



Designation: D8193 – 18

Standard Test Method for Total Oil and Grease (TOG) and Total Petroleum Hydrocarbon (TPH) in Water and Wastewater with Solvent Extraction Using Non-Dispersive Mid-IR Transmission Spectroscopy¹

This standard is issued under the fixed designation D8193; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This test method covers the determination of total oil and grease (TOG) that can be extracted from water or wastewater samples by cyclohexane and measured by non-dispersive IR spectroscopy from 1370–1380 cm^{-1} . Treating the extract with Florisil² to remove polar substances prior to the IR measurement enables determination of the total petroleum (TPH).

1.2 This method also considers the volatile fraction of petroleum hydrocarbons which is lost by gravimetric methods that require solvent evaporation prior to weighing, as well as by solventless IR methods that require drying of the employed solid phase material prior to measurement. Similarly, a more complete fraction of extracted petroleum hydrocarbon is accessible by this method as compared to GC methods that use a time window for quantification, as petroleum hydrocarbons eluting outside these windows are also quantified.

1.3 This method defines total oil and grease in water as material that can be extracted with cyclohexane and measured by IR absorption in the region of 1370–1380 cm^{-1} (7.25–7.3 μm). Similarly, total petroleum hydrocarbon in water is defined as material that can be extracted with cyclohexane, remains in the extract after filtration over Florisil and is measured by IR absorption in the region of 1370–1380 cm^{-1} (7.25–7.3 μm). The concentration of total grease is defined as the difference between the total oil and grease and total petroleum hydrocarbon concentrations.

1.4 This method covers the range of 0.5 to 1000 mg/L for total oil and grease as well as for total petroleum hydrocarbons and has a method detection limit (MDL) of 0.5 mg/L. The range and method detection limit may be extended to higher or

lower concentrations by adjusting the water or solvent volume used in the liquid-liquid extraction.

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

1.6 *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.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization 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*:³
- D1129 Terminology Relating to Water
 - D1141 Practice for the Preparation of Substitute Ocean Water
 - D1193 Specification for Reagent Water
 - D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
 - D3370 Practices for Sampling Water from Closed Conduits
 - D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
 - D7678 Test Method for Total Oil and Grease (TOG) and Total Petroleum Hydrocarbons (TPH) in Water and Wastewater with Solvent Extraction using Mid-IR Laser Spectroscopy
 - E168 Practices for General Techniques of Infrared Quantitative Analysis

¹ This test method 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 Florisil is a trademark by U.S. Silica Company, Frederick, MD.

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.

2.2 *ISO Standards*:⁴

ISO 9377-2 Determination of Hydrocarbon Oil Index

2.3 *Code of Federal Regulations (CFR) Publications*:⁵

40 CFR Part 136 Guidelines Establishing Test Procedures for the Analysis of Pollutants

49 CFR Part 172 Hazardous Materials Table, Special Provisions, Hazardous Materials Communications, Emergency Response Information, Training Requirements, and Security Plans

3. Terminology

3.1 *Definitions*:

3.1.1 For definitions of terms used in this test method, refer to Terminology **D1129** and Practices **E168**.

3.1.2 *total oil and grease (TOG), n*—material that can be extracted from water or wastewater by this test method and which can be measured by infrared absorption in the region from 1370 cm^{-1} to 1380 cm^{-1} .

3.1.3 *total petroleum hydrocarbon (TPH), n*—non-polar organic material that can be extracted from water or wastewater, and which can be measured by infrared absorption in the region from 1370 cm^{-1} to 1380 cm^{-1} .

3.2 *Definitions of Terms Specific to This Standard*:

3.2.1 *grease, n*—the difference between TOG and TPH of a sample.

4. Summary of Test Method

4.1 An acidified 900-mL sample of water or wastewater is extracted with 50 mL of cyclohexane. A part of the extract is measured with infrared spectroscopy to quantify the total oil and grease (TOG) concentration. The remaining part of the extract is treated by Florisil to remove polar substances. The treated extract is measured with infrared spectroscopy to quantify the total petroleum hydrocarbon concentration (TPH). The difference between TOG and TPH provides the amount of grease extracted from the sample.

5. Significance and Use

5.1 The presence and concentration of total petroleum hydrocarbons, as well as total oil and grease, in domestic and industrial wastewater is of concern to the public because of its deleterious aesthetic effect and its impact on aquatic life.

5.2 Regulations and standards have been established that require monitoring of total petroleum hydrocarbons as well as total oil and grease in water and wastewater.

6. Interferences

6.1 Soaps, detergents, surfactants, and other materials may form emulsions that could reduce the amount of oil and grease as well as petroleum hydrocarbons extracted from a sample.

This test method contains procedures that can assist the analyst in breaking such emulsions.

6.2 Organic compounds and other materials not considered as oil and grease or petroleum hydrocarbons based on their chemical structure (for example, halogenated or cyclic hydrocarbons) may be extracted and measured by the method.

7. Apparatus

7.1 All glassware that will come in contact with the sample shall be thoroughly cleaned, rinsed with distilled water, and dried at 130°C.

7.2 Temperature controlled absorption spectrometer with an automatic filling system and a transmission cell. The spectrometer should use a light source and an optical interference filter transmitting in the range from 1370–1380 cm^{-1} . The path length of the transmission cell shall be between 1–1.5 mm. In order for the spectrometer to qualify, the standard deviation of 10 blank measurements should be less than 0.06 mAU.

7.3 Glass wide mouth sample bottle, suggested 1 L, either with screw cap having a fluoropolymer liner or a wide-necked glass flask with a ground neck with either glass or fluoropolymer stopper. The sampling bottle shall allow direct extraction from the bottle.

7.4 Micro-separator, for example see figure in **Annex A2** or other suitable device for phase separation (optional).

7.5 Solid phase extraction cartridges containing Florisil with PTFE or stainless steel frits (for TPH).

7.6 Beakers 50–100 mL.

7.7 Magnetic stirrer, with PTFE-fluorocarbon stirring bar (optional).

7.8 Volumetric flasks, glass, various (50, 100, and 200 mL).

7.9 Teflon spritz bottle, one-piece wash bottle for rinsing.

7.10 Volumetric pipettes, glass, various (10, 20, and 40 mL).

7.11 Analytical balance.

7.12 Graduated glass syringes, 250 μL (optional).

7.13 Benchtop shaker, (optional).

7.14 Glass stirring rod, (optional).

8. Reagents and Materials

8.1 *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 specification of the committee on analytical reagents of the American Chemical Society, where such specifications are available.⁶ 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.

⁴ Available from International Organization for Standardization (ISO), ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <http://www.iso.org>.

⁵ Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, <http://www.access.gpo.gov>.

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC, www.chemistry.org. For suggestions on the testing of reagents not listed by the American Chemical Society, see the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD, <http://www.usp.org>.

8.2 *Cyclohexane*, minimum purity 99.5 %, used for extraction.

8.3 *Purity of Water*—Unless otherwise indicated, references to laboratory or reagent water shall be understood to mean reagent water conforming to Specification **D1193**, Type II.

8.4 *n-Octane*, 99.0 % minimum purity, for use in calibration.

8.5 *2,2,4 Trimethylpentane*, 99.0 % minimum purity, for use in calibration.

8.6 *1:1 (w/w) Mixture of Mineral Oil Type A (Diesel Oil Without Additives) and Mineral Oil Type B (Lubricating Oil Without Additives)*, for use as laboratory control sample (LCS). A readily prepared 1:1 (w:w) mixture of these oils may be used (for example, BAM K010⁷).

8.7 *Florisil*, grain size 75 µm to 150 µm (100 mesh to 200 mesh), heated to 140°C for 16 h and stored in a desiccator. Florisil is a trade name for a prepared diatomaceous substance, mainly consisting of anhydrous magnesium silicate.

8.8 *Sodium Sulfate (Na₂SO₄)*, anhydrous, granular.

8.9 *Sulfuric Acid (1+1)*—Slowly and carefully add 1 volume of sulfuric acid (H₂SO₄, sp gr 1.84) to 1 volume of water, stirring and cooling the solution during addition.

8.10 *Hydrochloric acid, ACS, (1 + 1)*—Mix equal volumes of concentrated HCl and water.

8.11 *Stearyl stearate (C₃₆H₇₂O₂)*, minimum purity 98.0 %, for qualification of Florisil used for TPH measurements.

9. Hazards

9.1 Normal laboratory safety applies to this method. Analysts should wear safety glasses, gloves and lab coats. Analysts should review the Safety Data Sheets (SDS) for all reagents used in this method. Additional hazards may be presented by the particular sample being tested so proper care must be taken.

10. Sampling

10.1 Weigh the dried bottle before sample collection. Rinse the sample bottle and cap with the solvent (8.2) and dry it prior to sample collection. Do not rinse the sample bottle with the sample to be analyzed.

10.2 Collect the sample in accordance with the principles described in Practices **D3370**, using a glass bottle as specified in **7.3**.

10.3 Fill the bottle to approximately 80 %. Filling the bottle above 80 % of total volume or allowing the bottle to overflow will make extraction more difficult and lead to erroneous results.

10.4 A sample volume of about 900 mL is recommended for this test. Weigh the bottle containing the sample to determine the actual sampled amount. Alternatively, record the sampled

volume. Use the entire sample because removing a portion would not apportion the hydrocarbons that adhere to the bottle surfaces. The high probability that extractable matter may adhere to sampling equipment and result in measurements that have a low bias precludes the collection of composite samples for determination of total oil and grease and total petroleum hydrocarbon. Therefore, samples must be collected as grab samples. If a composite measurement is required, individual grab samples collected at prescribed time intervals may be analyzed separately and the concentrations averaged. Alternatively, samples can be collected in the field and composited in the laboratory. For example, collect three individual 300-mL samples over the course of a day. In the laboratory, extract each 300-mL sample with 15 mL and combine the extracts in a 50-mL volumetric flask and fill up to mark with solvent prior to measurement (**12.2** and **12.3**).

10.5 Preserve the sample with a sufficient quantity of sulfuric acid (see **8.9**) or hydrochloric acid (see **8.10**) to a pH of 2 or lower and refrigerate at 1–6°C from the time of collection until extraction. The amount of acid required will be dependent upon the pH and buffer capacity of the sample at the time of collection. If the amount of acid required is not known, make the pH measurement on a separate sample that will not be analyzed. Introduction of pH paper to an actual sample or sample cap may remove some oil from the sample. In case the bottle containing the sample cannot be weighed before addition of the acid, the volume of acid added to each sample can be recorded and then subtracted from the final measured sample amount. If the sample is to be shipped by commercial carrier, U.S. Department of Transportation regulations limit the pH to a minimum of 1.15 if H₂SO₄ is used and 1.96 if HCl is used (see 40 CFR Part 136, Table II Footnote 3 and 49 CFR Part 172).

10.6 All samples must be refrigerated at 1–6 °C from the time of collection until extraction. All samples must be analyzed within 28 days of the date and time of collection (40 CFR 136, Table II). Extracted samples can be stored up to two weeks between 7°C and 10°C.

11. Quality Control

11.1 To ensure analytical values obtained using this test method are valid and accurate within the confidence limits of the test, the instrument manufacturer's instructions and the following procedures must be followed when performing the test method. Calibrations made by the instrument manufacturer may be used for analysis.

11.2 Instrument Calibration:

11.2.1 Bring all solutions to 22 ± 3°C.

11.2.2 Calibration Solution S:

11.2.2.1 Prepare a stock solution by weighing in 9.00 g n-octane and 1.00 g 2,2,4 Trimethylpentane.

NOTE 1—A 10 % solution of 2,2,4 Trimethylpentane in n-Octane was found to provide representative values for TOG and TPH for a broad range of samples, ranging from heavy crude oil to lighter condensates including fuels and lubricants.

NOTE 2—The calibration standard specified in this procedure reflects the objective of the test to detect recoverable oil and grease and petroleum

⁷ The sole source of supply of BAM K010 known to the committee at this time is German Federal Institute for Materials Research and Testing, Berlin. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

hydrocarbon material in water and wastewater with an unknown composition of oil and grease. In a few cases, the composition of the oil and grease in a sample will be known. In such cases, it is possible to develop a calibration with the known target oil. As long as all other steps in this test method are followed, such calibrations may be used for internal monitoring or internal reporting. However, for such calibrations it is not possible to develop reproducibility statements and the repeatability statement of this test method will not be valid. In order to obtain consistent results between laboratories, it is required to use the standard calibration outlined in Section 11 when reporting TOG or TPH values citing the ASTM designated number.

11.2.3 Calibration Solution A:

11.2.3.1 Weigh 1.8 g of Calibration Solution S in a 100 mL volumetric flask and fill to the mark with cyclohexane.

11.2.3.2 Calibration Solution A = 18000 mg/L (1000 mg/L oil in water).

11.2.4 Calibration Solution B:

11.2.4.1 Place 40.0 mL of Calibration Solution A in a 100-mL volumetric flask and fill to mark with solvent.

11.2.4.2 Calibration Solution B = 7200 mg/L (400 mg/L oil in water).

11.2.5 Calibration Solution C:

11.2.5.1 Place 20.0 mL of Calibration Solution B in a 100-mL volumetric flask and fill to mark with solvent.

11.2.5.2 Calibration Solution C = 1440 mg/L (80 mg/L oil in water).

11.2.6 Calibration Solution D:

11.2.6.1 Place 10.0 mL of Calibration Solution C in a 100-mL volumetric flask and fill to mark with solvent.

11.2.6.2 Calibration Solution D = 144 mg/L (8.0 mg/L oil in water).

11.2.7 Calibration Solution E:

11.2.7.1 Weigh 1.35 g of Calibration Solution S in a 100 mL volumetric flask and fill to the mark with cyclohexane.

11.2.7.2 Calibration Solution E = 13500 mg/L (750 mg/L oil in water).

11.2.8 Calibration Solution F: [http://standards/sis/1a80e59d-ASTM D8193-18](http://standards.sis/1a80e59d-ASTM D8193-18)

11.2.8.1 Place 20.0 mL of Calibration Solution E in a 100-mL volumetric flask and fill to mark with solvent.

11.2.8.2 Calibration Solution F = 2700 mg/L (150 mg/L oil in water).

11.2.9 Calibration Solution G:

11.2.9.1 Place 20.0 mL of Calibration Solution F in a 100-mL volumetric flask and fill to mark with solvent.

11.2.9.2 Calibration Solution G = 540 mg/L (30 mg/L oil in water).

11.2.10 Calibration Solution H:

11.2.10.1 Place 10.0 mL of Calibration Solution G in a 100-mL volumetric flask and fill to mark with solvent.

11.2.10.2 Calibration Solution H = 54 mg/L (3 mg/L oil in water).

11.2.11 Measurement of the Calibration Standards:

11.2.11.1 The calibration must contain a minimum of 8 non-zero points.

11.2.11.2 Use cyclohexane from the same bottle used for preparing the calibration samples to measure a new reference (background).

11.2.11.3 Obtain the absorbance values for the calibration standards A to H. Make a new reference measurement before measuring the next calibration sample.

11.2.11.4 Determine the constants of a second order polynomial which, in a least squares sense, represents the best fit to the absorbance measured and the concentration of the calibration solutions.

NOTE 3—Even though solvent of high purity is used for analysis, it can contain small amounts of non-cyclic hydrocarbons and even polar components. Furthermore, there will be a variation in this content between production batches (lot numbers), even from the same producer. To avoid that variation in product quality affects the results of this test method, solvent of the same lot number must be used for reference and sample measurement.

11.3 Calibration Verification:

11.3.1 Use the calibration constants obtained in 11.2.11.4 and the absorbance values measured in 11.2.11.3 to calculate the predicted concentrations for all calibration samples. The calibration is verified if the difference between the actual and predicted concentration is smaller than $\pm 1.5\%$ of the measured value or ± 13 mg/L oil in solvent concentration (± 0.7 mg/L oil in water), whichever is greater.

11.3.2 If calibration cannot be verified, recalibrate the instrument.

NOTE 4—Periodic calibration verification is carried out by measurement of the 50 mg/L LCS. If the LCS fails, a measurement of one of the calibration standards can be used to verify the calibration. In this case the result shall fall within the limits defined in 11.3.1.

11.4 Standardization of Sample Cleanup:

11.4.1 The sample cleanup procedure required for the measurement of total petroleum hydrocarbons uses Florisil solid phase extraction cartridges. Such cartridges can be bought ready-made or can be prepared in the lab. Each time a new batch of Florisil cartridges is used, the suitability shall be tested. Cartridges may be qualified by the manufacturer and used as delivered.

11.4.2 If solid phase extraction cartridges with plastic housing are used, ensure that the cartridges do not affect the results. Measure a blank using only cyclohexane. The instrument reading must be ≤ 0.5 mg/L and ≥ -0.5 mg/L.

11.4.3 Prepare 1800 mg of Mineral Oil Type A and Type B (1:1 (w/w)) (8.6) in a 100 mL volumetric flask. Fill to the mark with cyclohexane.

11.4.4 Measure the solution without any cleanup and note the result on the flask.

11.4.5 Draw the solution through the Florisil cartridge and perform a measurement of the treated extract. The instrument reading shall be at least 95 % of the untreated value obtained in 11.4.4.

11.4.6 Prepare 65 mg stearyl stearate (8.11) in a 100 mL volumetric flask. Fill to the mark with cyclohexane.

11.4.7 Measure the solution without any cleanup and note the result on the flask.

11.4.8 Draw the solution through the Florisil cartridge and perform the measurement of the treated extract. The instrument reading shall be less than 1/30 of the reading of the original extract obtained in 11.4.7.

11.4.9 If the signal is higher, activate the Florisil by heating it to 140°C for 16 h and repeat the qualification procedure.

NOTE 5—The use of 900-mg Florisil cartridges is sufficient to clean samples up to at least 70 mg/L (stearyl stearate). If higher grease

concentrations are expected, either increase the amount of Florisil or dilute the sample.

11.5 Preparation of the Laboratory Control Sample (LCS):

11.5.1 Pour 900-mL reagent water into a sample bottle. Record exact volume or weight.

11.5.2 Using a micro-syringe, add 45.0 mg of Mineral Oil Type A and Type B (1:1 (w/w)) (8.6) to obtain a nominal concentration of 50.0 mg/L (oil in water concentration). Obtain the exact concentration by difference weighing of the micro-syringe and the exact water volume.

NOTE 6—A mixture of a Mineral Oil Type A and Type B has been selected as material for initial demonstration of laboratory capability and for establishing LCS as it is readily available worldwide and also used for calibration of ISO 9377-2, which determines the hydrocarbon oil index in water using solvent extraction and gas chromatography, as well as LCS in Test Method D7678. It is therefore suited to verify the correct performance of the test method despite of its different chemical composition to most crude and condensate oil types.

11.6 Initial Demonstration of Laboratory Capability:

11.6.1 If a laboratory has not performed the test before or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

11.6.2 Analyze a reagent water test blank. The total oil and grease concentration in the blank must be in the range ± 0.5 mg/L. If the total oil and grease concentration is outside this range, analysis of samples is halted until the contamination is eliminated and the blank gives concentrations in the range ± 0.5 mg/L.

11.6.3 Prepare 7 samples by each weighing in 45.0 mg of a mixture of a Mineral Oil Type A and Type B (8.6) in 900 mL of reagent water. Each sample must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

11.6.4 Calculate the mean value and the standard deviation and compare to the acceptable ranges of precision and bias obtained through the single laboratory study. The found mean value for TOG shall lie between 48.2 and 50.2 mg/L and the standard deviation shall be below 2.1 mg/L. For TPH the mean value shall lie between 47.7 and 50.1 mg/L and the standard deviation shall be below 2.5 mg/L. All values are calculated based on Practice D5847 at the 99 % level.

11.6.5 This study should be repeated until the single operator precision and the mean recovery are within the limits given above.

11.7 Laboratory Control Sample (LCS):

11.7.1 To ensure that the test method is in control, analyze the LCS containing 50 mg/L of a 1:1 (w:w) mixture of mineral oil type A and B with each batch of 20 samples. The selected LCS follows recommendation of Practice D5847 to use an independent reference material as the LCS. If large numbers of samples are analyzed in the batch, analyze the LCS after every 50 samples. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The TOG result obtained for the LCS shall fall within the limits 46.4–51.9 mg/L. The TPH result obtained for

the LCS shall fall within the limits 45.6–52.2 mg/L. These limits are based on Practice D5847 evaluation at the 99 % level.

11.7.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

11.8 Method Blank:

11.8.1 Analyze a reagent water test blank with each batch of 20 samples. The total oil and grease concentration in the blank must be in the range ± 0.5 mg/L. If the total oil and grease concentration is outside this range, analysis of samples is halted until the contamination is eliminated and the blank gives concentrations in the range ± 0.5 mg/L.

11.9 Matrix Spike (MS):

11.9.1 To check for interferences in the specific matrix being tested, perform an MS on at least one sample from each batch by spiking an aliquot of the sample with a known amount of Mineral Oil Type A and Type B (1+1) and taking it through the analytical method. Addition of Mineral Oil Type A and Type B (1+1) shall be carried out using a glass syringe and by difference weighing.

11.9.2 The spike concentration plus the background concentration of total oil and grease must not exceed 1000 mg/L. The spike must produce a concentration in the spiked sample 2 to 5 times the background concentration or 10 to 50 times the detection limit of the test method, whichever is greater.

11.9.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = 100 \frac{AV - BV}{C} \quad (1)$$

where:

- A = concentration of total oil and grease found in the spiked sample (mg/L),
- B = concentration of total oil and grease found in the un-spiked sample (mg/L),
- C = amount added during spiking (mg), and
- V = volume of sample used (L).

11.9.4 The percent recovery of the spike shall fall within the limits 70–130 %. This margin considers difficulties associated with splitting a sample into aliquots of the same concentration due to the nature of the analyte which tends to adhere to surfaces. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

12. Procedure

12.1 Extraction:

12.1.1 Bring the sample to a temperature of $22 \pm 3^\circ\text{C}$.

12.1.2 Add 50 mL of cyclohexane (8.2) to the sample in the original sample bottle. Recap immediately and shake vigorously for 2 minutes. Alternatively, add a magnetic stirrer bar and stir the sample for 30 min on a magnetic stirrer. Allow contents to settle and bubbles to disappear.

12.1.3 In the case of formation of emulsions, add $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ during the liquid-liquid extraction step. Typically an amount of 5–10 g will be sufficient.

12.1.4 If a micro-extractor as in Annex A2 is used, remove the cap from the bottle and replace it by the micro-separator. Add enough distilled water to allow withdrawal of the organic phase from the micro-separator.

12.1.5 If no micro-separator is used for phase separation, add distilled water to the bottle to facilitate withdrawing the organic phase (top layer) using a glass pipette or glass syringe.

12.1.6 When transferring the organic phase to a beaker, ensure that no free water is transferred. Free water will interfere with the measurement of TOG and the cleanup procedure and measurement of TPH.

12.1.7 If the sample is turbid, use an additional Na_2SO_4 drying cartridge to prevent water from interfering with the sample cleanup and measurement.

12.1.8 Centrifuge the extract before the measurement if emulsion is still seen in the extract.

12.2 Measurement of Total Oil and Grease (TOG):

12.2.1 Use cyclohexane from the same batch (lot number) used for extraction to measure a reference.

12.2.2 Record the infrared absorbance of the extract obtained in 12.1.

12.2.3 Determine the concentration of oil and grease in the solvent by applying the calibration constants.

12.2.4 If the concentration of total oil and grease exceeds the calibration range, dilute the extract to bring the concentration within the calibration range using the same batch of cyclohexane as used for extraction and repeat the measurement.

12.3 Measurement of Total Petroleum Hydrocarbon (TPH):

12.3.1 Use a fresh cartridge for each measurement.

12.3.2 Draw cyclohexane from the same batch (lot number) used for extraction through the Florisil solid phase extraction cartridges and perform a reference measurement.

12.3.3 Draw the extract obtained in 12.1 through the Florisil solid phase extraction cartridge and record the infrared absorbance of the treated extract.

12.3.4 Determine the concentration of petroleum hydrocarbons in solvent by applying the calibration constants.

12.3.5 If the concentration of total hydrocarbons exceeds the calibration range, or the difference between TOG and TPH values is larger than 70 mg/L, or if the cartridges show indication of break-through (colored throughout the cartridge), dilute the extract 10 times and repeat the measurement.

13. Calculation of Results

13.1 Calculate the total oil and grease (TOG) concentration in the original water sample and report to the nearest 0.1 mg/L:

Test Method D8193:

$$\text{TOG (mg/L)} = D \frac{R_{\text{TOG}}}{E} \quad (2)$$

where:

R_{TOG} = measured concentration of total oil and grease in mg/L in extract,

D = dilution factor (volume of diluted extract / volume undiluted extract), if any, as utilized in 12.2.4, and

E = enrichment factor (volume of water / volume of solvent) due to the liquid-liquid extraction.

13.2 Calculate the total petroleum hydrocarbon (TPH) concentration in the original water sample report to the nearest 0.1 mg/L:

Test Method D8193:

$$\text{TPH (mg/L)} = D \frac{R_{\text{TPH}}}{E} \quad (3)$$

where:

R_{TPH} = measured concentration of total petroleum hydrocarbons in mg/L in extract after treatment with Florisil,

D = dilution factor (volume of diluted extract / volume undiluted extract), if any, as utilized in 12.3.5, and

E = enrichment factor (volume of water / volume of solvent) due to the liquid-liquid extraction.

14. Precision and Bias

14.1 A single laboratory validation study was carried out with ocean substitute water (Practice D1141) samples. The sample set included 3 crude oils with densities 811 kg/m^3 (oil 1), 839 kg/m^3 (oil 2) and 896 kg/m^3 (oil 3). Two different crude oils were used per concentration in the range from 5 to 500 mg/L. In addition, the lightest crude oil (oil 1) was used for 900 mg/L. Each sample was prepared by spiking a given amount of oil in 900 mL water and extracting with 50 mL cyclohexane. For each extract, a single measurement of each TOG and TPH was carried out. For the concentrations where more than one oil type was used, the pooled mean, pooled standard deviation and pooled recovery were calculated. The raw data are shown in Tables A1.1 and A1.2 in Annex A1. For the QC section, 8 samples with a mixture of Mineral Oil Type A and Type B (BAM K010) in reagent water (Specification D1193) at a concentration of 50 mg/L was taken through the entire analytical method for both TOG and TPH. The results are summarized in Tables A1.3 and A1.4 in Annex A1.

14.2 *Repeatability*—Based on the single lab study, a preliminary repeatability for the different concentrations was estimated based on Practice D2777. A full interlaboratory study will be completed within five years to determine the repeatability of the method. See Tables 1 and 2.

NOTE 7—The ratio of TOG and TPH recovery reflect the amount of polar substances that are removed by means of the treatment with Florisil.

14.3 *Method Detection Limit*—Eight samples of ocean substitute water spiked with oil 3 at a nominal concentration of 1.7 mg/L were used to determine the method detection limit (MDL) according to 40 CFR Pt. 136, Appendix B. The raw data are shown in Tables A1.1 and A1.2 in Annex A1. See Table 3.