Designation: D3328 – 06

StandardTest Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography[1]

This standard is issued under the fixed designation D3328; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the comparison of petroleum oils recovered from water or beaches with oils from suspect sources by means of gas chromatography (**1, 2, 3**).[2] Such oils include distillate fuel, lubricating oil, and crude oil. The test method described is for capillary column analyses using either single detection (flame ionization) or dual detection (flame ionization and flame photometric) for sulfur containing species.

1.2 This test method provides high resolution for critical examination of fine structure that is resistant to weathering. The flame-photometric detection for sulfur components is an adjunct, not a substitute, for flame-ionization detection in the identification of waterborne petroleum oils (**4-12**). For this reason, flame photometric detection is optional.

1.3 *This standard does not purport to address 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2549 Test Method for Separation of Representative Aromatics and Nonaromatics Fractions of High-Boiling Oils by Elution Chromatography
D3325 Practice for Preservation of Waterborne Oil Samples
D3326 Practice for Preparation of Samples for Identification of Waterborne Oils
D3415 Practice for Identification of Waterborne Oils
D4489 Practices for Sampling of Waterborne Oils
D5739 Practice for Oil Spill Source Identification by Gas Chromatography and Positive Ion Electron Impact Low Resolution Mass Spectrometry
E355 Practice for Gas Chromatography Terms and Relationships

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Practice D3415, Terminology D1129, and Practice E355.

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. The known oils are collected from suspected sources. Samples of such known oils *must* be collected and submitted along with the unknown for analysis. At present, identification of the source of an unknown oil by itself cannot be made (for example, from a library of known oils).

4.2 The use of a flame-photometric detector in addition to the flame-ionization detector provides a second, independent profile of the same oil, that is, significantly more information is available from a single analysis with dual detection.

4.3 Many close similarities (within uncertainties of sampling and analysis) will be needed to establish identity beyond a reasonable doubt. The analyses described will distinguish many, but not all samples. For cases in which this method does not clearly identify a pair of samples, and for important cases where additional comparisons are needed to strengthen conclusions, other analyses will be required (refer to Practice D3415). In particular, Practice D5739 is useful for such cases.

5. Interferences

5.1 Compounds that have the same retention time as petroleum hydrocarbons will interfere in the comparison of the unknown with known oils. This is particularly true if animal fat or vegetable oil, naturally occurring hydrocarbons, or spill-treatment chemicals are present in relatively large amounts. Independent analysis, for example, infrared spectroscopy, will

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

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[2] The boldface numbers in parentheses refer to the references at the end of these test methods.

[3] 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.

*A Summary of Changes section appears at the end of this standard

establish the presence of these contaminants if their presence is suspected. Animal or vegetable oils can be removed effectively by Test Method D2549 or by Practices D3326 (Method D).

NOTE 1—Test Method D2549 will also remove the aromatic fraction.

6. Reagents and Materials

6.1 *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]

6.2 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 presented in Specification D1193.

6.3 *Air*—For use with the flame-ionization and flame-photometric detectors; may be obtained using a laboratory pure air generator, or from a zero grade tank supply.

6.4 *Carrier Gas*—High-purity grade helium is used as carrier gas.

6.5 *Cyclohexane*—High-purity (HPLC-grade). For sample preparation and for use in reference standards.

6.6 *Hydrogen*—For use with the flame-ionization and flame-photometric detectors; may be obtained using a hydrogen generator, or from a prepurified grade tank supply.

6.7 *Methylene Chloride*—For use in reference standards and glassware cleaning.

6.8 *Normal Alkane Standards*—Normal alkanes, decane through hexatriacontane, for use as reference compounds.

6.9 *Thiophene*—For use in optimization of flame-photometric detector.

7. Reference Standards

7.1 *Normal Paraffinic Hydrocarbons*—Prepared mixtures of approximately decane to hexatriacontane, or selected individual normal paraffins, are run under normal analysis conditions to determine retention times of compounds.

7.2 *Resolution Mixture*—Equal mixtures of *n*-heptadecane, *n*-octadecane, pristane and phytane in solution. See Annex A1 for details (A1.2.1).

8. Sampling

8.1 Collect a representative sample in accordance with Practice D4489.

8.2 If the sample is not to be analyzed within 1 week, it should be preserved in accordance with Practice D3325 because of the possibility of bacterial decomposition of normal paraffins in the sample.

8.3 The sample should be prepared for analysis in accordance with Practices D3326, because of the great variety of materials and circumstances associated with collecting petroleum oils from the environment. For heavier oils, a procedure to deasphalt the oil may be necessary.

9. Summary of Test Method

9.1 This test method uses a gas chromatographic capillary column system for the separation of petroleum hydrocarbons. The effluent of the column may be detected with a flame-ionization detector, or it may be split (1 + 2) between a flame ionization and a flame-photometric detector. The flame photometric detector is equipped with a narrow bandpass interference filter for spectral isolation of the sulfur emission at 394 nm. The relative peak size of each component (as indicated by retention time) of recovered oil is compared visually with the relative peak size of each component (of like retention time) of the suspected source.

NOTE 2—This duel detector method is based on the early work done by Kahn (**13**), Garza (**4**), and Adlard (**7**).

9.2 In this test method, elution of characteristic hydrocarbons occurs generally in order of increasing boiling point.

10. Apparatus

10.1 *Chromatographic Column*—Fused silica capillary column with bonded phase SE-30 or equivalent, 30 m by 0.32 mm inside diameter (0.1 µm film thickness).

NOTE 3—Other columns, providing equivalent or better resolution may be substituted (see Annex A1), but the analysis time will be increased with longer columns.

10.2 *Gas Chromatograph*—A commercial or custom designed gas chromatograph with heated injection and detector zones and a column oven capable of being programmed from 75°C to at least 325°C for heavier oils (higher boiling than gasolines, jet fuels, etc.).

10.2.1 For light distillate fuels, the chromatograph must be capable of programming from 50°C and also be capable of maintaining isothermal control at 50°C.

10.2.2 *Carrier Gas Pressure Regulator* is substituted pressure regulator for the mass flow controllers to give more precise rates in the low flow ranges (1 to 5 mL/mm).

10.2.3 *Injection Port*—The use of glass injector inserts that can be replaced or cleaned frequently, or both, will prolong the useful life of the column (**3**).

10.2.4 *Detectors*—A hydrogen-flame ionization detector is always used for analyses. A flame-photometric detector with a 394 nm bandpass filter is used for dual detection (**9, 10, 11, 12**).

10.2.5 *Carrier Gas Makeup* is required at the effluent of the column with a temperature independent mass flow controller.

10.2.6 *Effluent Splitter*—An effluent splitter with a split ratio of 1 + 2 (FID/FPD) is required for dual detection.

10.2.7 *Bleeder for Reference Compound*—A device for in-line bleed of a reference compound (thiophene and cyclohexane) into the carrier flow for detector optimization is required, when using a flame-photometric detector.

10.2.8 *Recorder,* or an integrator or computer data handling system capable of acquiring data at a rate compatible with the

[4] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

high resolution of the capillary column. Alternatively, a strip-chart recorder is required to measure detector response at full-scale range of 1 mV with a response time of 1 s (or less). A second recorder, or dual-pen recorder, is required for dual detection..

10.3 *Syringe*—A microsyringe of 0.5 to 1 µL capacity.

10.4 *Gas Traps*—Any commerically available gas filter traps to be placed in line to remove trace hydrocarbon and water impurities from the helium, hydrogen, nitrogen, and air gas supplies.

10.5 *FPD Linearizer*—Optional accessory to facilitate comparison of FPD chromatograms.

10.6 *Glass Insert,* packed with glass wool (optional).

NOTE 4—For instruments that can use this instrument, splitless injection of an oil in cyclohexane solution simplifies the analysis by eliminating the need to deasphalt most oil samples.

11. Preparation of Chromatograph

11.1 Install the column in the chromatograph, as described in the manufacturer's instructions.

11.2 Shut off the downstream end of the system and pressurize the carrier gas supply to a gage pressure of approximately 15 psi (103 kPa) above the operating pressure. Shut off the cylinder valve and observe the pressure gage. Consider the system tight if no pressure drop is noted in 10 to 15 min. Use a small amount of aqueous soap solution to locate minor leaks. Do not use the soap solution near the ionization detector.

11.3 *Column Conditioning for New Columns:*

NOTE 5—For previously conditioned columns, proceed to 11.3.4.

11.3.1 During conditioning, disconnect the column at the detector end to avoid deposition of volatiles on the detector(s).

11.3.2 For new columns, follow the manufacturer's instructions for column conditioning.

11.3.3 Adjust the carrier gas flow as indicated in Table 1.

11.3.4 Adjust the hydrogen and air flow, and the air/hydrogen flow ratio to the detector(s), as specified for the instrument being used. Ignite the flame(s) (see 11.4 for optimization).

11.3.5 Adjust the carrier gas flow as indicated in Table 1.

11.3.6 Program the column temperature as indicated in Table 1, and hold at the maximum temperature while monitoring the effluent. If there are no peaks in the chromatogram and there is minimal baseline shift at high temperatures, then the column is ready for use; otherwise, recondition it.

11.3.7 Return the oven temperature to 75°C.

11.3.8 If the column is to be moved or stored, disconnect and seal the ends of the column. When the column is to be reused, even after conditioning, it is always necessary to cycle through the temperature program to remove any accumulated volatiles.

11.4 *Optimization of Detectors*—Adjust hydrogen and air flows to give optimal detector responses for a given signal provided by the reference compound bleeder (10.2.7). Use cyclohexane for FID optimization and thiophene for the FDP optimization.

12. Operating Conditions for Analysis (Notes 6-8)

NOTE 6—One of the problems frequently encountered with the flame photometric detector is "flameout" when large amounts of solvent are injected with the sample. The recommended sample preparation procedure avoids this problem at the same time that it permits the use of small samples. For those who may encounter this problem, a simple modification has been suggested (**8**) which consists of reversing the hydrogen gas and air/oxygen gas inlets to the detector.

NOTE 7—For oil identification under the recommended procedure, air has been found satisfactory for combustion for the FPD, that is, oxygen is not necessary.

NOTE 8—See the manufacturer's manual for maintenance information for the FPD. Present flame photometric units should not be heated above 250°C, unless the photometer is removed from the heated zone by fiber optics.

TABLE 1 Operating Conditions for Chromatographic Columns (11, 12, 13)

Column	30 m by 0.32 mm ID by 0.1 µm film thickness, fused capillary
Packing	bonded phase SE-30, or equivalent
Carrier gas:	helium
Flow, mL/min:	
Column	1 to 2
Makeup gas	40
Temperature, °C:	
Injection port	250
Column:	
Heavier oils:	
Initial	60 hold 4 min
Final	280 (FID) 250 (FID/FPD) hold 30 min
Lighter oils:	
Initial	40 hold 10 min
Final	280 hold 10 min
Detector	300 (FID) 250 (FID/FPD)
Program Rate, °C/min[A]	3–8 [A]
Chart speed, in/min (mm/min)	2.5 (10)
Sensitivity, mV	1
Sample size, µL[A]	1.0 (cyclohexane solution)
Effluent split ration (FPD procedures)	1 + 2 (FID/FPD)

[A] The precise rate is dictated by the design of the gas chromatograph.