Washington State Department of Ecology

Spill Prevention, Preparedness, & Response Program

Standard Operating Procedure for Collecting Oil Spill HCID Samples

Version 1.0

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SPL002

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Please note that the Washington State Department of Ecology's Standard Operating Procedures (SOPs) are adapted from published methods, or developed by in-house technical and administrative experts. Their primary purpose is for internal Ecology use, although sampling and administrative SOPs may have a wider utility. Our SOPs do not supplant official published methods. Distribution of these SOPs does not constitute an endorsement of a particular procedure or method.

Any reference to specific equipment, manufacturer, or supplies is for descriptive purposes only and does not constitute an endorsement of a particular product or service by the author or by the Department of Ecology.

Although Ecology follows the SOP in most instances, there may be instances in which Ecology uses an alternative methodology, procedure, or process.

SOP Revision History

Revision Date	Rev number	Summary of changes	Sections	Reviser(s)
09-30-2011	1.0			

Washington State Department of Ecology

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Standard Operating Procedure for Collecting Oil Spill HCID Samples

1.0 Purpose and Scope

1.1 This document is the Spill Prevention, Preparedness, & Response (Spills) Program Standard Operating Procedure (SOP) for collecting oil spill environmental samples for Hydrocarbon Identification (HCID) analysis. Oil in environmental samples (water, sediment, tissue, etc.) is compared to oil from the source of the spill using the HCID analysis to determine if they match. Source oil should be sampled following SOP#SPL001.

1.2 **Objectives** – 1) To collect samples of products associated with an oil spill from the environment for characterization and fingerprinting to match the environmental samples with source oil. 2) To maintain the integrity of the sample(s) during sampling, transport, and storage.

1.3 It is critical to determine if the oil collected in environmental samples matches the source oil to clearly identify the responsible party and assign liability for clean-up costs and natural resource damages. If the spill source is not known initially, samples can be collected from all potential sources and then compared to environmental samples to identify the source. Oil in environmental samples matched to source oil samples documents violations of applicable laws and natural resource exposures. To assign liability, samples must be carefully collected to prevent contamination and strict chain-of-custody must be maintained throughout collection, transport, and analysis.

1.4 Hydrocarbon Identification (HCID) is the analysis used to characterize and fingerprint petroleum based oil samples. For some oils, an additional a bio-marker analysis can be performed to confirm a match. HCID is a qualitative analysis and does not result in the measurement of a concentration of oil in the sample. The amount of oil in a sample for the HCID analysis is not important as long as enough oil is present to perform the analysis. Very little oil is needed for the HCID analysis, but the amount of oil collected in a sample should be maximized to ensure that enough is present to perform the analysis. One or two ounces of concentrated oil is adequate for multiple HCID analyses, therefore collection of a large quantity of concentrated oil for each sample is unnecessary and presents disposal problems for the laboratory. If the concentration of oil in environmental samples is needed (quantitative analysis), other SOPs are available for a variety of media (water, sediment, tissue, etc.).

2.0 Applicability

2.1 This procedure is based on protocols developed by Research Planning, Inc. (http://www.researchplanning.com/services/damage-assessment-restoration/) for NOAA for oil spill Natural Resource Damage Assessments (NRDA). The protocols were based on sampling and analytical methods developed for the National Status and Trends Program. These protocols are widely accepted and used by oil handling companies, consultants, and other trustees and should be used for all oil spill related sampling. This procedure is based on and closely follows the SOP for source oil sampling, but expands the procedure to include sampling of oil in water, sediment/soil, and tissue.

3.0 Definitions

3.1 NOAA – National Oceanic and Atmospheric Administration.
3.2 GC/FID – Gas Chromatograph/Flame Ionizing Detector
3.3 GC/MS – Gas Chromatograph/Mass Spectrometer
3.4 TRAP – Trustee Resource Assessment and Protection.
3.5 NRDA – Natural Resource Damage Assessment.
3.6 SOSC – State On Scene Coordinator

4.0 Personnel Qualifications/Responsibilities

4.1 Any Ecology employee expecting to collect oil spill related samples must attend appropriate training from a Spills Program Sampling Specialist. Oil spill sample collection for HCID analyses can be conducted by any employee that has completed basic sampling training and has collected at least one field sample under the supervision of an experienced sampler. All Spills Program employees (including managers and administrative staff) are encouraged to attend basic sampling training. Due to safety requirements, at least two people are recommended for any field sampling and anyone that has taken the training, with or without field experience, can assist an experienced sampler.

5.0 Equipment, Reagents, and Supplies

5.1 Equipment

5.1.1 Samples should be collected in certified clean glass containers. Alternatively, new glass containers (such as Mason jars or uncertified jars) can be used if certified containers are not available, but at least one empty container of the same type and kind should be submitted with the samples as a container blank. Metal containers, such as buckets, can be used to collect the samples if necessary as long as they are thoroughly cleaned first, but the samples should be transferred to glass containers for shipment to the laboratory. This method should not be used for sheens because most of the oil will stick to the metal container and will not be transferred to the glass container. Plastic containers should never be used.

5.1.2 Concentrated product is oil that has been spilled into the environment that is in pools, tar balls, or heavy coatings where there is more oil present than other material (water, sediment, etc.). Concentrated product can be transferred directly into wide-mouth glass jars with pre-cleaned stainless steel spoons or other appropriate tools.

5.1.3 Essentially any oiled material associated with an oil spill (debris, vegetation, beach wrack, etc.) can be collected for HCID analysis, using an appropriate sized glass container and a pre-cleaned tool to transfer the material.

5.1.4 Water samples can be collected directly into the sample container, minimizing risks of contamination. Water samples analyzed for HCID are typically collected in narrow mouthed one-liter amber glass bottles with Teflon lined caps.

5.1.5 Sediment or soil samples are collected in 8 oz. wide-mouth glass jars by directly transferring the sediment or soil into the jar with a pre-cleaned stainless steel spoon.

5.1.6 Tissue samples for HCID analysis only require an appropriate sized container (usually a 4 or 8 oz. glass jar) to collect oil from impacted fish or wildlife with pre-cleaned fiberglass cloth or Teflon mesh, or stainless steel spoons.

5.1.7 GPS (set datum to WGS-84).

5.1.8 Digital camera.

5.1.9 Ice chests with wet or blue ice (preferably equipped with chain of custody security cables).

5.2 **Reagents**

5.2.1 Pesticide grade acetone and hexane for decontamination.

5.3 **Supplies**

5.3.1 Sample tags and labels
5.3.2 Field notebook
5.3.3 Chain-of-custody seals
5.3.4 Chain-of-custody forms
5.3.5 Nitrile disposable gloves
5.3.6 Ziploc bags
5.3.7 Paper towels
5.3.8 Stainless steel spoons or spatulas
5.3.9 Liquinox or equivalent soap
5.3.10 Aluminum foil
5.3.11 Cleaning brush
5.3.12 Distilled water

6.0 Summary of Procedure

6.1 Sample Collection Procedure

6.1.1 Safety is of greatest concern. Be aware of physical and chemical hazards at the site. Get a safety briefing before entering the area. Do not enter confined spaces unless they have been determined to be safe. Use recommended safety equipment and procedures.

6.1.2 Develop a sampling plan. Identify the number and type of samples that are to be collected, the type of containers that will be used, and unique identifiers for each sample. Make a drawing of the area being sampled, including points of reference and the location of each site where samples are collected so the sites could be located later if necessary. Identify the sampling procedure(s) that will be used. Include any preservation techniques used for the samples, the type of analyses that will be done, and the laboratory that the samples will be sent to. The plan can be recorded in a field notebook or on a separate piece of paper; there is no required form or specific format that must be followed. Each plan will be different depending on the number and type of samples being collected and the complexity of sampling site.

6.1.3 Concentrated product is oil that has been spilled into the environment that is in pools, tar balls, or heavy coatings where there is more oil present than other material (water, sediment, etc.). Concentrated product can be transferred directly into wide-mouth jars with pre-cleaned stainless steel spoons or other appropriate tools. Concentrated product floating on water can be collected with spoons, by soaking the oil up with pre-cleaned fiberglass cloth, scooping the oil up with pre-cleaned Teflon nets, or by scooping the oil up directly into glass bottles or jars (the outside of the containers should be cleaned off before sending to the laboratory). Coatings of concentrated product on rocks or solid structures can be sampled by wiping the surface with pre-cleaned fiberglass cloth or Teflon mesh, or by scraping with a pre-cleaned spoon. Teflon nets or mesh and fiberglass cloth must be put into glass containers for transport to the lab.

6.1.4 Most oil spilled into an aquatic environment will be floating on water, either as concentrated product (which should be collected as described above) or as a sheen. Sheens can be a variety of colors depending on the type of oil and the thickness of the floating layer. Thicker sheens are metallic or rainbow colored and thin sheens are silver. Some oil can mix with water and form an emulsion or “mousse”. For sheens or emulsified oil, collect as much oil as possible, while minimizing the amount of water collected. Using a narrow-mouth one-liter amber bottle, submerge the bottle at an angle with the mouth at the surface of the water and slowly fill the bottle. Keep half of the bottle mouth above water so air coming out of the bottle does not produce bubbles. Do not fill the bottle to the top; try to keep about one-inch of head space. One bottle will be sufficient for most sheen and emulsified oil samples, but two or more bottles can be collected and combined at the lab if the sheen is very thin. Do not collect a sample in one container and then transfer to another container; oil will stick to the container and much of the sample may not be transferred. Teflon nets can be used to collect oil in sheens; pull the net through the sheen until the net is saturated with oil and is not picking up any additional oil. Transfer the net into a glass container.

6.1.5 Most oils will readily soak into sediment or soil so that the sediment or soil just appears to be wet. If any water is present, the sediment or soil surface will sheen. If the oil has pooled on the surface of the sediment or soil, then the oil should be collected as concentrated product. For all oils except gasoline, sediment or soil samples are collected by filling an 8 oz. glass jar ¾ full with a pre-cleaned stainless steel spoon. Other cleaned tools (glass, Teflon, etc.) can be used to transfer the product, but do not use plastic items. Collect material that will maximize the amount of oil in the sample; fine grained sediment or soil will have more oil than coarse material. Water, vegetation, or other debris can be collected along with the sediment or soil and will not affect the results. However, be careful not to collect any creosote contaminated debris. For collecting sediment or soil associated with a gasoline spill, see SOP#SPL006.

6.1.6 When fish or wildlife are impacted by an oil spill (oiled), samples of the oil on the fish or wildlife need to be collected to document injury. Oil probably will not stick to fish so a sample should be collected of any oil in the proximity of dead or dying fish. See SOP#SPL007 for collection of dead fish associated with an oil spill. When possible, oil should be collected directly from impacted wildlife. Do not collect the whole animal; collection of dead wildlife associated with an oil spill should be coordinated with Wildlife Rescue. Collect oil from the impacted wildlife by wiping with a pre-cleaned square of fiberglass cloth or Teflon mesh, scraping with a pre-cleaned stainless steel spoon, or clipping hair/fur or feathers with pre-cleaned scissors. Place the sample into a 4 or 8 oz. wide-mouth glass jar.

6.1.7 Any oiled material in the vicinity of an oil spill can be collected for HCID analysis as long as it will fit in a jar and it is not contaminated with petroleum products unrelated to the spill (e.g., creosote). Commonly collected materials include beach wrack, vegetation (live or dead), and small rocks or pieces of concrete. Plastic debris should be avoided, including absorbent material used for spill clean-up. Transfer the oiled material into jars using appropriate pre-cleaned tools.

6.1.8 Label each container with an adhesive label directly applied to the container and with a paper tag attached to the container with an elastic band. Use a waterproof pen or marker to record the project or incident name, a station identifier, a unique sample identifier, the collection date and time, the sample type (HCID), and the sampler's name or initials on each label. The adhesive label should be filled out and applied to the container prior to sample collection.

6.1.9 After labeling, place each sample container in a separate Ziploc bag to reduce the chance of contamination should a container leak or break.

6.1.10 Immediately place all samples in a cooler and keep at ≤6°C (do not freeze).

6.1.11 Use packing material, such as bubble wrap, around containers to prevent breakage.

6.1.12 Fill out the chain-of-custody form; be sure to record all information for each sample. Record the same information in a field notebook and add specific information about where each sample was collected from, including latitude-longitude and a map if necessary. Also include the sampling devices used, container sizes and types, if any preservative was used, and sampler name.

6.1.13 Make special notation on the chain-of-custody form about any problems or observations during sampling, such as potential sources of contamination, etc.

6.1.14 Maintain strict chain-of-custody during sample storage and transportation.

6.1.15 If possible, ship source samples separately from environmental samples to reduce risk of cross contamination.

6.1.16 Samples can be held at ≤6°C in the dark for up to 7 days without loss of sample integrity. HCID samples can be extracted within the 7 days and the holding time for the extract is 40 days.

6.2 **Analytical Methods**

6.2.1 **Hydrocarbon Identification** (HCID). A GC/FID is used to analyze petroleum source and environmental samples to determine if they match, i.e. the source oil is the same as the oil spilled into the environment. When there is any doubt to the origin of a spill, some oils can be analyzed for bio-markers for confirmation.

6.2.2 **Bio-markers, Steranes and Triterpanes**. These compounds are highly resistant to degradation and have a unique distribution for each batch of oil (unique to a specific load of crude oil). Thus, they are valuable for differentiating among different sources of hydrocarbons. This analysis is a specialized method using GC/MS in the selected ion monitoring mode.

6.3 **Decontamination Procedure**

6.3.1 Wash with soap (Liquinox or equivalent) and water (preferably hot), scrubbing all surfaces thoroughly with the cleaning brush. If the item being cleaned is heavily contaminated (oiled), this step should be repeated after washing to remove gross contamination.

6.3.2 **Procedure**:

6.3.2.1 Rinse with tap water and then triple rinse with distilled water.

6.3.2.2 Rinse with acetone.

6.3.2.3 Rinse with hexane.

6.3.2.4 Allow to air dry.

6.3.2.5 If item is not used immediately, wrap in solvent rinsed aluminum foil.

7.0 Records Management

7.1 Sampling Plan Template – Use this form as an aid for developing a complete and comprehensive sampling plan. This form is not required for developing a sampling plan, but provides ready access to guidelines and reminders.

7.2 Sampling Documentation Form – Use this form as an aid and reminder for recording complete and comprehensive sampling information, and provides a single place to record information for multiple samples.

7.3 Both forms are available at:
http://teams/sites/SPPR/response/trap/Sampling/Forms/AllItems.aspx (SharePoint)
or X:\Spills_Program\Response Section\TRAP-NRDA\Sampling\

7.4 Oil Spill Chain-of-Custody Form (ECY 050-42 (11/01))

8.0 Quality Control and Quality Assurance Section

8.1 There are no QA/QC requirements specific or unique to this procedure. Field splits should be avoided. If splits are requested, the samples should be submitted to the laboratory and the laboratory can be asked to split the samples. Typically, the laboratory will extract the samples and then split the extracts. The laboratory will usually provide splits directly to the requester or their laboratory if the sample contains enough material.

9.0 Safety

9.1 Sample collection can present some unusual circumstances that could have equally unusual associated safety hazards. Samplers should consult with the Safety Officer or SOSC and review the incident safety plan or Hazard Assessment Worksheet (HAW) prior to developing a sampling plan so known hazards can be avoided. Samplers should also be aware that sampling will often take place in areas that may not be adequately addressed in the safety plan or HAW. If there is any question, then a separate HAW should be prepared prior to sampling. A Sampling HAW is available at:
http://teams/sites/SPPR/response/trap/default.aspx (SharePoint) or X:\Spills_Program\
Response Section\TRAP-NRDA\Sampling, that includes action levels appropriate for sampling various petroleum products.

9.2 Some hazards that could be associated with sampling are:
9.3 Low areas that could collect fumes (vapors) or have reduced oxygen levels (confined space)
9.4 Higher concentrations of fumes at ground level where samples are collected
9.5 General water hazards when collecting samples on a shoreline or from a boat or dock, etc.
9.6 Increased risk of slips, trips, and falls
9.7 Traffic when sampling near a highway

9.8 Dangerous animals
9.9 Exposure to elements (hot or cold)
9.10 Eye damage from splashes or brush/branches

10.0 References

10.1 NOAA, 1993. Sampling and analytical methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Water Projects, 1984-1992. Volume IV, Comprehensive descriptions of trace organic analytical methods. Lauenstein, G.G. and A.Y. Cantillo (eds.). NOAA Tech. Memo NOS ORCA 71, Silver Spring, MD. 181 pp.