label of each pan on the TSS Filter Preparation datasheet (Appendix 1).
2. Prepare glass-fiber filter disc as follows:

- a. Place the glass-fiber filter into the membrane filter funnel with the wrinkled side facing up.
- b. Insert the rubber stopper of the filter holder into the neck of the filtration flask and connect the vacuum pump to the side arm on the filtration flask using vacuum tubing.
- c. Apply the vacuum, rinsing the filter with three 20 mL aliquots of deionized water. Continue the suction to remove all traces of water and discard the washings.
- d. After all traces of water have been removed, continue to draw air through the filter for approximately 1 minute. This will help to ensure that the filter does not stick to the aluminum weighing pan after it is dried in the oven.
- e. Carefully remove the washed filter from the filter holder and transfer it to a prepared aluminum weighing pan.
- f. Place the pan containing the filter into a drying oven at 103 - 105 °C and dry for a minimum of 1 hour. Record the date and time when filter was placed into oven on the TSS Filter Preparation Datasheet (Appendix 1).
- g. After drying, remove the weighing pan containing the filter from the oven and place in a desiccator to cool. Record the date and time when filter was removed from oven (Appendix 1).
- h. Weigh the pan containing the filter on an analytical balance to 0.01 mg. Record the weight (Appendix 1).
- i. Repeat the drying, cooling in the desiccator, and weighing (Steps f-h) at least one more time; until the weight change is less than 4% of the previous weight or 0.5 mg, whichever is less.

### **Sample Filtration**

1. For samples with expected low suspended solids concentrations, a volume of 1000 mL should be filtered. If filtration requires more than five minutes, reduce the sample volume being filtered. Record the volume of filtered sample in a log book or the TSS Sample Analysis datasheet (Appendix 2).
2. Sample filtration procedure:
  - a. Assemble the filtering apparatus containing a previously prepared glass-fiber filter (“Aluminum Weigh Pan and Glass-Fiber Filter Preparation”, Step 2).
  - b. Wet the filter with a small amount of deionized water to seat it properly in the filter holder.
  - c. If filtering a sample volume of 100 mL or less, thoroughly mix the sample, and transfer the homogenized sample from the sample bottle into a beaker. Stir the sample with a magnetic stirrer and pipette the volume of sample to be filtered from a point both mid-depth and midway between wall and vortex of the stirred sample.
  - d. If filtering a sample volume of greater than 100 mL, shake the sample bottle vigorously and immediately pour the volume of sample to be filtered into a 1000 mL graduated cylinder. Filter the sample transferred to the filter holder by applying a vacuum to the filtration flask. Rinse the graduated cylinder with

- several aliquots of deionized water to ensure that all solids have been transferred to the filter apparatus.
- e. Rinse the walls of the filter holder with three aliquots of deionized water to transfer any particles adhering to the walls onto the filter. Continue the vacuum for several minutes after the filtration is complete.
  - f. Carefully transfer the filter containing the residue back into its aluminum pan. Record the date and time filter was placed into oven on the TSS Sample Analysis data sheet (Appendix 2).
  - g. Dry for a minimum of 1 hour at 103-105 °C (record date and time filter was removed from oven, see Appendix 2), cool in a desiccator, and weigh the pan and filter to 0.01 mg. Record the weight (Appendix 2).
  - h. Repeat the drying, cooling in the desiccator, and weighing at least one more time; until the weight change is less than 4 % of the previous weight or 0.5 mg, whichever is less.
  - i. Duplicate determinations should be conducted on at least 10 % of the samples and duplicates should have RPDs of less than 5 %.

### **Total Suspended Solids Concentration Calculation**

1. Calculate the total suspended solids in each sample:

$$\text{Total Suspended Solids (mg/L)} = \frac{(A - B) * 1000}{\text{Sample volume (L)}}$$

Where:

A = weight of aluminum pan, filter, and dried residue (g)

B = weight of aluminum pan and filter (g)

### **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 (2011)* or *GSI/QAQC/QAPP/BS/1 - Quality Assurance Project Plan for Great Ships Initiative (GSI) Bench-Scale Tests (2010)*.
2. Analyze data to ensure that all applicable data quality criteria are met.
3. Collect and analyze in duplicate at least 10 % of the samples to document sampling and analytical variability. Duplicates should have a Relative Percent Difference (RPD) of less than 5 %. A certified reference standard may be purchased and analyzed to document procedural accuracy. Certified reference standards will be analyzed at least twice with each ballast water treatment system (BWTS) being tested at the GSI Land-Based RDTE Facility. The value obtained for the reference standard should fall within the acceptance range provided for the standard. A TSS blank will be analyzed with each set of samples. The blank will involve filtering 1000 mL of deionized water through a previously prepared glass fiber filter (“Aluminum Weigh Pan and Glass-Fiber Filter Preparation”, Step 2). The value obtained for the blank should be less than the method detection limit.

4. Follow all procedures outlined in this SOP. Any SOP amendments 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 SOP 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 (for Land-Based or Bench-Scale Studies) as soon as practicable.
5. Record data on data collection forms (i.e., Appendix 1 and 2) or in specific laboratory notebooks. All instrument data output (e.g., chromatograms, absorbance scans, and/or measurements) and data forms must be stored in a project-specific three-ring binder. Ensure hard copies of all raw data (e.g., instrument 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 only implemented during treatment technology certification testing at the GSI Land-Based RDTE Facility.

## **DATA STORAGE AND ARCHIVING**

1. Store and archive data according to *GSI/QAQC/QAPP/LB/1 - Quality Assurance Project Plan for Great Ships Initiative (GSI) Land-Based Tests (2011)* 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 generated for a period of at least seven years.

## **REFERENCES AND RELATED DOCUMENTS**

American Public Health Association (2005). Total suspended solids dried at 103-105 °C. Part 2540 D. In *Standard Methods for the Examination of Water and Wastewater*, 21<sup>st</sup> edition. Washington, DC, pp 2-58 to 2-59.

*GSI/QAQC/QMP/1 – Great Ships Initiative Quality Management Plan (2011)*.

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

*GSI/QAQC/QAPP/LB/1 - Quality Assurance Project Plan for Great Ships Initiative (GSI) Land-Based Tests (2011)*.

*GSI/SOP/BS/RA/CD/1 – Procedure for Examining the Aquatic Degradation of Active Substance(s) in a Ballast Treatment System*

*GSI/SOP/BS/RA/CD/2 – Procedure for Examining the Degradation of Active Substance(s) in a Ballast Treatment System using Large-Volume Influent and Effluent Tanks*

*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.*

*GSI/SOP/LB/RA/SC/8 – Procedure for Collecting Water Chemistry Samples and Data at the GSI Land-Based RDTE Facility*

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

Great Ships Initiative website: [www.greatshipsinitiative.org](http://www.greatshipsinitiative.org).

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

# **APPENDIX 1**

## **Total Suspended Solids (TSS): Filter Preparation Datasheet**



## **APPENDIX 2**

### **Total Suspended Solids (TSS): Sample Analysis Datasheet**

