



United States
Environmental Protection
Agency

Office of Water
Washington DC 20460
www.epa.gov/npdes

EPA 800-B-14-001
September 2014
Final Report



VESSEL DISCHARGE SAMPLE COLLECTION & ANALYTICAL MONITORING

A How-To Reference for EPA's 2013 Vessel General Permit (VGP)



[This page intentionally left blank.]

Table of Contents

SUMMARY OF KEY POINTS..... 1

SECTION 1 GETTING STARTED 5

 1.1 Finding A Sampling Service Provider and/or an Analytical Laboratory 5

 1.2 Questions to Ask When Identifying a Laboratory or Sampling Service
 Provider..... 7

SECTION 2 MONITORING REQUIREMENTS FOR EACH DISCHARGE 11

 2.1 Bilgewater/Oily Water Separator Effluent 11

 2.2 Graywater 14

 2.2.1 Additional Considerations for Field Tests (pH and Total Residual
 Chlorine) 15

 2.2.2 Additional Considerations for Multiple Graywater Discharge Points 15

 2.3 Exhaust Gas Scrubber Washwater..... 18

 2.3.1 Additional Considerations for Field Tests (pH and Total Residual
 Chlorine) 20

 2.4 Ballast Water 21

 2.4.1 Biological Monitoring..... 21

 2.4.2 Additional Considerations for Field Tests (Total Residual Chlorine) 23

 2.4.3 Residual Biocides from Ballast Water Treatment 23

 2.4.4 Other Ballast Water Sampling Approaches 24

SECTION 3 SAMPLING 27

 3.1 List of Sampling Equipment..... 27

 3.2 Sample Collection Steps 28

 3.3 Dissolved Metals Filtration..... 31

 3.4 Sample Packing and Shipping 33

 3.5 Bottle Labels and Chain of Custody (COC) Forms..... 37

List of Tables

Table 2-1. Bilgewater Analytical Method Details	13
Table 2-2. Graywater Analytical Method Details.....	15
Table 2-3. Analytes for Exhaust Gas Scrubber Washwater.....	18
Table 2-4. Exhaust Gas Scrubber Washwater Analytical Method Details	19
Table 2-5. Indicator Organism Monitoring Parameters*	22
Table 2-6. Example Ballast Water Indicator Organism Sample Collection and Preservation Techniques	22
Table 2-7. Monitoring Schedule for Residual Biocides or Derivatives of the Residual Biocide	23
Table 2-8. Residual Biocides and Biocide Derivative Monitoring Requirements.....	25

List of Figures

Figure 2-1. A Comparison of the Bilgewater Samples Taken Before and After Bilgewater Treatment	12
Figure 2-2. Sampling of Bilgewater from a Bilgewater Treatment System	13
Figure 2-3. Examples of Oil Content Meter and Monitoring System.....	14
Figure 2-4. Composite Sample of Treated Mixed Graywater/Sewage Effluent.....	16
Figure 2-5. Two Examples of Sample Collection Points for Graywater Discharge.....	17
Figure 2-6. The EcoSilencer® Scrubber Installed on the <i>Pride of Kent</i>	20
Figure 2-7. Sampling Tap At the Pump of a Ballast Water Treatment System.....	23
Figure 3-1. Vessel Discharge Being Collected in a Labeled Sample Bottle	27
Figure 3-2. Example of Various Types of Sample Bottles and Various Preservation Chemicals in Dropper Bottles.....	28
Figure 3-3. Typical Field Measurement Meters and Strips for Chlorine and pH.	29
Figure 3-4. Sample Collectors Conducting Field Measurements	29
Figure 3-5. Sodium Thiosulfate	29
Figure 3-6. Sample Collection	30
Figure 3-7. Filled Sample Bottles Preserved on Ice	31
Figure 3-8. Samplers Performing Dissolved Metals Filtration.....	32
Figure 3-9. A Typical Peristaltic Pump	32
Figure 3-10. Disposable Filter Cartridges and Tubing	33
Figure 3-11. Packing Glass and Plastic Bottles	34
Figure 3-12. Garbage Bags Used to Line a Cooler.....	34
Figure 3-13. Individually Packed Samples in a Cooler	35
Figure 3-14. Samples in a Sealed Bag and Bags of Ice to Keep the Samples Cold During Shipping	35
Figure 3-15. Place the Chain of Custody in a Plastic Bag to Keep it Dry.....	36
Figure 3-16. A Packed Cooler Showing the Custody Seal and Strapping Tape.....	36

[This page intentionally left blank.]

SUMMARY OF KEY POINTS

The purpose of this document is to provide vessel owners/operators with tips and tools for meeting the sample collection and analysis monitoring requirements in the 2013 VGP. The document is written primarily to better educate vessel owners/operators who intend to conduct some or all of the sampling themselves rather than contracting these sampling activities to experienced third-party sampling service providers. However, EPA expects many vessel owners/operators will look to sampling service providers and laboratories to perform these activities for them and this document should serve as a resource for them as well.

Many NPDES permittees hire full-service “turnkey” operations to sample and analyze their discharges in lieu of building these capabilities in-house. Such service providers are currently available in many ports and EPA is aware that additional entities are considering offering similar services soon. When an owner/operator is not interested or unable to perform these sampling activities, use of a full-service provider is a viable alternative.

This summary of key points provides the most crucial information on the following aspects of sampling collection:

- Finding a Sampling Service Provider and/or an Analytical Laboratory
- Sample Preparation
- Collecting and Handling Samples
- Shipping Samples to a Laboratory.

Refer to the detailed sections of this document for information on the types of discharges required to be sampled as well as more comprehensive information on how to ensure sampling activities provide results consistent with the VGP requirements.

HOW DO I FIND A SAMPLING SERVICE PROVIDER OR AN ANALYTICAL LABORATORY?

Since different laboratories offer different services, a vessel owner/operator will need to find an analytical laboratory capable of meeting the monitoring requirements specified in the permit before conducting the actual sample collection. In addition to analyzing the samples (or arranging to have them analyzed), some services will provide prepared sampling bottles and sampling gear, conduct the actual sampling, and complete any necessary paperwork and forms. Conversely, some laboratory services only include analysis of a sample delivered to their lab. Finding the right sampling service provider and laboratory is similar to finding any other specialty service contractor in that you need to find entities that are capable of meeting all of your needs. Most commercial laboratories have websites that list their services and can be found through internet searches or word of mouth. The *National Environmental Laboratory Accreditation Program (NELAP)* maintains a list of about 1,500 laboratories here: <http://nelac-institute.org/lams/search>. NELAP also maintains a list of laboratories accredited through each of the 50 states; however, about 20 percent of states only list laboratories accredited for drinking water testing. See <http://www.nelac-institute.org/abdb.php> for details on state programs. The American Council of Independent Laboratories (ACIL) website also has a search function to find environmental laboratories by location. See <https://m360.acil.org/frontend/search.aspx?cs=1018>.

Also, while most of the laboratories identified from these sources are in the United States, vessel owners/operators are not required to use laboratories located in the United States so long as the lab meets the requirements of each test methods. Note that EPA does not endorse these laboratories and does not require use of a NELAP lab, but is providing this information as a resource. EPA does not require use of a “certified” or “accredited” laboratory for sampling and analytical analysis to comply with the VGP’s monitoring conditions.

Since some samples have short holding times between sample collection and analysis (i.e., less than a day in many instances), vessel owners/operators will need to consider the timing of sample collection to allow sufficient time for transport to the laboratory for analysis. Therefore, the physical location of the laboratory may be important because of the ability to arrange for sample pickup by laboratory personnel or a courier service.

WHAT QUESTIONS SHOULD I ASK WHEN IDENTIFYING A SAMPLING SERVICE PROVIDER AND/OR LABORATORY?

- ***Is the laboratory capable of providing the analyses for every pollutant parameter for each of the discharges that the permit requires? Will the laboratory’s reported results meet all the requirements of the approved analytical methods of the 2013 VGP?***
 - In some cases, a single laboratory cannot be identified that can provide all of the vessels’ analytical needs. In these situations, multiple laboratories may be needed to perform the range of analyses. Discuss each of the required analyses and explain to the laboratory the characteristics/source of the samples.
- ***Can the laboratory or sampling service provider offer a complete service which would include sample collection and transport. In the event they cannot offer such service (or you are not interested in such a service), can the laboratory provide bottles or other supplemental equipment for sampling such as bottles pre-labeled with your specific information, bottles with preservation chemicals already added, extra bottles in case of breakage and coolers/shipping materials?***
 - If laboratories do not currently offer these services, ask if an exception can be made. Otherwise the vessel owner/operator will need to acquire these materials separately and ensure that they meet the method requirements.
- ***Can the laboratory provide or arrange for courier services to pick up the samples directly from the vessel and all necessary paperwork? If not, how will the samples be delivered to the laboratory? What are the holding times for each sample and are there any other logistical and sampling limitations to consider?***
 - If you are seeking courier service from the laboratory, ensure they have escorted or unescorted access to the dock from which the sample will need to be picked up.
- ***How and when will the results be reported back to the vessel? What will the data package contain?***

- You need to be certain that the sample service provider is able to complete sampling and analysis and provide any necessary documentation and in time for you to be able to meet the VGP reporting requirements for the results of that monitoring.

COLLECTING SAMPLES AND SHIPPING

This section lists equipment commonly used for vessel sampling, steps for sampling collection, and procedures for sample packing and shipping. Note that you may not need all equipment listed or may omit certain steps depending on which samples you must collect.

If I collect the samples myself, what equipment will I need?

- Sampling Pole
- Sample Bottles
- Field Test Equipment
- Buckets and Disposable Bucket Liners
- Bottle Labels
- Pens
- Disposable Gloves
- Preservation Chemicals
- Zip Ties
- Log Book
- Bubble Wrap/Bubble Bags
- Shipping Paperwork/Traffic Reports
- Garbage Bags
- Clear and Strapping Tape
- Ice/Refrigeration/Coolers
- Zipper storage bags
- Chain of Custody Forms
- Custody Seals
- Coolers

How does my crew Collect, Pack, and Ship Samples?

1. Assemble all the necessary sampling equipment, materials, and supplies onsite.
2. Ensure that bottles are appropriately labeled (waterproof labels are best as they remain intact and legible).
3. Collect a discharge sample aliquot to perform any necessary field measurements (e.g., pH, free residual chlorine). Refer to the user manuals for the field test instruments to ensure proper use and maintenance of these meters.
4. Determine whether sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) is needed for preservation due to the presence of chlorine in the sample and add to the sample bottles as appropriate.
5. Fill the sample bottles with the appropriate discharge samples.
6. If necessary, filter the sample for dissolved metals. See instructions for sample filtering in Section 3.3 below.
7. If the laboratory was unable to add preservation chemicals to each bottle, add any appropriate preservation chemicals at this point and test the pH or chlorine to ensure that the enough has been added.

8. Cool the samples on ice as dictated by the analytical methods. If the discharge water is hot to the touch, consider the need to allow samples to cool for a few minutes prior to placing in ice water to prevent shattering of the sample container or loss of the lid liner into the sample.
9. Repeat steps 2 through 9 if more than one discharge needs to be sampled.
10. Complete chain of custody forms.
11. Wrap glass sample bottles with “bubble wrap” and place all bottles (glass and plastic) in individually sealed zipper storage bag to contain liquids and preservation chemicals in case of shattering, punctures, or leaks.
12. Line the cooler with a large garbage bag to further ensure nothing leaks from the cooler.
13. Place sample bottles and a temperature blank upright in the garbage bag in the cooler and close bag with twist-tie.
14. Arrange sealed plastic freezer bags filled with ice (or chemical ice) on top of the sample bottles (if sample cooling is required for preservation) to maintain preservation temperature during shipping.
15. Place the completed chain of custody form in the cooler (retain a copy for your records).
16. Close cooler and secure with strapping tape to ensure that the lid will remain closed if the latch is accidentally released or damaged. Also tape the cooler drain plug closed so it will not open during shipment.
17. Place a custody seal on the cooler to verify the cooler has not been opened or tampered with during shipment and secure with clear tape to prevent loss during transport.

The following is an example of a bottle label:

Sample Number:	000001
Sampling Port:	Miami, Florida
Vessel Name/Number:	Container Vessel 123
Sampling Point Description:	Exhaust Gas Scrubber Inlet Water
Day and Time of Sample Collection:	8/8/2013 4:30 PM EST
Analysis to be Performed:	Total Metals
Sample Bottle Type:	500-mL Plastic Bottle
Preservation Used:	HNO ₃ to pH<2
Sampler Initials:	FH and GW

SECTION 1 GETTING STARTED

Purpose of this Document: To provide tips and tools for complying with the sample collection and analysis monitoring requirements in the 2013 VGP.

Target Audience: Anyone (vessel owners/operators, crew, service providers, and laboratories) collecting or analyzing samples of discharges from vessels as required under the 2013 VGP.

Vessel Required to Collect and Analyze Samples under the 2013 VGP:

- Any vessel discharging bilgewater to waters subject to the VGP constructed on or after December 19, 2013 and greater than 400 gross tons (see Part 2.2.2 of the VGP)
- Any large cruise ship discharging graywater to waters subject to the VGP within 3 nautical miles of shore (see Part 5.1 of the VGP)
- Any medium cruise ship discharging graywater to waters subject to the VGP within 1 nautical mile of shore (see Part 5.2 of the VGP)
- Any vessel constructed on or after December 19, 2013, having a maximum crew capacity of at least 15 crew, and providing overnight accommodation to those crew, and discharging graywater to waters subject to the VGP (see Part 2.2.15 of the VGP)
- Any vessel operating on the Great Lakes, that is not a “commercial vessel,” and discharging graywater to waters subject to the VGP (see Part 2.2.15 of the VGP)
- Any vessel discharging exhaust gas scrubber washwater to waters subject to the VGP (see Part 2.2.26 of the VGP)
- Any vessel operating a ballast water treatment system and discharging ballast water to waters subject to the VGP (see Part 2.2.3 of the VGP).

Results of monitoring are required to be reported to the EPA as part of the annual reporting requirements of the 2013 VGP. See Part 4 of that permit for specific reporting and recordkeeping requirements. Also, visit EPA’s electronic (eNOI) system, accessible at: <http://water.epa.gov/polwaste/npdes/vessels/>, for specifics on how monitoring results are to be reported to EPA.

1.1 FINDING A SAMPLING SERVICE PROVIDER AND/OR AN ANALYTICAL LABORATORY

Once it is determined that a vessel is required to collect samples of bilgewater, graywater, exhaust gas scrubber wastewater, and/or ballast water discharges, the owner/operator of the vessel will have to determine how those samples will be collected, handled, analyzed, and reported, and what documentation is necessary to be retained. In many instances, these activities will require the owner/operator to find a sampling service provider and/or an analytical laboratory capable of meeting the monitoring requirements specified in the permit. Finding the right sampling service provider or analytical laboratory is similar to finding any other specialty service contractor. Most service providers and commercial laboratories have websites that list their services and can be found through internet searches or word of mouth. The *National Environmental Laboratory Accreditation Program (NELAP)* maintains a list of about 1,500

laboratories (there are about 6,000 to 10,000 laboratories in the US) that are accredited through their program organized by analytical method, which may also be useful in identifying a qualified laboratory. See <http://nelac-institute.org/lams/search>. NELAP also maintains a list of laboratories accredited through each of the 50 states; however, about 20% of states only list laboratories accredited for drinking water testing. See <http://www.nelac-institute.org/abdb.php> for details on state programs. American Council of Independent Laboratories (ACIL) is the trade association representing about 100 independent, commercial scientific and engineering firms across the U.S. Their website also has a search function to find environmental laboratories by location. See <https://m360.acil.org/frontend/search.aspx?cs=1018>. Note that EPA does not endorse these laboratories, but is providing this information as a resource. Also, while most of the laboratories identified from these sources are in the United States, vessel owners/operators are not required to use laboratories located in the United States to meet the requirements of the 2013 VGP. However, EPA notes that any non-U.S. laboratory must use appropriate quality assurance and quality control procedures to ensure that sample results are accurate.

Section 2 of this document contains a summary of VGP monitoring requirements and can be used as the starting point for the types of services needed from a service provider and/or laboratory. This section will help in determining answers to the following questions, which will be important to understand before contacting a service provider or laboratory:

- Which vessels and vessel discharges require sampling?
- Are vessel sampling points accessible (can the sample be collected easily from either a pre-installed tap or discharge point)? If not, what arrangements need to be made to collect the sample?
- What analyses are required of each discharge?
- What is the timeframe and frequency of sampling?
- What is the anticipated vessel location/condition during sampling?
- Who is the point of contact for sampling, follow-up questions, etc? Is that a contact in your headquarters operation, a vessel agent, a member of your crew, or someone else?

Also, since some samples have short allowable holding times between sample collection and analysis, vessel owners/operators will need to consider both the timing of sample collection and the time for transport to the laboratory for analysis when selecting the appropriate sampling service provider and/or laboratory. Therefore, the physical location of the laboratory and the ability of the service provider to gain access to the vessel to collect samples while a discharge is occurring may be important to ensure that samples can be analyzed within the appropriate holding times required to demonstrate compliance with permit requirements (see allowable holding times in Title 40 Code of Federal Regulations Part 136). For example, the ability to arrange for sample pickup by laboratory personnel or a courier service (which can take a few minutes to a few hours) instead of shipping the samples through a commercial parcel delivery service like DHL, FedEx, or UPS (which can take a day or more).

When contacting potential sampling service providers or laboratories, be sure to discuss the details of the planned sample collection and analysis with them. Below are some questions to ask and the types of services that should be considered.

1.2 QUESTIONS TO ASK WHEN IDENTIFYING A LABORATORY OR SAMPLING SERVICE PROVIDER

1. ***Although not required, is the laboratory NELAC (National Environmental Laboratory Accreditation Conference) certified to perform all of the analyses for each of the discharges that the vessel requires? If not, what other indications do you have that the laboratory can and will perform the monitoring consistent with the methods specified in 40 CFR Part 136 or other methods specifically allowed in the permit?***

If a single laboratory cannot be identified that can provide all of the vessels' analytical needs, multiple laboratories may be needed to provide the full range of required analyses. Discuss each of the required analyses and explain to the laboratory the characteristics/source of the samples and any associated allowable holding times for those sample parameters.

2. ***What experience does the laboratory or sampling service provider have with sampling and analyzing samples consistent with the analytical methods required for your discharge?***

Sampling service providers and laboratory personnel may have additional insights and tips for avoiding sampling and analysis problems. Consider the volume of sample needed, range of analytical results, preservation requirements, sample collection schedule/timing, etc.

3. ***Can the laboratory or sampling service provider offer a complete "turnkey" service which would include sample collection and transport?***

This is often the best way to ensure that samples are collected, handled, and analyzed properly and avoids the vessel owner/operator from having to learn all the details of proper sample collection and handling techniques. Some laboratories and sampling service providers offer a full range of services, which can include actual sample collection, transport, analysis, and preparation of all required recordkeeping documents. In these instances, you should be certain that the service provider is able to board your vessel at the appropriate time and location (e.g., appropriate access to the port).

4. ***If collecting samples on your own, check to see if the laboratory can provide bottles or other supplemental equipment for sampling? Are the bottles pre-labeled with vessel-specific information? Will there be extra bottles available in case of breakage? Does the laboratory provide sample bottles with the preservation chemicals already added?***

If the laboratory does not typically offer these services, ask if an exception can be made. Often these laboratories are willing to perform such services, that being when they will collect the samples, transport the samples to the laboratory, analyze the samples, and prepare any necessary reports with the sampling results.

Otherwise, the vessel owner/operator will need to acquire appropriate laboratory-grade bottles and preservation chemicals from a laboratory equipment supplier. See an example bottle label in Section 3.5. If these services are available, discuss the logistics of receiving the needed equipment.

If the sampling service provider or laboratory does not provide sample bottles with the preservation chemicals already added, the appropriate preservation chemicals will need to be purchased separately. In addition, the amount of preservation chemicals required will need to be calculated based on the pH of the discharge. Generally speaking, a few milliliters of preservation chemicals are needed to appropriately preserve 500 mL of wastewater at a pH of 7. If the laboratory is able to provide this service, the pH of the discharge will need to be provided to the laboratory so they can estimate the amount of preservation chemical to add to each bottle (details of the type of preservation needed by discharge is provided in tables in Section 2).

5. ***Will the sampling service provider and/or laboratory be able to provide filters and other supplies to perform any necessary filtering in the field?***

See Section 3.3 for more information regarding dissolved metals filtering equipment and procedures.

6. ***Can the sampling service provider or laboratory provide or arrange for courier services to pick up the samples directly from the vessel? If not, how will the samples be delivered to the laboratory? Will the samples meet their holding times in consideration of any logistical and sampling limitations?***

Generally speaking, a sample with a 5-day holding time or greater could be shipped over-night to the laboratory, but a sample with less than a 5-day holding time will require a faster shipping method (i.e. courier service). Additional time considerations for packaging and shipping, coordination, weekend schedules, etc. must be considered. If samples will be shipped using a commercial delivery service, see the section on “Sample Packing and Shipping” in Section 3.4 below.

7. ***If shipping samples is necessary, will the laboratory provide the shipping coolers and packaging materials?***

See the “List of Sampling Equipment” in Section 3.1 below.

8. ***Will the laboratory provide all necessary paperwork for the samples such as bottle labels, field logs, chain of custody forms, sample custody seals, etc?***

See an example of a standard chain of custody form in Section 3.5 of this document.

9. ***How and when will the results be reported back to the vessel? What will the data package contain?***

A standard laboratory data package may include the following items:

- **Narrative Report:** including a cover page containing the following information: laboratory name, episode number, sample numbers, method number and date, and a list of laboratory analysis ID numbers. The

narrative should include any difficulties encountered in the production of the analytical and QA/QC data, resolution of those difficulties, deviations from the methods, any comments on the method performance, and any problems associated with the analysis of specific samples (including reasons and recommendations).

- **Summary Report Forms:** including forms summarizing all sample, instrument, and method QC results, including calibration and calibration verification information as well as percent recovery information.
- **Miscellaneous Data:** including sample and standard preparation logbooks, and the current Method Detection Limit/ Initial Precision and Recovery (MDL/IPR).

10. *What other sampling logistics should be considered to ensure accurate and high quality data are attained, while minimizing your burden and specialized training needed for your crew?*

For example, can sampling be accomplished during a vessel's annual survey or in locations with established sampling infrastructure (e.g., in areas where services exist which conduct actual sampling for you)? Alternatively, will you designate a dedicated crew member to be responsible for sampling obligations?

[This page intentionally left blank.]

SECTION 2

MONITORING REQUIREMENTS FOR EACH DISCHARGE

This section provides an overview of monitoring required under the 2013 VGP.

Consistent with Part 4.2 of the 2013 VGP, records of all monitoring information, including all calibration and maintenance records, continuous monitoring instrumentation records (including strip chart recordings if applicable), sampling and testing results, and laboratory quality assurance (QA) documentation, must be retained onboard or kept electronically for a period of 3 years and must include:

- The date, exact place, and time of sampling or measurements;
- The individual(s) who performed the sampling or measurements;
- The individual(s) who performed the analyses and any meter recalibration;
- The techniques or methods used for sample analyses; and
- The results of such analyses and oil content meter (OCM) readings.

Consistent with Part 4 of the 2013 VGP, monitoring data must be submitted electronically (or on paper if EPA grants a waiver) at least once per calendar year no later than February 28 of the year after the data are collected. EPA has developed an electronic reporting system accessible from EPA's 2013 VGP homepage at <http://water.epa.gov/polwaste/npdes/vessels/Vessel-General-Permit.cfm>. Data must be submitted on the applicable VGP discharge monitoring reports (DMRs) as shown in Appendix H of the 2013 VGP (which have been incorporated into the electronic reporting system) and are to be submitted as part of the vessel's annual report (except for initial cruise ship graywater monitoring that may be due before the annual report). As appropriate, you must also report any waivers or other documentation on your annual report.

As described in Section 1, owners/operators required to monitor will have to contact one or more sampling service providers or contract laboratories to coordinate logistics to collect and or analyze the samples. Owners/operators should be certain to communicate the documentation requirements of the permit to these service providers and laboratories as summarized above.

2.1 BILGEWATER/OILY WATER SEPARATOR EFFLUENT

Part 2.2.2 of the 2013 VGP requires owners/operators of new build vessels constructed on or after December 19, 2013 and greater than 400 gross tons that may discharge bilgewater into U.S. waters, to collect a sample of bilgewater effluent (discharge from the vessel after bilgewater treatment system) annually¹ for analysis of oil and grease content by one of the following methods:

¹ Part 2.2.2.1 of the 2013 VGP provides a monitoring waiver provision after two years of monitoring provided certain conditions are met. Applicable vessel owners/operators may cease conducting analytical monitoring if:

- The analytical monitoring results are below 5 parts per million (ppm) oil and grease for two consecutive years of permit coverage;

- EPA Method 1664; or
- ISO 9377-2 (2000) Water Quality–Determination of Hydrocarbon Oil Index–Part 2: Method Using Solvent Extraction and Gas Chromatography (incorporation by reference, see 46 CFR §162.050–4).

In addition, the 2013 VGP requires that a reading of the OCM be recorded at the time of sample collection so that the oil content measured by the laboratory can be compared to that measured by the OCM.



Figure 2-1. A Comparison of the Bilgewater Samples Taken Before and After Bilgewater Treatment

EPA Method 1664 measures oil and grease content as Hexane Extractable Material (HEM), and also measures Silica Gel Treated N-Hexane Extractable Material (SGT-HEM). Both HEM and SGT-HEM samples are extracted using hexane, but for the SGT-HEM samples, the hexane extract undergoes an additional silica gel treatment process to remove polar material, and therefore, measurements include only nonpolar material. The weight of extracted oil and grease after the solvent is evaporated is then reported. EPA Method 1664 is approved by EPA at 40 CFR Part 136 (http://www.epa.gov/region9/qa/pdfs/40cfr136_03.pdf) for measuring oil and grease under the Clean Water Act; therefore, EPA Method 1664 is routinely offered by commercial analytical laboratories in the United States.

Alternatively, ISO Method 9377-2 runs a portion of the dried solvent extract through a gas chromatography instrument (reported as oil index). The ISO 9377-2 (2000) method is that

-
- The vessel has an oil water separator that has been type approved by any flag administration to be capable of meeting a 5 ppm standard or has an alarm and overboard discharge control unit which prevents the discharge of any bilgewater with an oil content of greater than 5 ppm oil and grease;
 - The vessel owner/operator calibrates the OCM annually; and
 - The vessel's OCM never reads above 5 ppm during discharges into U.S. waters.
-

specified by the US Coast Guard at 46 CFR 162.050-39 for measuring oil content in samples taken in approval testing of bilgewater separators, monitors, and alarms; this method is not commonly offered by US commercial analytical laboratories. There is a disparity in costs between the two methods with ISO 9377-2 (2000) potentially costing five to ten times more than EPA Method 1664. However, the hydrocarbon oil index method may be more likely to produce results consistent with type approval testing. The vessel owner/operator can choose which method they wish to employ. Table 2-1 summarizes sample collection and analysis procedures for bilgewater monitoring.

Table 2-1. Bilgewater Analytical Method Details

Analyte	Method	MRL	Unit	Container	Sample Volume	Preservation	Holding Time
HEM	EPA-1664A	5	mg/L	Any Color Wide-mouth Glass Bottles	Two 1-Liter Bottles	Cool to $\leq 6^{\circ}\text{C}$, HCl or H_2SO_4 to pH <2	28 days
Hydrocarbon Oil Index	ISO 9377-2:2000	0.1	mg/L	Amber Glass Bottles with Teflon® lid	Two 1-Liter Bottles	Cool to $\leq 6^{\circ}\text{C}$	4 days

MRL = Method Reporting Limit.



Figure 2-2. Sampling of Bilgewater from a Bilgewater Treatment System



Figure 2-3. Examples of Oil Content Meter and Monitoring System

2.2 GRAYWATER

Part 2.2.15.2 of the 2013 VGP specifies that new build vessels constructed on or after December 19, 2013 and with a maximum crew capacity greater than or equal to 15, and providing overnight accommodations to those crew are required to collect samples of graywater discharge for analysis.² For these vessels, the 2013 VGP requires two samples a year³ to be collected, at least 14 days apart, and analyzed for the following:

- Biological Oxygen Demand (BOD)
- Fecal Coliform or *E. coli*
- Total suspended solids
- pH
- Total residual chlorine

The analyses must be conducted according to 40 CFR Part 136 methods and the results must be reported in the vessel's Annual Report. Samples for fecal coliform or *E. coli* may be collected and analyzed only once per year if the owner/operator is having difficulties meeting the short holding times. Table 2-2 summarizes sample collection and analysis procedures for graywater monitoring.

² Large and medium cruise ships discharging graywater to waters subject to this permit have additional graywater monitoring requirements. See Parts 5.1.2 and 5.2.2 of the VGP for graywater monitoring requirements for large and medium cruise ships, respectively. Additionally, vessels operating on the Great Lakes that are not "commercial vessels" that discharge graywater are also required to monitor that graywater. See part 2.2.15.1.

³ Monitoring is not required in any calendar year that the vessel does not enter waters subject to this permit; however, the vessel's Annual Report must clearly state that the vessel did not enter waters subject to this permit.

Table 2-2. Graywater Analytical Method Details

Analyte	Method*	MRL	Unit	Container	Sample Volume	Preservation	Maximum Holding Time
BOD	SM 5210 B	2	mg/L	1 Plastic Bottle	500-mL	Cool, ≤6°C	48 hours
Fecal Coliform	SM 9222D or 9221E	1	CFU or MPN/100 mL	1 Plastic Bottle	120-mL	Cool, ≤10°C, Na ₂ S ₂ O ₃ if Chlorine Present	8 hours
<i>E. coli</i>	EPA 1603	1	CFU or MPN/100 mL	1 Plastic Bottle	120-mL	Cool, ≤10°C, Na ₂ S ₂ O ₃ if Chlorine Present	8 hours
Total Suspended Solids	SM 2540 D	3	mg/L	1 Plastic Bottle	1-Liter	Cool, ≤6°C	7 days
pH	SM 4500-H B	Field Tests					
Total Residual Chlorine	SM 4500-Cl G						

MRL = Method Reporting Limit.

* Sampling and testing shall be conducted according to 40 CFR Part 136. The listed methods are suggested methods but EPA will also accept sufficiently sensitive methods that are considered equivalent.

2.2.1 Additional Considerations for Field Tests (pH and Total Residual Chlorine)

Note that pH and total residual chlorine need to be measured within 15 minutes of sample collection and therefore need to be measured and recorded at the time of sample collection rather than at a commercial laboratory. This monitoring is performed using test meters equipped with the appropriate sensors designed to meet the analytical method listed. Generally, a 1-liter sample container jar is filled during sample collection for use in performing these measurements. Typically, samples for field measurements are collected first, because if total residual chlorine is detected, sodium thiosulfate (Na₂S₂O₃) will need to be added as a preservative for the fecal coliform or *E. coli* samples. (ASTM D7365-09a specifies preservation options for samples containing chlorine.) Vessel owners/operators should calibrate all equipment used for field measurements using the applicable calibration procedures specified by the instrument manufacturer.

2.2.2 Additional Considerations for Multiple Graywater Discharge Points

For vessels with multiple graywater discharge points (e.g., sinks, laundry facilities, showers, galley kitchens, etc), consider collecting a sample of each of the discharge points and compositing them together for a representative sample of the vessel’s entire graywater discharge, or sampling from an existing combined graywater collection tank. Compositing protocols should consider the relative discharge volumes of the various graywater sources. Regardless of where

graywater is sampled, the sampling point must be reported to EPA when you submit your monitoring data.



Figure 2-4. Composite Sample of Treated Mixed Graywater/Sewage Effluent

All records of the graywater sampling must identify the proportions of waste streams being sampled (such as mixed graywater, mixed graywater and blackwater, and galley). If actual amounts are not available, then estimated proportions should be provided.



Figure 2-5. Two Examples of Sample Collection Points for Graywater Discharge

2.3 EXHAUST GAS SCRUBBER WASHWATER

Part 2.2.26 of the 2013 VGP specifies that twice during the first year of permit coverage or system operation, whichever is later, each vessel operating a wet exhaust gas scrubber system must collect and analyze exhaust gas scrubber related samples.⁴ One of those samples may be conducted as part of a vessel’s annual or other survey, and during the first year of system operation, one of those sampling events may be conducted as part of system installation to ensure it is functioning properly. The two samples must be collected at least 14 days apart. After the first year, samples must be collected at least once per calendar year and may be collected as part of the vessel’s annual survey as appropriate.

For each sampling event, samples must be collected of each of the following:

- Exhaust gas scrubber inlet water (for background),
- Untreated water leaving the scrubber (but before any treatment system), and
- The discharged water (after any treatment).

The 2013 VGP requires these exhaust gas scrubber related samples to be analyzed for the analytes listed in Table 2-3.

Table 2-3. Analytes for Exhaust Gas Scrubber Washwater

Analytical Group	Specific Compounds
Dissolved Metals	Arsenic Cadmium Chromium Copper Lead Nickel Selenium Thallium Vanadium Zinc
Total Metals	Arsenic Cadmium Chromium Copper Lead Nickel Selenium Thallium Vanadium Zinc
Polycyclic Aromatic Hydrocarbons (PAHs)	Acenaphthylene Acenaphthene Anthracene Benz[a]anthracene Benzo[ghi]perylene

⁴ These monitoring conditions do not apply to inert gas scrubbers used as part of a safety system in a vessel tank.

Table 2-3. Analytes for Exhaust Gas Scrubber Washwater

Analytical Group	Specific Compounds
	Benzo[a]pyrene Benzo[b]fluoranthene Benzo[k]fluoranthene Chrysene Dibenz[a,h]anthracene Fluoranthene Fluorene Indeno[1,2,3-cd]pyrene Naphthalene Phenanthrene Pyrene
Nitrate/Nitrite	
pH	

Table 2-4 summarizes sample collection and procedures for analyzing exhaust gas scrubber washwater samples.

Table 2-4. Exhaust Gas Scrubber Washwater Analytical Method Details

Analyte	Method*	MRL	Unit	Container	Sample Volume	Preservation	Holding Time
Dissolved Metals ^d	EPA-200.8 or EPA-200.9 ^a	1-5	µg/L	One Plastic Bottle	500-mL	0.45 µm filter ^b , HNO ₃ to pH<2	6 Months
Total Metals	EPA-200.8 or EPA-200.9 ^a	1-5	µg/L	One Plastic Bottle	500-mL	HNO ₃ to pH<2	6 Months
Nitrate/Nitrite	EPA 353.2	0.01	mg/L	One Plastic Bottle	1-Liter	Cool, ≤6°C, H ₂ SO ₄ to pH <2	28 Days
PAHs	EPA-550.1, EPA-610, EPA-625, EPA-8100, EPA-8270c or EPA-8310	5	µg/L	One Amber Glass Bottle with Teflon® Lid	1-Liter	Cool, ≤6°C, Na ₂ S ₂ O ₃ if chlorine present	Extraction within 7 days; Analysis of extract within 40 days
pH	SM 4500-H B	Field Tests					
Total Residual Chlorine ^c	SM 4500-Cl G						

MRL = Method Reporting Limit.

* The listed methods are suggested methods but EPA will also accept sufficiently EPA Part 136 methods that are considered equivalent.

^a Because matrix interference is a known issue for arsenic and selenium in saltwater samples, EPA strongly recommends using Octopole Reaction Cell ICP-MS, Dynamic Reaction Cell ICP-MS, hydride generation with a graphite furnace, or other appropriate approach consistent with 200.8 or 200.9 to minimize this interference.

^b These samples will need to be filtered immediately after collection. See the Dissolved Metals Filtration section of this document.

^c Collected to determine PAHs sample preservation requirements.

^d Vessel owner/operators may want to consider seeking laboratories that can conduct metal filtration of the samples at the lab. This will simplify onboard sampling and processing requirements.



Figure 2-6. The EcoSilencer® Scrubber Installed on the *Pride of Kent*⁵

2.3.1 Additional Considerations for Field Tests (pH and Total Residual Chlorine)

Note that pH and total residual chlorine need to be measured within 15 minutes of sample collection and therefore need to be measured and recorded at the time of sample collection rather than at a commercial laboratory. Also, while total residual chlorine is not identified in the permit as a required analyte, it is needed to determine if preservation is needed for PAHs samples. This monitoring is performed using test meters equipped with the appropriate sensors designed to meet the analytical method listed. Generally, a 1-liter sample container is filled during sample collection for use in performing these field measurements. If total residual chlorine is detected, sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) will need to be added as a preservative for any PAHs sample. (ASTM D7365-09a specifies treatment options for samples containing chlorine.) Vessel owners/operators should ensure that all equipment used for field measurements are calibrated following applicable calibration procedures specified by the instrument manufacturer.

⁵ Source: Entec. 2005. European Commission Directorate General Environment, Service Contract on Ship Emissions: Assignment, Abatement and Market-based Instruments, Task 2c – SO₂ Abatement Final Report. August 2005. Entec UK Limited.

2.4 BALLAST WATER

2.4.1 Biological Monitoring

The 2013 VGP specifies that vessels using a ballast water treatment system (i.e., those subject to Part 2.2.3.5.1.1.1 of the 2013 VGP) must sample and analyze ballast water discharges for the following biological indicators:

- Total heterotrophic bacteria,
- E. coli, and
- Enterococci.

The vessel's ballast water system must be provided with sampling ports arranged in order to collect representative samples of the vessel's ballast water. In addition to the sampling ports designed and installed in accordance with the specifications in the ETV Protocol (<http://nepis.epa.gov/Adobe/PDF/P10097A4.pdf>). Sampling ports must be located:

- As close as practicable to the ballast water management system prior to treatment to determine concentrations of living organisms upon uptake; and
- As close as practicable to the ballast water management system overboard outlet prior to the discharge point to determine concentrations of living organisms prior to discharge.⁶

Sampling of ballast water discharges for these vessels must be conducted two times during the first year the system is installed or used for vessels with devices for which high quality data are available (See Part 2.2.3.5.1.1.4 of the 2013 VGP for definition of high quality data). For vessels with high quality data, if sampling results are below permit limits for two consecutive events, the vessel owner/operator may reduce monitoring to one time per year after the first year. However, if the vessel owner/operator exceeds a permit limit on any sampling event, they must return to monitoring two times per year until they have two additional results below permit limits.

For vessels required to perform ballast water monitoring for which high quality data are not available, monitoring must be conducted four times per year.

For all vessels required to perform ballast water monitoring, one of the samples may be conducted as part a vessel's annual or other survey, and during the first year, one of those sampling events may be conducted as part of the installation of the system to ensure it is functioning properly.

Table 2-5 summarizes applicable analytical methods that can be used for ballast water monitoring for indicator organisms. Table 2-6 provides a few examples of ballast water indicator organism sample collection and preservation techniques for some of the most common analytical methods.

⁶ See 46 CFR 162.060-28

Table 2-5. Indicator Organism Monitoring Parameters*

Measurement	Instrument or Analysis	EPA Method	Standard Method	ASTM	ISO	Other
Total Heterotrophic Bacteria	Plate Counts		SM 9215	ASTM D5465	ISO 6222:1999	
<i>E. coli</i>	Selective Substrate	EPA Method 1103.1 and 1603	SM 9223B	ASTM D5392 – 93	ISO 9308-1:2000	Colilert®
Enterococci	Selective Substrate	EPA Method 1106.1 and 1600	SM 9230C	ASTM D5259 – 92(2006)	ISO 7899-2:2000	Enterolert®

* Sampling and testing shall be conducted according to 40 CFR Part 136. The listed methods are suggested methods, but EPA will also accept Part 136 methods that are considered equivalent.

Table 2-6. Example Ballast Water Indicator Organism Sample Collection and Preservation Techniques

Analyte	Method	MRL	Unit	Container	Sample Volume	Preservation	Holding Time
Total Heterotrophic Bacteria	SM 9215	1	CFU or MPN/100 mL	Plastic Bottle	120-mL	Cool, ≤4°C, Na ₂ S ₂ O ₃ if Chlorine Present	8 hours
<i>E. coli</i>	EPA 1603 or Colilert®	1	CFU or MPN/100 mL	Plastic Bottle	120-mL	Cool, ≤10°C, Na ₂ S ₂ O ₃ if Chlorine Present	8 hours
Enterococci	EPA 1600 or Enterolert®	1	CFU or MPN/100 mL	Plastic Bottle	120-mL	Cool, ≤10°C, Na ₂ S ₂ O ₃ if Chlorine Present	8 hours
Total Residual Chlorine ^a	SM 4500-Cl G	Field Test					

MRL = Method Reporting Limit.

^a Collected to determine sample preservation requirements and not for compliance monitoring.

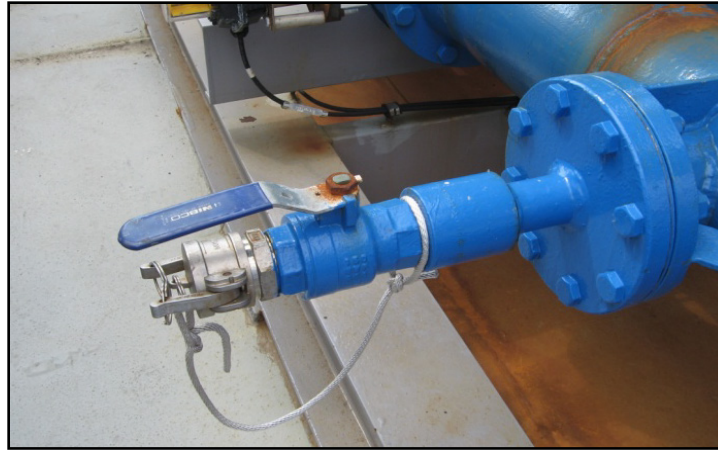


Figure 2-7. Sampling Tap At the Pump of a Ballast Water Treatment System

2.4.2 Additional Considerations for Field Tests (Total Residual Chlorine)

Note that total residual chlorine needs to be measured in the field to determine the type of preservation needed for the three biological indicators samples. This monitoring is performed using test meters equipped with the appropriate sensors designed to meet the analytical method listed. Generally, a 1-liter sample container is filled during sample collection for use in performing field measurements. If total residual chlorine is detected, sodium thiosulfate (Na₂S₂O₃) will need to be added as a preservative for any biological indicators samples. (ASTM D7365-09a specifies treatment options for samples containing chlorine.) Vessel owners/operators should ensure that all equipment used for field measurements are calibrated following applicable calibration procedures specified by the instrument manufacturer.

2.4.3 Residual Biocides from Ballast Water Treatment

Vessels subject to Part 2.2.3.5.1.1.1 of the 2013 VGP must conduct monitoring of the ballast water discharge for any residual biocides or derivatives used in the treatment process to demonstrate that residual biocides or derivatives are in compliance with this permit. Table 2-7 below summarizes required sampling frequency based on ballast water treatment type and available data. Table 2-8 summarizes sample collection and analysis procedures for ballast water monitoring for residual biocides.

Table 2-7. Monitoring Schedule for Residual Biocides or Derivatives of the Residual Biocide⁷

Type of Monitoring	Devices for Which High Quality Type Approval Data Are Available	Devices for Which High Quality Data Are Not Available
Initial Monitoring	3 times in the first 10 discharge events (not to exceed a 180 day period).	5 times in the first 10 discharge events (not to exceed a 180 day period).
Maintenance Monitoring	2 times per year.	4 times per year.

⁷ See Section 2.2.3.5.1.1.5.2 of the 2013 VGP for definition of high quality data.

2.4.4 Other Ballast Water Sampling Approaches

The VGP's ballast water sampling requirements are not as extensive as living organism sampling currently being contemplated in other forums, including by the International Maritime Organization (IMO), or under other efforts, including EPA and US Coast Guard's development of shipboard based sampling protocols for under the ETV program. Those approaches help to better understand ballast water treatment system performance for both type approval testing and onboard compliance. For example, the EPA ETV protocols are used by the U.S. Coast Guard to define methods required for the land-based portion of U.S. type approval (see <http://nepis.epa.gov/Adobe/PDF/P10097A4.pdf> for a copy of the ETV ballast water protocol). Likewise, numerous test facilities have been established in Asia, Europe, and North America to characterize ballast water treatment system performance in the context of land-based testing using the G8 guidelines and/or the ETV protocols. EPA will continue to track the development of testing methodologies, and may modify future permit monitoring conditions as appropriate to maximize consistency with other approaches and produce better monitoring information.

Table 2-8. Residual Biocides and Biocide Derivative Monitoring Requirements

Biocide	Analyte	Analytical Methods	Minimum Volume	Sample Holding Time	MDL	Effluent Limit or Action	Limit Type
Alkylamines	Alkylamines	EPA Method 8360B and 8270D	25 mL (8260B)	14 days (8260B)	Varies by compound (8260D); 10 µg/L (8270C)	Report	NA
Chlorine or Chlorine dioxide	Chlorine Dioxide	EPA Method 327.0-1; SM 4500 ClO ₂ E	16 mL (327.0-1)	4 hours (327.0-1); As soon as possible (SM)	Varies (327.0-1); 10 to 100 mg/L (SM)	200 µg/L	Instantaneous Maximum
	Total Residual Oxidizers (TRO) as Cl ₂	SM 4500-Cl G; ISO 7393/2	50 mL	15 minutes	10 µg/L, under ideal conditions	100 µg/L	Instantaneous Maximum
	Chlorite*	EPA Method 300.1	250 mL	14 days	Varies	Report	NA
	Chlorate*	EPA Method 300.1	250 mL	28 days	Varies	Report	NA
	Total Trihalomethanes ^{a*}	EPA Method 8260	25 mL	14 days	Varies	Report	NA
	Haloacetic Acids ^{b*}	EPA Method 552.2	40 mL	14 days	Varies by compound	Report	NA
Menadione	Menadione	NA				Report	NA
Ozone	Total Residual Oxidizers (TRO) as Cl ₂	SM 4500-Cl G; ISO 7393/2	50 mL	15 minutes	10 µg/L, under ideal conditions	100 µg/L	NA
	Bromate*	EPA Method 317 ; EPA Method 300.1; ASTM D 6581-00	250 mL	28 days (317; 300.1)	Varies (317; 300.1)	Report	NA
	Bromoform*	EPA Method 8260	25 mL	14 days	Varies	Report	NA
	Total Trihalomethanes ^{a*}	EPA Method 8260	25 mL	14 days	Varies	Report	NA
	Haloacetic Acids ^{b*}	EPA Method 552.2	40 mL	14 days	Varies by compound	Report	NA
Peracetic Acid	pH	SM 4500 H+	25 mL	As soon as possible		6.5 – 9 s.u.	Instantaneous Maximum

Table 2-8. Residual Biocides and Biocide Derivative Monitoring Requirements

Biocide	Analyte	Analytical Methods	Minimum Volume	Sample Holding Time	MDL	Effluent Limit or Action	Limit Type
	Peracetic Acid	Photometric analysis (Pinkernell, 1997; EMD Chemicals, 2011; CHEMetrics 2010)	25 mL	As soon as possible	500 µg/L	Report	NA
	Hydrogen Peroxide	Titimetric analysis (JIS K 1463:2007; EMD Chemicals, 2011; CHEMetrics 2010))	25 mL	As soon as possible	500 µg/L	Report	NA

* Potential byproduct or derivative.

MDL - Method Detection Limit.

NA - Not applicable.

^a Total trihalomethanes is the sum of the concentrations of chloroform, bromodichloromethane, dibromochloromethane, and bromoform.

^b Haloacetic acids is the sum of the concentrations of mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acids.

SECTION 3 SAMPLING

This section lists equipment commonly used for vessel sampling, steps for sample collection, and procedures for sample packing and shipping. These tips are provided as a way to get started. Sampling procedures may have to be customized or adjusted to suit the specific requirements of each vessel.



Figure 3-1. Vessel Discharge Being Collected in a Labeled Sample Bottle

3.1 LIST OF SAMPLING EQUIPMENT

The following is a list of sampling equipment, materials, and supplies that may be needed for proper sampling, depending on both the sample type being collected and the sampling location.

- Sampling Pole (to access sample ports in hard to reach locations)
- Sample Bottles (plastic, glass, etc.) (to collect samples)
- Field Test Equipment (for pH, chlorine)
- Buckets and Disposable Bucket Liners (if taking a large volume of sample)
- Bottle Labels
- Pens
- Disposable Gloves
- Preservation Chemicals
- Zip Ties

- Log Book
- Bubble Wrap/Bubble Bags (to protect the samples during shipping)
- Shipping Paperwork/Traffic Reports
- Garbage Bags (to wrap the samples in shipping)
- Clear and Strapping Tape
- 0.45 μm Filters and Other Filtering Equipment (if needed for dissolved metals)
- Ice/Refrigeration/Coolers (some samples need to be chilled until reaching the lab)
- Zipper Storage Bags
- Chain of Custody Forms
- Peristaltic Pump/Tubing (if needed)
- Custody Seals



Figure 3-2. Example of Various Types of Sample Bottles and Various Preservation Chemicals in Dropper Bottles

3.2 SAMPLE COLLECTION STEPS

The following are the general steps for sample collection.

1. Assemble all the necessary sampling equipment, materials, and supplies onsite.
2. Ensure that bottles are appropriately labeled (waterproof labels are best as they remain intact and legible). See example bottle label in Section 3.5.
3. Ensure that the vessel discharge system is fully operational and has adequate flow.
4. Collect a discharge sample aliquot to perform any necessary field measurements (e.g., pH, free residual chlorine). Refer the user manuals for the field test instruments to ensure proper use and maintenance of these meters.



Figure 3-3. Typical Field Measurement Meters and Strips for Chlorine and pH.



Figure 3-4. Sample Collectors Conducting Field Measurements

5. Determine whether sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) is needed for preservation due to the presence of chlorine in the sample and add to the sample bottles as appropriate. See in Section 2 to determine the samples and the conditions in which sodium thiosulfate needs to be added.



Figure 3-5. Sodium Thiosulfate

6. Fill the sample bottles with the appropriate discharge samples. Wear disposable gloves and use clean equipment to avoid contaminating and cross-contaminating samples.



Figure 3-6. Sample Collection

7. If necessary, filter the sample for dissolved metals. See instructions for sample filtering in Section 3.3 below.
8. If the laboratory was unable to add preservation chemicals to each bottle, add any appropriate preservation chemicals at this point and test the pH or chlorine, if need be to ensure that the enough has been added.
9. Cool the samples on ice as dictated by the analytical methods. If the discharge water is hot to the touch, consider the need to allow samples to cool for a few minutes prior to placing in ice water to prevent shattering of the sample container or loss of the lid liner into the sample. To avoid contamination, avoid submerging sample containers in ice water.



Figure 3-7. Filled Sample Bottles Preserved on Ice

10. Repeat steps 2 through 9 if more than one discharge needs to be sampled.
11. Complete chain of custody forms. See example chain of custody form in Section 3.5.
12. Once the samples have been cooled to their appropriate preservation temperature, pack the samples for transport to the laboratory. If air or overnight shipping is necessary, see the section on “Sample Packing and Shipping” in Section 3.4 below. Otherwise pack the samples in the coolers to avoid breakage.
13. Transfer custody of the samples to the laboratory and retain a copy of the chain of custody form for your records.

3.3 DISSOLVED METALS FILTRATION

Note: Some labs will filter metals once the sample is shipped/delivered to the laboratory. This may be preferable to avoid on-site sample filtration (as described below).

Equipment Needed:

- Peristaltic pump;
- Approximately 3 feet of New 3/8” Inner Diameter (I.D.) pump silicone tubing;
- 0.45 um cartridge filter with 3/8” Outer Diameter (O.D.) push barbs; and
- A 1-liter plastic sample bottle to collect the filtrate (sample).

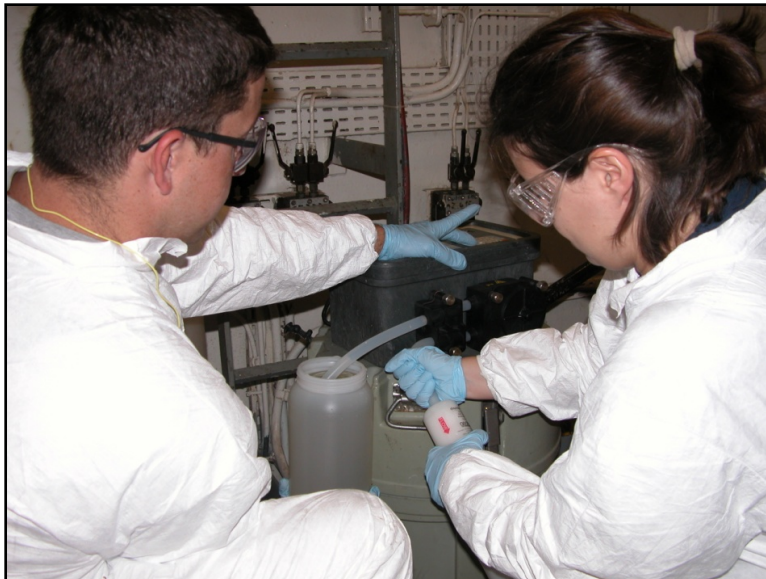


Figure 3-8. Samplers Performing Dissolved Metals Filtration

Filtration Procedure:

1. Place new silicone tubing in the peristaltic pump to prevent cross contamination from previous samples. Allow approximately 2 feet of tubing to extend from both sides (suction and discharge) of the pump head.
2. Place a 0.45 um disposable cartridge filter on the discharge end of the pump tubing. Verify the direction of flow through the cartridge filter (direction of the flow arrow indicated on the filter housing).
3. Start the peristaltic pump and place the suction end of the pump tubing into the unfiltered sample.



Figure 3-9. A Typical Peristaltic Pump

4. Fill the 1-liter plastic sample bottle to approximately $\frac{3}{4}$ full by collecting the discharge from the cartridge filter directly into the sample bottle. Change filter

between samples to prevent contamination of samples or when the flow out of the filter decreases significantly indicating filter is clogged.

5. Add nitric acid into the filtered sample for preservation to pH <2.

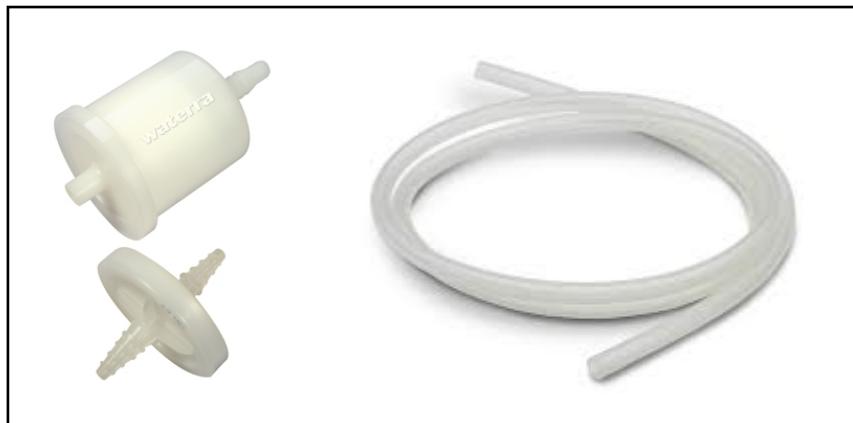


Figure 3-10. Disposable Filter Cartridges and Tubing

3.4 SAMPLE PACKING AND SHIPPING

When samples must be shipped, all samples must be packaged and shipped in accordance with Department of Transportation (DOT) or International Air Transport Association (IATA) regulations. Below are a few tips to ensure the integrity of the samples is maintained through receipt at the laboratory, that the coolers meet the shipping requirements, and that the samples and coolers do not leak. Note that a leaking package will not be delivered.

1. Ensure all bottles are tightly closed and have a waterproof label.
2. Wrap each glass sample bottle with “bubble wrap” and place all bottles in individually sealed zipper storage bags to contain liquids and preservation chemicals in case of shattering, punctures, or leaks. Place plastic bottles in individual zipper storage bags as well to contain any leaks.





Figure 3-11. Packing Glass and Plastic Bottles

3. Line the cooler with a large garbage bag to further ensure nothing leaks from the cooler.



Figure 3-12. Garbage Bags Used to Line a Cooler

4. Place sample bottles and a temperature blank upright in the garbage bag in the cooler and close bag with twist-tie.



Figure 3-13. Individually Packed Samples in a Cooler

5. Arrange sealed plastic freezer bags filled with ice (or chemical ice) on top of the sample bottles (if sample cooling is required for preservation). This will ensure that the preservation temperature of the samples is maintained through receipt at the laboratory, which may take several days.



Figure 3-14. Samples in a Sealed Bag and Bags of Ice to Keep the Samples Cold During Shipping

6. Place the completed chain of custody form in the cooler (retain a copy for your records).

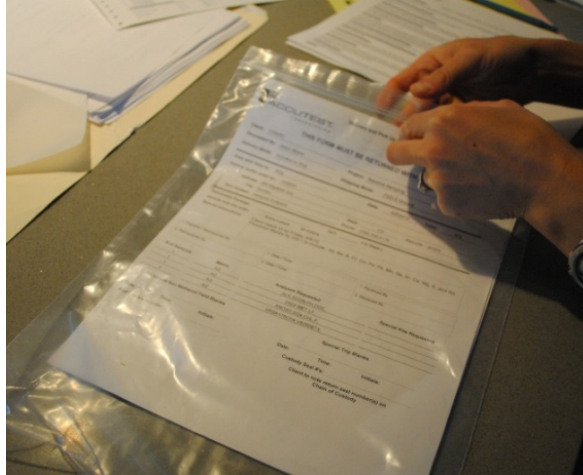


Figure 3-15. Place the Chain of Custody in a Plastic Bag to Keep it Dry.

7. Close cooler and secure with strapping tape to ensure that the lid will remain closed if the latch is accidentally released or damaged. Also tape the cooler drain plug closed so it will not open during shipment.



Figure 3-16. A Packed Cooler Showing the Custody Seal and Strapping Tape

8. Place a completed address label on the lid of the cooler including name, address, and telephone number of the receiving laboratory and the return address and telephone number of the shipper.
9. Place a custody seal on the cooler in a manner that will allow the laboratory to verify the cooler has not been opened or tampered with during shipment. Place clear tape over the custody seal to ensure the custody seal remains on the cooler during transport to the laboratory.

3.5 BOTTLE LABELS AND CHAIN OF CUSTODY (COC) FORMS

Each sample container should have a label that clearly provides information identifying and describing the sample. Ideally, sample container labels should provide the following information:

- Site name
- Sample identification number
- Date and time the sample was collected
- Sampling location (e.g., site name or address)
- Container size
- Container type
- Type of sample (grab or composite)
- Analysis
- Preservatives added, if applicable
- Name or initials of sample collector(s)

All of the information on the sample label should be identical to the information on the COC form. The sample collector should be able to extrapolate based on field notes, bottle labels, and COCs where and when the samples were taken in case additional sampling or analysis is necessary.

To facilitate sample collection activities and ensure proper labeling, sample containers should be pre-labeled as much as is practical prior to sample collection. Sample labels should be completed with waterproof ink and securely affixed to each sample container to identify each sample clearly. If waterproof ink is not used, it is recommended that the sampler cover the label(s) with clear packaging tape after writing the sampling information onto the label.

The COC form should include any available information regarding the potential hazards associated with the sample, handling procedures required for the samples, sample identification number, sample concentration, if known, sampling location, sample date and time, sample matrix, names and signatures of the samplers, and signatures of all individuals who had custody of the samples. A COC form should remain with the samples from collection to laboratory receipt. If samples are split into two or more shipping containers, copies of the COC form should be placed with each container and directly indicate the contents.

A COC form creates an accurate written record that can be used to trace the creation, possession, and handling of the sample from the moment it is collected through analysis. A COC form is used and required, without exception, for the tracking and recording of on-site or off-site sample collection, transport and analysis. A COC form accompanies each sample or group of samples as custody of the sample(s) is transferred from one custodian to another. One copy of the form is retained by the original sample collector, and the original is obtained by the receiving laboratory. If multiple laboratories are receiving a sample, individual COC forms should be submitted; each COC form represents the contents of the sample shipment. Each laboratory or facility representative who accepts an incoming sample shipment signs and dates the COC form. It is typically the laboratory or facility's responsibility to maintain internal logbooks and custody records throughout sample preparation and analysis. Sample custodians are typically responsible for initiating, maintaining, and completing COC tracking. A sample custodian is the person responsible for the custody of a sample or samples at a particular time, until custody is transferred to another person (and so documented), who then becomes the new custodian. A sample is under a person's custody if:

- It is in that person's possession,
- It is in that person's view, after being in that person's physical possession,
- It was in that person's physical possession and then he/she locked it up to prevent tampering, or
- It was in that person's physical possession and then he/she placed it in a designated and identified secure area.

Handling of COC forms during sample transportation depends on the method of transport. If the laboratory is within driving distance, the sample containers can be couriered to the laboratory. In this case, then the courier should sign off on the COC. It is important to note that common commercial carriers will not usually accept responsibility for handling and completing COC forms. This often necessitates packing the COC form in the shipping container (enclosed with other documentation in a plastic zipper-type bag). As long as COC forms are sealed inside the shipping or transport container and the container's custody seals are intact, commercial carriers are not required to sign the COC form. Using a computer and the Web, the tracking information generated by a common carrier can be obtained if complete COC tracking is required. This documentation is attached to the COC form to show that the sample container was in the possession of the carrier during the missing COC time. This time period should be noted as "common carrier" on the COC form between the final custodian at the sample site location and laboratory receipt.

Although COC forms vary in style, format, and detail, the forms should contain the same minimal information required to identify the sample. Procedures for filling out other styles of COC forms will be very similar. It is best for the samplers to fill out the COC form provided by the party receiving the samples. Sample screening can influence the strategy used for sample analysis. Consult with the laboratory service to see if they have existing COC templates and whether they can prefill some of the known information. The following information should be provided and the following steps should be followed to complete COC forms:

- General information (sample owners, contact information, site name)

- Sample specific information for each sample that will be traveling in the same cooler/transport container (i.e., sample identification number, sample type [matrix], grab or composite, number and type of sample containers, and date and time sample was collected)
- Sign, date, and enter the time under “Relinquished by” entry. Have the person receiving the sample sign the “Received by” entry. If shipping samples by a common carrier, print the carrier to be used in this space (e.g., Federal Express, UPS).
- If a common carrier is used, a copy of the airbill is to be kept for recording purposes by both the sender and recipient.
- Place the original signed copy of the COC form in a plastic zipper-type bag or other appropriate waterproof sample shipping package. Retain a copy with the field records.
- Complete carrier-required shipping papers.
- If possible, fax or scan and email a copy of the COC form and field report to the party receiving the samples.

The following is an example of a bottle label:

Sample Number:	000001
Sampling Port:	Miami, Florida
Vessel Name/Number:	Container Vessel 123
Sampling Point Description:	Exhaust Gas Scrubber Inlet Water
Day and Time of Sample Collection:	8/8/2013 4:30 PM EST
Analysis to be Performed:	Total Metals
Sample Bottle Type:	500-mL Plastic Bottle
Preservation Used:	HNO ₃ to pH<2
Sampler Initials:	FH and GW

The following is a sample Chain of Custody form:

Name of Lab Lab Address and contact information	CHAIN OF CUSTODY	Comments:																	
Location:	Ship To:																		
Sampling Contact:	ATTN:																		
Email Address:	Carrier:																		
Phone:	Airbill:																		
Shipped by:	Ship Date:																		
Received by:	Received Date:																		
Sample Point Description		Analysis																	
Sample Number	Date and Time	Collector	Vessel or Ambient Source	Discharge Type	Additional Sample Description	Preservation (y/n)	Filtration (y/n)	Oily (y/n)	Salt Water (y/n)										

Temperature blank – Ship: _____

Temperature blank – Receipt: _____