

Protocols For Collecting NRDA Samples

SPILL SOURCE

Sampling Objectives

- To obtain a sample(s) of the original product(s) involved in the incident, for characterization, fingerprinting, predicting fate and effects (via bioassays) of the spilled oil.
- To maintain the integrity the spill source sample(s) during sampling, transport, and storage.

Sample Volume

- Ideally, collect a minimum of 1 liter per source sample. That is, for each location sampled (e.g., per tank, hold, etc.), one 1-L sample should be taken. If there are many different holds or tanks, take a small sample (250 mL) from each.

Sampling Equipment/Containers

- Source samples can be collected directly into the sample container, minimizing risks of contamination. Use a device which holds the container, such as a Wheaton grab sampler (holds a 1-L bottle strapped to a metal rod with the ability to unscrew the cap remotely) or a Volskom sampler (frame which holds the container is lowered on a rope). For black oils, these methods can be messy, coating the device and container with oil.
- Other types of samplers for transferring to a container include: drum thief; coliwasa (narrow tube with positive end seal); bailer; bomb sampler; and air-driven metallic pumps.
- Sampler material, in order of preference: teflon (there are inexpensive disposable models); PVC (may contribute phthalates, but should not interfere with interpretation); and glass.
- Under emergency conditions, a new metal (preferred) or plastic (a last resort) bucket can be used after cleaning with soap and water.
- Use glass containers, certified-clean as organic-free (i.e., solvent rinsed), with teflon-lined lids. Wide-mouth containers are easier to fill. As a last resort, use clean “mason” jars.
- Paper, metal, or plastic funnels are useful when transferring samples. Clean prior to use.

Sample Collection Methods

- 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.
- Collect the source sample as soon as possible, even for potential releases. Collect the freshest sample of the spilled material, even if it is from the water, shoreline, etc.
- Decon equipment after unique tank or hold is sampled with rinses of acetone or methanol, then methylene chloride. Collect all rinsate for proper disposal.
- Give the source sample used for NRDA purposes a name other than just the spill name, since there could be multiple “source” samples collected for different purposes.
- Label each sample container uniquely and sequentially, whether it is a replicate or from different storage tanks on a vessel. For example, Spill Name NRDA Source Oil No. 1-2P- rep 1 would be the first sample collected, from #2 port hold, replicate #1.
- Fill out the chain-of-custody form, noting where each source sample was collected from, sampling device used, time/date of collection, size and container type, and sampler name .
- Make special notation on the chain-of-custody form about any problems or observations during sampling, such as visual differences in samples from different tanks, presence of water in the sample, etc.
- Maintain strict chain of custody during sample storage and transportation.
- Ship source samples separately from environmental samples to reduce risk of cross contamination.

Preservation/Holding Times

- Immediately place all samples in cooler and keep at 4°C (do not freeze).
- Use packing material, such as bubble wrap, around containers to prevent breakage.
- Petroleum samples can be held at 4°C in the dark for up to 3-4 months without loss of sample integrity, as long as there is no organic material or water present to serve as nutrients for bacterial growth.

Analytical Methods

- **Petroleum products** are usually analyzed for fingerprinting purposes, so that the spilled oil can be differentiated from other petroleum sources. Chemical analyses for this purpose include:
 - Saturated Hydrocarbons (SHC).** These compounds include n-alkanes and saturated isoprenoids. They are contained in the f_1 fraction obtained after column chromatography and measured by GC-FID analysis. The chromatographic trace can be used to differentiate among oils and is valuable for predicting the short-term weathering and fate of the oil.
 - Polynuclear aromatic hydrocarbons (PAH).** PAHs are used to fingerprint the spilled oil, monitor weathering, and predict toxicity. If PAHs are to be measured, it is important that the analytes include the alkyl-substituted PAH homologs, in addition to the standard PAH “priority pollutants”. This method is referred to as Modified EPA Method 8270, because the list of PAHs is expanded to include the alkylated homologs, using GC/MS in the selected ion monitoring mode.
 - Steranes and triterpanes.** These compounds are highly resistant to degradation and have a unique distribution for each oil type. Thus, they are valuable for differentiating among different sources of hydrocarbons. However, few laboratories have the ability for this analysis, which is a specialized method using GC/MS in the selected ion monitoring mode.
- There are no general analytical guidelines for chemical products because of their variability.

Other Considerations

- There may be different products loaded in different compartments or tanks, even when only one type of product is involved (e.g., two different types of No. 2 fuel oil could be loaded). Before sample collection, get a loading diagram and as much data as possible on the products. Slight differences in product properties, such as specific gravity, may indicate different products. Each unique product should be sampled.
- Make sure that the source sample(s) collected represent the material actually released. Again, product in intact holds may not be the same as the released product.
- Be aware of sources of contamination or mixing of products onscene, such as transferring of product between holds, dilution with fire-fighting water, or application of a foam blanket.

Key References

- NOAA, 1993. Sampling and analytical methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Watch 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.
- Sauer, T.C. and P.D. Boehm, 1995. Hydrocarbon chemistry for analytical methods for oil spill assessments. Marine Spill Response Corporation Technical Report Series 95-032, Washington, D.C. 114 pp.
- USEPA, 1979. Methods for chemical analysis of water and wastes. EPA-600/4-79/020. USEPA Environmental Monitoring Systems Laboratory, Office of Research and Development, Cincinnati, Ohio.
- USEPA, 1986. Test methods for evaluating solid waste. SW 846 Third Edition (and updates).