Designation: D 4489 – 95

Standard Practices for Sampling of Waterborne Oils[1]

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1. Scope

1.1 These practices describe the procedures to be used in collecting samples of waterborne oils (see Practice D 3415), oil found on adjoining shorelines, or oil-soaked debris, for comparison of oils by spectroscopic and chromatographic techniques, and for elemental analyses.

1.2 Two practices are described. Practice A involves“ grab sampling” macro oil samples. Practice B can be used to sample most types of waterborne oils and is particularly applicable in sampling thin oil films or slicks. Practice selection will be dictated by the physical characteristics and the location of the spilled oil. These two practices are:

	Sections
Practice A (for grab sampling thick layers of oil, viscous oils or oil soaked debris, oil globules, tar balls, or stranded oil)	9 to 13
Practice B (for TFE–fluorocarbon polymer strip samplers)	14 to17

1.3 Each of the two practices is designed to collect oil samples with a minimum of water, thereby reducing the possibility of chemical, physical, or biological alteration by prolonged contact with water between the time of collection and analysis.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazards statements, see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[2]

D 3415 Practice for Identification of Waterborne Oils[3]

3. Terminology

3.1 *Definitions*—For the definitions of terms used in these practices, refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *chain of custody*—a documented accountability of each sample, that is, date, time, and signature of each recipient when the sample changes hands, from the time of collection until the requirement for each sample is terminated.

3.2.2 *waterborne oil*—refer to Practice D 3415.

4. Significance and Use

4.1 Identification of the source of a spilled oil is established by comparison with known oils selected because of their possible relationship to the spill, that is, potential sources. Generally, the suspected source oils are from pipelines, tanks, etc., and therefore pose little problems in sampling compared to the spilled oil. This practice addresses the sampling of spilled oils in particular, but could be applied to appropriate source situations, for example, a ship’s bilge.

5. Apparatus

5.1 *Sample Containers*, 100 to 125-mL wide-mouth glass jars that have been thoroughly cleaned. When field expedients must be employed, an empty container of each type used should be included in the shipment to the laboratory, to be used as a blank to measure inadvertent contamination.

5.2 *Closures*—Lids for the glass jars should have TFE-fluorocarbon polymer film or aluminum-coated insert.

5.3 *Strip Samplers*, 5 by 7.5 cm pieces of TFE-fluorocarbon polymer sheets (0.25 mm thickness, or screen or fabric (50–70 mesh)).

5.4 *Wooden Tongue Depressor*.

5.5 *TFE-Fluorocarbon Polymer Net Sampling Kit.*[4]

6. Reagents

6.1 *High Purity Solvents,*[5] that must be used for rinsing samplers and sample containers. The solvents which may be used are *n*-hexane, mixed hexanes, cyclohexane, pentane, or dichloromethane, acetone, or chloroform.

7. Hazards

7.1 **Precaution:** Extreme care should be exercised so as not to contaminate the samples or cause their integrity to be questioned.

7.2 **Warning:** The rinsing solvents are volatile and, except for dichloromethane, are flammable, and therefore should be

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[1] These practices are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.02.

[4] Sampling kit available from General Oceanics, Miami, FL, or equivalent, is suitable.

[5] MCB Spectroquality solvents, available from MCB Manufacturing Chemists, Inc. (Associate of E. Merck, Darmstadt, Germany), 480 Democrat Rd., Gibbstown, NJ 08027, or equivalent are suitable.

handled with appropriate care. Dichloromethane will release toxic vapors when heated.

7.3 Minimize contact with oil even when wearing gloves.

8. General Sampling Guidelines

8.1 The objective is to obtain a sample for analysis that is representative of the spilled oil. The most critical factors in sampling are selecting a suitable location, collecting a sample of oil with the least water possible (to minimize possible sample alteration), and maintaining the sample integrity.

8.2 It is recommended that at least three samples be taken of each waterborne oil in order to demonstrate the homogeneity of the spill. These samples should be taken in different regions of the oil slick at points where the accumulation is heaviest. This will increase the volume of oil available for analysis. In the event that multiple samples cannot be collected, then a single sample should be collected from the area where the accumulation of oil visually appears to be the heaviest.

8.3 The following general rules are applicable to sampling of waterborne oils:

8.3.1 Take a sample that contains sufficient oil for the method or methods of analysis to be employed and for any replicate analyses that may be required.

8.3.2 Affix a label or tag to the sample jar in such a manner that it becomes an integral part of the container. The label or tag should contain the following information: sample identification, date and time of collection, location of collection, signature of person collecting the sample, and at least one witness to the collection.

8.3.3 Pack the samples, ship, and manipulate prior to analysis in a manner that maintains a continuous chain of custody and safeguards against tampering or changes in the properties of the samples.

8.4 Store collected samples at refrigerator temperatures (4 to 5°C).

NOTE 1—Storage at lower temperatures (−10°C or lower) may cause irreversible crystallization of waxes. Storage at 4 to 5°C obviates this problem; biological degradation at 4 to 5°C has been found negligible over a 3 to 5 year storage with respect to qualitative identification of oil.

PRACTICE A—GRAB SAMPLING

9. Scope

9.1 This practice is applicable to thick layers of waterborne oil films, viscous oils, oil globules, and tar balls.

9.2 This practice is also applicable to sampling oil stranded on shorelines or oil-soaked debris.

10. Summary of Practice

10.1 The sampling consists of collecting the sample directly with the sample container, that is, scooping the sample up in the sample jar and sealing.

11. Apparatus

11.1 The sample container serves as the sampling device (see 5.1). The glass jars and lid liners should be rinsed three times with a high purity solvent (see 6.1), allowed to air dry, and assembled prior to use. Sample jars that are precleaned using EPA recommended wash procedures for organics are acceptable.

NOTE 2—To avoid possible sample contamination, do not reuse sample containers, lids, or liners.

11.2 Nitrile gloves are to be worn during sampling.

11.3 A detachable ring for the sample jar and sampling pole may be useful to extend sampling range.

12. Procedure for Floating Samples

12.1 Select the sampling site.

12.2 Unscrew the lid from the sample jar. Hold the jar in position for sampling; hold the lid in a free hand or place the lid in a safe position. Gently lower the sample jar into the water and gently skim the oil layer or oil globules from the water surface into the sample container. Continue the process until the sample container is approximately three-quarters full.

12.3 Remove the sample container from the water surface, replace and tighten the lid. Invert the jar and allow the container to stand in this position for 2 to 3 min.

12.4 Gently unscrew the sample jar lid and allow the water layer to drain out of the inverted container. Seal the lid and return the jar to the upright position.

12.5 Repeat 12.2 to 12.4, if necessary, until approximately 60 mL of oil is collected, or until there is no increase in the amount of recovered oil.

12.6 When the collection is complete, invert the jar and allow to stand for 10 min. Gently unscrew the lid to drain off excess water a final time. Tighten the lid and return the jar to the upright position. Wipe excess water and oil from the outside surface of the sample container.

12.7 Attach a sample label or tag to the container, bearing the information cited in 8.3.2.

13. Procedure for Shoreline Sampling (Oil on Sand and Debris)

13.1 Select a sampling site where oil accumulation is largest.

13.2 Open the sample jar; hold the jar in one hand and lid in the other. Using either the sample jar or the lid as a scoop, fill the jar three-quarters full with oil-saturated material. Use a wooden tongue depressor to maneuver the sample into the jar, if necessary.

13.3 Replace and tighten the lid. Wipe excess material from the outside surfaces of the sample container and lid.

13.4 Attach the sample label or tag to the container, bearing the information cited in 8.3.2.

PRACTICE B—TFE-FLUOROCARBON POLYMER SAMPLERS

14. Scope

14.1 This practice is applicable to sampling all types of oil by preferential adherence to a film or sheet of TFE-fluorocarbon material. It depends in principle on the lipophilic properties of TFE-fluorocarbon polymer, that is, the preferential adhesion of oil rather than of water to TFE-fluorocarbon polymer.

14.2 In general, the use of TFE-fluorocarbon polymer screening (approximately 50 to 70 mesh) will collect significantly more oil than strips of sheet material. The screen reduces the rate at which oil rolls off the surface and presents more surface openings to trap oil droplets, thereby collecting more oil per unit area of film.

14.3 TFE-fluorocarbon polymer mesh fabric sheets are commercially available. These are the most efficient form of TFE-fluorocarbon polymer for sampling oil. Although they can be used directly in sheet form, this material can be fabricated into nets of design similar to a miniature plankton net, further increasing the ease with which the collection device can be brought into contact with the oil sheen. There is little difference in the performance of the nets ranging from 100 to 200 micron mesh size.

14.4 The efficiency of collecting oil increases as the viscosity of the oil increases. This practice is particularly useful in sampling highly weathered oils.

15. Summary of Practice

15.1 Sampling is accomplished by slowly dragging the TFE-fluorocarbon polymer through the slick and using its natural affinity to collect the oil.

15.2 The procedure is for the use of strips of TFE-fluorocarbon polymer sheet, TFE-fluorocarbon screen or fabric screen, or commercially available prefabricated nets with support rings.

16. Materials

16.1 TFE-fluorocarbon polymer can be obtained in sheets of 0.25 mm thickness. To increase the efficiency of oil collection, sheets can be obtained containing five 1.5-mm holes per square centimetre. Higher oil collecting efficiency can be obtained by using the previously mentioned 50 to 70-mesh screen (see 14.2) or fabric (see 14.3).

16.2 TFE-fluorocarbon polymer is cut into 5 by 7.5 cm strips. Carefully rinse the strips with high purity solvent (see 6.1) and air dry. Place eight strips in each sample jar that has been precleaned as described in 11.1, and tightly seal the lids.

16.3 Each jar, containing eight strips, is used for taking a single sample. One jar is set aside in each sampling situation for use as a blank in subsequent analyses.

16.4 Clean tweezers, hemostats, or pliers are required for handling the TFE-fluorocarbon strips to avoid contamination.

16.5 TFE-fluorocarbon polymer mesh fabric, with 150 µm distance between the polymer threads, is available prefabricated into nets that are detachable from support rings. The nets and rings are cleaned and prepackaged with nitrile gloves in plastic bags. To avoid contaminating the nets with finger oils, it is critical to handle the nets only with the nitrile gloves.

17. Sampling Waterborne Oils

17.1 Select the sampling site where oil accumulation is heaviest.

17.2 For the strip technique, remove the lid from the sample jar. Using precleaned tweezers, hemostats, or pliers as holders, carefully lay the TFE-fluorocarbon strips on the inverted lid. Using the holder, take the strips one at a time, and gently drag them through the slick. Expose both sides of the TFE-fluorocarbon polymer strip to the slick by turning the strip over and dragging it again through the slick, taking care not to get oil on the tweezers, hemostats, or pliers. Place the strip in the empty sample jar as quickly as possible to prevent loss of oil.

17.3 Repeat 17.2 until all eight strips have been used.

NOTE 3—For extremely thin sheets, it is recommended that 16 strips be used, rather than 8.

17.4 For the net technique, remove the nitrile gloves from the kit. Do not handle anything other than the sample kit. Remove the net from its sealed bag using the handle of the support ring to which it is attached. If necessary, attach the net support ring to the extension pole. Do not allow the net to come into contact with anything other than the spill.

17.5 Take the sample by skimming through the sheen and straining the oily water through the net. Make sure that the sheen is entering through the mouth of the net and straining through the fine mesh of the net. Slowly skim the surface with the net back and forth through the full length of the sheen at least eight times.

17.6 While still wearing the gloves, unclip the net from the support ring and place the net into a clean sample jar. Expect some water to remain in the jar. Touch the net material as little as possible. Discard the gloves.

17.7 Attach each jar lid and tighten.

17.8 Attach a sample label or tag to each container, bearing the information cited in 8.3.2.

18. Keywords

18.1 oil identification; sampling; spilled oil; TFE-fluorocarbon polymer sampler; waterborne petroleum oils