



Designation: D3326 – 07 (Reapproved 2024)

Standard Practice for Preparation of Samples for Identification of Waterborne Oils¹

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1. Scope

1.1 This practice covers the preparation for analysis of waterborne oils recovered from water. The identification is based upon the comparison of physical and chemical characteristics of the waterborne oils with oils from suspect sources. These oils may be of petroleum or vegetable/animal origin, or both. Seven procedures are given as follows:

	Sections
Procedure A (for samples of more than 50 mL volume containing significant quantities of hydrocarbons with boiling points above 280 °C)	8 to 12
Procedure B (for samples containing significant quantities of hydrocarbons with boiling points above 280 °C)	13 to 17
Procedure C (for waterborne oils containing significant amounts of components boiling below 280 °C and to mixtures of these and higher boiling components)	18 to 22
Procedure D (for samples containing both petroleum and vegetable/animal derived oils)	23 to 27
Procedure E (for samples of light crudes and medium distillate fuels)	28 to 34
Procedure F (for thin films of oil-on-water)	35 to 39
Procedure G (for oil-soaked samples)	40 to 44

1.2 Procedures for the analytical examination of the waterborne oil samples are described in Practice D3415 and Test Methods D3328, D3414, and D3650. Refer to the individual oil identification test methods for the sample preparation method of choice. The deasphalting effects of the sample preparation method should be considered in selecting the best methods.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific caution statements are given in Sections 6 and 32.

1.5 *This international standard was developed in accordance with internationally recognized principles on standard-*

ization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:²

D95 Test Method for Water in Petroleum Products and Bituminous Materials by Distillation
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D3325 Practice for Preservation of Waterborne Oil Samples
D3328 Test Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography
D3414 Test Method for Comparison of Waterborne Petroleum Oils by Infrared Spectroscopy (Withdrawn 2018)³
D3415 Practice for Identification of Waterborne Oils
D3650 Test Method for Comparison of Waterborne Petroleum Oils By Fluorescence Analysis (Withdrawn 2018)³
D4489 Practices for Sampling of Waterborne Oils
E1 Specification for ASTM Liquid-in-Glass Thermometers
E133 Specification for Distillation Equipment

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *animal/vegetable-derived oils, n*—a mixture made of mono-, di-, and triglyceride esters of fatty acids and other substances of animal or vegetable origin, or both.

3.2.2 *simulated weathering of waterborne oils by distillation, n*—considers only the effect of evaporation, which likely is the most significant short-term weathering effect in the environment.

¹ This practice is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

3.2.3 *simulated weathering of waterborne oils by evaporation, n*—under ultraviolet light simulates the loss of light components on weathering, as well as some oxidative weathering.

4. Significance and Use

4.1 Identification of a recovered oil is determined by comparison with known oils selected because of their possible relationship to the particular recovered oil, for example, suspected or questioned sources. Thus, samples of such known oils must be collected and submitted along with the unknown for analysis. It is unlikely that identification of the sources of an unknown oil by itself can be made without direct matching, that is, solely with a library of analyses.

5. Reagents and Materials

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.⁴ Special ancillary procedures such as fluorescence may require higher purity grades of solvents. Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water that meets the purity specifications of Type I or Type II water, as specified in Specification **D1193**.

6. Caution

6.1 Solvents used in this practice are volatile, flammable, or may cause the harm to the health of the user. Specifically, benzene is a known carcinogen, while chloroform and carbon tetrachloride are suspected carcinogens. Consequently, it is important that extractions and separations utilizing these substances must be carried out in a laboratory hood with a minimum linear face velocity of 38 m/min to 45 m/min (125 ft/min to 150 ft/min) located in a regulated area posted with signs bearing the legends: NO SMOKING or (if appropriate) DANGER — CHEMICAL CARCINOGEN—AUTHORIZED PERSONNEL ONLY, or both.

7. Sampling

7.1 Collect representative samples in accordance with Practices **D4489**.

7.2 Preserve the waterborne oil samples in accordance with Practice **D3325**.

7.3 The portion of the sample used must be representative of the total sample. If the material is liquid, thoroughly stir the sample as received, warming if necessary to ensure uniformity.

⁴ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

PROCEDURE A—LARGE SAMPLES

8. Scope

8.1 This procedure covers the preparation for analysis of samples in which the volumes of waterborne oil in the environmental and suspect source samples equal or exceed 50 mL and in which the oil portion contains significant amounts of hydrocarbons with boiling points above 280 °C.

NOTE 1—The boiling point may be ascertained by injecting the neat samples into the gas chromatograph and checking the elution times above that of pentadecane on a nonpolar column.

8.2 The preparation of samples containing mostly hydrocarbons of boiling points below 280 °C, such as petroleum distillate fuels, is beyond the scope of this procedure (see Procedure C or E).

9. Summary of Procedure

9.1 A neat portion of the waterborne oil is retained. If not possible to obtain a neat portion, then retain a portion of the waterborne oil as received. This is to be used in those analyses performed on samples containing significant quantities of hydrocarbons with boiling points below 280 °C. Preparation of these samples is beyond the scope of this procedure, but are covered in Procedure C.

NOTE 2—Waterborne oil samples containing significant quantities of hydrocarbons with boiling points below 280 °C (see **Note 1**), such as gasoline and kerosene, can usually be obtained as neat samples without any sample preparation.

9.2 The waterborne oil sample is dissolved in an equal volume of chloroform or dichloromethane and centrifuged to remove the free water, solids, and debris. The water layer, if present, is separated from the organic layer. Other debris, if present, is removed by filtration through glass wool.

NOTE 3—The use of spectrograde cyclohexane is required for the extraction of samples to be analyzed by fluorescence spectrometry by Test Method **D3650**. Separation of water may be accomplished by centrifugation or drying, or both, with anhydrous sodium sulfate.

9.3 When centrifugation will not separate the water from the chloroform solution of the sample, it is refluxed with an aromatic or petroleum distillate solvent in accordance with Test Method **D95**.

NOTE 4—Pressure filtration has also been found useful for breaking emulsions.

9.4 A portion of the solvent/sample solution is retained. The solvent may be removed by evaporation. This portion of the sample may be used in the preliminary gas chromatographic analysis, Test Methods **D3328** (Test Method A), and other analyses in which the results are unaffected by weathering.

9.5 The remainder of the solvent/sample solution is distilled using nitrogen purge to a liquid temperature of 280 °C to remove the solvent and simulate weathering conditions as nearly as possible. The distillate may be discarded or saved for characterization by gas chromatography (Test Methods **D3328**). This simulated weathering treatment is necessary to bring the unweathered suspect samples and the waterborne oil sample to as nearly comparable physical condition for subsequent analysis as possible. Analyses requiring the use of this