Designation: D8478 – 23

Standard Test Method for N-Hexane Recoverable Total Oil and Grease and Total Petroleum Hydrocarbons in Water by ATR-Infrared Determination[1]

This standard is issued under the fixed designation D8478; 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 determination of total oil and grease, and total petroleum hydrocarbons in produced water and wastewater by an infrared (IR) determination of n-hexane extractable substances from the sample. Included in this estimation of total oil and grease are any other compounds soluble in the n-hexane.

1.2 This test method defines total oil and grease in produced water and wastewater as that which is extractable in the test method and measured by IR absorption from 3.34 µm to 3.54 µm (2825 cm^{-1} to 2994 cm^{-1}). Similarly, this test method defines total petroleum hydrocarbons in produced water and wastewater as that oil and grease which is not adsorbed by silica gel in the test method, and is measured by IR absorption from 3.34 µm to 3.54 µm (2825 cm^{-1} to 2994 cm^{-1}). Alternative methods for total oil and grease or total petroleum hydrocarbons, or both, can produce differing results.

1.3 This method covers the range of 5 mg/L to 175 mg/L for total oil and grease and the range of 5 mg/L to 50 mg/L for total petroleum hydrocarbons. The range may be extended to a lower or higher level by extraction of a larger or smaller sample volume collected separately.

1.4 This test method uses horizontal attenuated total reflectance (HATR) with a cubic zirconia crystal.

1.5 This test method is intended as a field test only and should be treated as such. This method is not intended to replace laboratory-based regulatory methods currently in use.

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

1.7 *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.* See Guide D3856 for more information.

1.8 *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:*[2]

D1129 Terminology Relating to 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 Flowing Process Streams

D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

E168 Practices for General Techniques of Infrared Quantitative Analysis

2.2 *CFR Publications:*[3]

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

49 CFR Part 172 Hazardous Materials Table, Special

[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] 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] Available from U.S. Government Publishing Office (GPO), 732 N. Capitol St., NW, Washington, DC 20401, http://www.gpo.gov.

Provisions, Hazardous Materials Communications, Emergency Response Information, Training Requirements, and Security Plans

2.3 *EPA Standards:*[4]

Method 1664, Revision A N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGTHEM; Non-polar Material) by Extraction and Gravimetry

3. Terminology

3.1 *Definitions:*

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *horizontal attenuated total reflection (HATR) crystal, n*—horizontally oriented infrared transmitting crystal shaped so that light will pass through the filter while reflecting off the top and bottom crystal face; as light strikes the top crystal the light will be attenuated by any sample placed on the top crystal at specific wavelengths corresponding to the molecular shape and chemistry of the sample; this attenuation can be used to generate an infrared spectrum of the sample.

3.2.2 *total oil and grease (TOG), n*—organic material that can be extracted from produced water or wastewater by this test method and which can be measured by infrared absorption in the region from 3.34 µm to 3.54 µm.

3.2.3 *total petroleum hydrocarbon (TPH), n*—non-polar organic material that can be extracted from produced water or wastewater, and which can be measured by infrared absorption in the region from 3.34 µm to 3.54 µm.

4. Summary of Test Method

4.1 A sample of produced water or wastewater between 100 mL and 250 mL is extracted with a proportional amount of n-hexane at a ratio of 10:1 (sample to n-hexane). A portion of the extract is evaporated on the HATR crystal and examined by infrared spectroscopy (IR) for a total oil and grease measurement.[5] If a total petroleum hydrocarbons measurement is required, a portion of the extract is contacted with silica gel to remove polar substances, thereby producing a solution containing non-polar material. The non-polar material is measured by infrared spectroscopy.

5. Significance and Use

5.1 The presence and concentration of 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 TOG and TPH in produced water and wastewater.

6. Interferences

6.1 Soaps, detergents, surfactants, and other materials can form emulsions that can reduce the amount of oil and grease 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 on the basis of chemical structure can be extracted and measured as total oil and grease. Of those measured, certain ones will be adsorbed by silica gel while others will not. Those not adsorbed are measured as total petroleum hydrocarbons.

6.3 Sulfur present in the sample can extract into n-hexane and cause a positive bias in the results. See Annex A2 for testing details.

7. Apparatus

7.1 *Filter Paper,* ashless, quantitative, general-purpose, 11 cm diameter, 8 µm pore size.

7.2 *Glass Sample Bottle,* minimum 125 mL, with screw cap having a fluoropolymer liner.

7.3 *Glass Graduated Cylinder,* 100 mL

7.4 *Glass Funnel.*

7.5 *Volumetric Flasks,* glass, various.

7.6 *Polytetrafluoroethylene (PTFE) Spritz Bottle,* one-piece wash bottle for rinsing.

7.7 *Syringes,* 100 µL, 25 mL.

7.8 *Glass Separatory-Funnel,* 500 mL, with fluoropolymer stopcock and stopper (optional).

7.9 *Volumetric Pipettes,* glass, various (optional).

7.10 *Analytical Balance* (optional).

7.11 *Infrared Analyzer,* scanning or non-scanning, capable of measuring absorption from 3.34 µm to 3.54 µm (2825 cm^{-1} to 2994 cm^{-1}). In order for the analyzer to comply, the standard deviation of 10 measurements with no sample present shall not exceed 0.1 mAU.

7.11.1 *HATR Crystal.* The apparatus shall use a cubic zirconia HATR crystal which contains a trough that prevents the n-hexane from spreading off the crystal.

8. Reagents and Materials

8.1 *Purity of Reagents*—Spectroscopic grade (preferred) or reagent grade chemicals shall be used in 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, where such specifications are available.[6] Other grades may be used, provided it is first

[4] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

[5] Consult the manufacturer's operation manual for the specific instructions related to the infrared spectrometer or analyzer to be used.

[6] *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.

ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *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.

8.3 *Isopropyl Alcohol*—95 % minimum purity.

8.4 *n-Hexane*—95 % minimum purity, evaporation residue less than 5 mg/L. Used for extraction.

8.5 *Hexadecane*—98 % minimum purity.

8.6 *Soybean Oil*—CAS No. 8001-22-7, analytical standard.

8.7 *Mineral Oil*—CAS No. 8042-47-5, 98 % minimum purity.

8.8 *Silica Gel,* anhydrous, 75 µm to 150 µm, high-purity grade 923—Dry at 200 °C to 250 °C for 24 h minimum and store in a desiccator or tightly sealed container. Determine the n-hexane soluble material content of the silica gel by extracting 10 g of silica gel with 25 mL of n-hexane and collect the elute in a flask. Filter and analyze the elute by IR. The n-hexane soluble material must be less than 5 mg/L.

8.9 *Sodium Sulfate* (Na_2SO_4), ACS, granular anhydrous—Dry at 200 °C to 250 °C for 24 h minimum and store in a tightly sealed container until use.

NOTE 1—Powdered sodium sulfate should not be used because water can cause it to solidify.

8.10 *Sulfuric Acid* (1 + 1)—Slowly and carefully add 1 volume of sulfuric acid (H_2SO_4, sp gr 1.84 g/cm^3) to 1 volume of water, stirring and cooling the solution during the addition (optional HCl replacement).

8.11 *Hydrochloric Acid,* ACS, 1 + 1—Mix equal volumes of concentrated HCl and water.

8.12 *Sodium Chloride* (NaCl), crystalline, ACS—for use in breaking emulsions, if needed. Wet thoroughly with n-hexane before using.

9. Sampling

9.1 Collect the sample in accordance with the principles described in Practice D3370, using a glass bottle equipped with a screw cap having a fluoropolymer liner. Pre-rinse the sample bottle and cap with the n-hexane prior to sample collection. Do not rinse the sample bottle with the sample to be analyzed. Fill bottle with a known amount of sample (100 mL to 250 mL), larger sample sizes may be collected if necessary. If the extraction is to be done in the sample bottle, leave enough headspace for the amount of n-hexane required for extraction, else keep the headspace at a minimum. Do not allow the sample to overflow the bottle during collection. Preventing overflow can be impossible in some sampling situations, however, measures should be taken to minimize overflow at all times.

9.2 Use the entire sample because removing a portion would not apportion the oil and grease that adheres to the bottle surfaces. The high probability that extractable matter can adhere to sampling equipment and result in measurements that are biased low precludes the collection of composite samples for determination of TOG and TPH. 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.

9.3 Preserve the sample with a sufficient quantity of either sulfuric acid (see 8.10) or hydrochloric acid (see 8.11) to a pH of 2 or lower and refrigerate at 2 °C to 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 can remove some oil from the sample. To more accurately calculate the final TOG or TPH concentration, or both, of the extract, the volume of acid added to each sample can be recorded, then subtracted from the final measured sample volume.

NOTE 2—If the sample is to be shipped by commercial carrier, see 40 CFR Part 136, Table II Footnote 3 (if HCl is used) or 49 CFR part 172 (if H_2SO_4 is used) for pH limits.

9.4 For those circumstances requiring the collection of multiple aliquots of one sample, each aliquot is to be collected in either of the following ways: *(1)* collect simultaneously in parallel, if possible, or *(2)* collect as grab samples in rapid succession, filling ⅓ of each container at a time and continuing until all containers are full, consistent with 9.1.

10. Preparation of Calibration and Spiking Solutions

10.1 *Oil Types:*

10.1.1 *Mineral Oil*—Used for calibrating the apparatus for TPH.

10.1.2 *50:50 Mix of Hexadecane/Soybean Oil*—Used for calibrating the apparatus for TOG.

10.1.3 *Known Oil*—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. However, for such calibrations it is not possible to develop reproducibility statements and the repeatability statement of this test method will not be valid.

10.2 *Calibration Mixtures:*

10.2.1 *Calibration Stock Solution*—Weigh 200 mg ± 2 mg of oil into a 100-mL volumetric flask and fill to the mark with n-hexane. Mix well. The resulting concentration is 2000 mg/L. This solution will be termed “stock solution.”

10.2.2 Using volumetric pipettes, transfer various amounts of stock solution into volumetric flasks and fill to the mark with n-hexane. The equation for calculating the calibration of the standard is as follows:

$$C_{std} = C_{stock} \times V_t \,/\, V_f \quad (1)$$

where:

C_{std} = final concentration of the standard in mg/L,
C_{stock} = concentration of the stock solution in mg/L,
V_t = volume of stock solution transferred in mL, and

V_f = final volume of the calibration solution in mL.

10.2.2.1 *Calibration Solution A*—Place 0.5 mL of stock solution in a 10-mL volumetric flask and fill to the mark with n-hexane. Calibration Solution A = 100 mg/L, equivalent to 10 mg/L TOG or TPH in a 150-mL water sample extracted into a 15-mL volume of n-hexane.

10.2.2.2 *Calibration Solution B*—Place 1.5 mL of stock solution in a 10-mL volumetric flask and fill to the mark with n-hexane. Calibration Solution B = 300 mg/L, equivalent to 30 mg/L TOG or TPH in a 150-mL water sample extracted into a 15-mL volume of n-hexane.

10.2.2.3 *Calibration Solution C*—Place 2.5 mL of stock solution in a 10-mL volumetric flask and fill to the mark with n-hexane. Calibration Solution C = 500 mg/L, equivalent to 50 mg/L TOG or TPH in a 150-mL water sample extracted into a 15-mL volume of n-hexane.

10.2.2.4 *Calibration Solution D*—Place 5.0 mL of stock solution in a 10-mL volumetric flask and fill to the mark with n-hexane. Calibration Solution D = 1000 mg/L, equivalent to 100 mg/L TOG or TPH in a 150-mL water sample extracted into a 15-mL volume of n-hexane.

10.2.2.5 *Calibration Solution E*—Place 7.5 mL of stock solution in a 10-mL volumetric flask and fill to the mark with n-hexane. Calibration Solution E = 1500 mg/L, equivalent to 150 mg/L TOG or TPH in a 150-mL water sample extracted into a 15-mL volume of n-hexane.

10.2.2.6 *Calibration Solution F*—Place 10.0 mL of stock solution in a 10-mL volumetric flask. Calibration Solution F = 2000 mg/L, equivalent to 200 mg/L TOG or TPH in a 150-mL water sample extracted into a 15-mL volume of n-hexane.

10.3 *TOG Precision and Recovery (TOG-PAR) Standard:*

10.3.1 Weigh in 45 mg ± 1 mg of a 50:50 mix of hexadecane and soybean oil into sample bottle.

10.3.2 Pour 900 mL ± 10 mL reagent water into the sample bottle in order to produce a TOG-PAR standard with approximately 50 mg/L.

10.4 *TPH Precision and Recovery (TPH-PAR) Standard:*

10.4.1 Weigh in 45 mg ± 1 mg of mineral oil into sample bottle.

10.4.2 Pour 900 mL ± 10 mL reagent water into the sample bottle in order to produce a TPH-PAR standard with approximately 50 mg/L.

11. Calibration and Standardization

11.1 Rely upon recommendations of the manufacturer of the analyzer because variations in design make it impractical to offer specific instructions for this method. Also, in relation to infrared filtometer operation, reference to scanning or running, or both, should be interpreted to mean obtaining a reading or a plot from 3.34 µm to 3.54 µm (2825 cm^{-1} to 2994 cm^{-1}).

11.2 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 calibration procedure (11.4) must be followed when performing the test method.

11.3 *Calibration Standards*—Refer to 10.1 and 10.2 for calibration standard description.

11.4 *Calibration:*

11.4.1 Equilibrate the instrument and all samples to the temperature of the operating environment (15 °C to 27 °C) prior to analysis.

11.4.2 Allow the instrument to warm up for the period of time recommended by the manufacturer before attempting a calibration.

11.4.3 Using a level, make sure the HATR sample plate and crystal are level. Since the method requires n-hexane to be evaporated off, only a thin film of oil is measured on the instrument.

11.4.4 Clean the HATR crystal of any residual oil or other contamination by applying about 1 mL of n-hexane to the crystal and wiping across the crystal in one direction with a disposable wipe. Avoid rubbing back and forth since this can re-contaminate the crystal. Repeat the cleaning of the crystal with isopropyl alcohol. Follow the instrument manufacturer's recommendation for determining crystal cleanliness.

11.4.5 Using a 100 µL glass syringe, deposit a specific amount of n-hexane on the crystal based on the instrument manufacturer's recommendation. It is crucial to use the same amount of volume for every measurement.

11.4.6 Allow enough time for the n-hexane to evaporate. The minimum evaporation time is 3 min and the maximum evaporation time is 5 min. If the n-hexane does not evaporate completely before taking a baseline detector response, the results will have a negative bias.

11.4.7 Obtain a baseline detector response (zero) according to the manufacturer's instructions. A zero should be obtained before the first use and at least once every 60 min the instrument is in use.

11.4.8 Clean the crystal according to 11.4.4.

11.4.9 Wash out the glass syringe with the first standard and deposit a specific amount of standard on the crystal based on the instrument manufacturer's recommendation. It is crucial to use the same amount of volume for every measurement.

11.4.10 Allow enough time for the standard to evaporate. The minimum evaporation time is 3 min and the maximum evaporation time is 5 min. If the standard does not evaporate completely, the results will have a positive bias. If the evaporation time is longer than 5 min, there can be an increased loss of volatile hydrocarbons causing a negative bias. All measurements (both calibration and sample measurements) must use the same evaporation time.

11.4.11 Obtain an infrared detector response according to the manufacturer's instructions and calculate the absorbance value from 3.34 µm to 3.54 µm (2825 cm^{-1} to 2994 cm^{-1}). The absorbance value may be calculated internally by the instrument.

11.4.12 Clean the crystal according to 11.4.4.

11.4.13 Repeat 11.4.9 – 11.4.12 at least two more times for the standard. Average the absorbance values recorded.

11.4.14 Repeat 11.4.9 – 11.4.13 for the remaining standards.

11.5 *Calibration Curve*—One of the following calibration fits may be used in generating the calibration curve.

11.5.1 *Linear Calibration*—A linear calibration may be used if at least five calibration standards are included in the calibration. Two separate linear calibrations may be used for

the ranges of 50 mg/L to 1000 mg/L (5 mg/L to 100 mg/L in the water sample) and 1000 mg/L to 2000 mg/L (100 mg/L to 200 mg/L in the water sample) as long as each calibration has at least five calibration standards.

11.5.2 *Quadratic Calibration*—A quadratic calibration may be used if at least six calibration standards are included in the calibration.

11.5.3 *Point-to-Point Calibration*—A point-to-point calibration may be used if the calibration using a quadratic equation is verified in accordance with 11.6. A point-to-point calibration requires at least six calibration standards.

11.6 *Calibration Verification:*

11.6.1 Using the calibration constants determined in 11.5 along with the absorbance values recorded in 11.4, calculate the predicted concentrations for all calibration standards. The error for any calibration standard shall not exceed the greater of 3 ppm (30 ppm in n-hexane concentration) or 10 % relative of the actual concentration of the standard. If one of the calibration standards does not meet the error limit, this point must be reanalyzed. If the point still does not meet the error limit, it may be excluded but still must contain the minimal points dictated in 11.5. The high or low point of the calibration may be excluded but the reporting range must be modified to reflect this change. If two points must be excluded, calibration must be repeated, and if this still is not achieved, calibration must be repeated with a new set of calibration standards.

11.6.2 Using the procedure outlined in 10.2, create a verification standard at approximately 50 mg/L that is of a separate batch, used to calibrate the instrument. Measure and record the infrared absorbance of the extract in a manner identical to that used for the calibration standards. Using the calibration constants determined in 11.5 along with the absorbance determined for the verification standard, calculate the predicted concentration for the verification standard. The error for the verification standard shall not exceed the greater of 3 ppm (30 ppm in n-hexane concentration) or 10 % relative of the actual concentration of the standard. If the verification standard does not meet the error limits, repeat 11.6.2 with a new verification standard. If verification is still not achieved, calibration must be repeated with a new set of calibration standards.

11.6.3 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 11.6. If the result does not fall within limits, re-calibrate the instrument according to Section 11.

12. Procedure

12.1 *Sample Pretreatment:*

12.1.1 Equilibrate the instrument and all samples to the temperature of the operating environment prior to analysis.

NOTE 3—Running samples outside the temperature range of 15 °C to 27 °C can affect TOG or TPH recovery, or both.

12.2 *Extraction:*

12.2.1 If there is not enough head space within the glass sample bottle to accommodate the n-hexane volume required for extraction, transfer the sample from the sample bottle to a clean separatory funnel via a clean transfer funnel.

12.2.2 Add n-hexane at a proportion of 10:1 (sample to n-hexane) to the original sample volume and cap with the original cap. If the sample has been transferred to a separatory funnel, shake the sample bottle to rinse all interior surfaces and pour the n-hexane into the separatory funnel.

12.2.3 Extract the sample by shaking vigorously for 2 min with periodic venting into a hood to release excess pressure. Vent the funnel slowly to prevent loss of sample.

12.2.4 Allow the phases to separate.

NOTE 4—Certain types of samples, such as those containing a large amount of detergent, can form an emulsion during the extraction. If emulsion forms between the phases and the emulsion is greater than one-third the volume of the extract layer, emulsion-breaking techniques should be employed to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, use of solvent phase separation paper, centrifugation, use of an ultrasonic bath with ice, addition of NaCl, increasing the temperature, lowering the pH, or other physical methods.

12.2.5 Place a filter paper in a filter funnel, add approximately 1 g of Na_2SO_4, rinse with a small portion of the extract and discard the rinsate.

NOTE 5—Use of the sodium sulfate is necessary to prevent water from interfering in the determination. If the sodium sulfate cakes when contacted with the extract, flush once with 2 mL of n-hexane into the 50-mL volumetric flask. Remove the solid with a clean spatula, and add about 1 g of fresh sodium sulfate to the filter. Re-wet the sodium sulfate with n-hexane before use.

12.2.6 Filter the extract (top) layer through the sodium sulfate into a pre-cleaned 50-mL volumetric flask.

NOTE 6—A milky extract indicates the presence of water. If the extract is milky, remove the sodium sulfate cake, add approximately 1 g of fresh sodium sulfate to the filter funnel, and pass the extract through the sodium sulfate into a pre-cleaned 50-mL volumetric flask.

12.3 *Total Oil and Grease Infrared Absorbance Measurement*—Measure and record the infrared absorbance of the extract using the following steps.

12.3.1 Allow the instrument to warm up for the period of time recommended by the manufacturer.

12.3.2 Using a level, make sure the HATR sample plate and crystal are level.

12.3.3 Clean the HATR crystal of any residual oil or other contamination by applying about 1 mL of n-hexane to the crystal and wiping across the crystal in one direction with a disposable wipe. Repeat cleaning with isopropyl alcohol. Follow the instrument manufacturer's recommendation for determining crystal cleanliness.

12.3.4 Using a 100 µL glass syringe, deposit a specific amount of n-hexane on the crystal based on the instrument manufacturer's recommendation. It is crucial to use the same amount of volume as used for calibration.

12.3.5 Allow enough time for the n-hexane to evaporate. The minimum evaporation time is 3 min and the maximum evaporation time is 5 min. It is crucial to use the same evaporation time as used for calibration.

12.3.6 Obtain a baseline detector response (zero) according to the manufacturer's instructions. A zero should be obtained before the first use and at least once every 60 min the instrument is in use.

12.3.7 Clean the crystal according to 12.3.3.

12.3.8 Wash out the glass syringe with the extract and deposit a specific amount of n-hexane on the crystal based on the instrument manufacturer's recommendation. It is crucial to use the same amount of volume as used for calibration.

12.3.9 Allow enough time for the n-hexane to evaporate. The minimum evaporation time is 3 min and the maximum evaporation time is 5 min. It is crucial to use the same evaporation time as used for calibration.

12.3.10 Obtain an infrared detector response according to the manufacturer's instructions and calculate the absorbance value from 3.34 µm to 3.54 µm (2825 cm^{-1} to 2994 cm^{-1}). The absorbance value may be calculated internally by the instrument.

12.3.11 If the concentration of total oil and grease exceeds the calibration range, dilute extract to bring sample within calibration range. Keep a record of each dilution for determination of the concentration in the sample in 13.1.

12.4 *Silica Gel Treatment*—For the removal of polar material for a nonpolar material measurement:

12.4.1 Place a filter paper in a filter funnel and add a minimum of 3 g of silica gel. Rinse with a small portion of extract and discard the rinsate.

NOTE 7—The amount of silica gel needed has been estimated at 3 g for every 100 mg of polar material. However, this amount can be insufficient for some samples. If there is doubt about whether the amount of silica gel is adequate, the amount needed should be determined by test.

12.4.2 Slowly pour an aliquot of the extract over the silica gel and collect in a clean volumetric flask.

12.5 *Total Petroleum Hydrocarbons Infrared Absorbance Measurement*—Measure and record the infrared absorbance of the silica-gel-treated extract in a manner identical to that used in 12.3. If the concentration of total petroleum hydrocarbons exceeds the calibration range, dilute the extract to bring the concentration within the calibration range. Keep a record of each dilution for use in 13.2.

13. Calculation or Interpretation of Results

13.1 Calculate the concentration of total oil and grease (TOG) material in the water sample (C_{TOG}) to the nearest 1 mg/L and report as TOG:

$$C_{TOG} = C_E \times D \times E/V \quad (2)$$

where:

C_{TOG} = concentration of TOG in the water sample (mg/L),
C_E = concentration of TOG in the extract (mg/L),
D = dilution factor of extract from 12.3,
E = extract volume (mL), and
V = sample volume (mL).

13.2 Calculate the concentration of total petroleum hydrocarbons (TPH) material in the water sample (C_{TPH}) to the nearest 1 mg/L and report as TPH:

$$C_{TPH} = C_E \times D \times E/V \quad (3)$$

where:

C_{TPH} = concentration of TPH in the water sample (mg/L),
C_E = concentration of TPH in the extract (mg/L),
D = dilution factor of extract from 12.5,
E = extract volume in mL, and
V = sample volume in mL.

14. Quality Control[7]

14.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when running the test:

14.2 *Calibration and Calibration Verification*—See Section 11 of this test method for the calibration procedure.

14.3 *Initial Demonstration of Laboratory Capability*—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.

14.3.1 Analyze seven replicates of a standard solution prepared from an aqueous independent reference material (IRM) containing 50 mg/L of TOG and seven replicates of an aqueous independent reference material (IRM) containing 50 mg/L of TPH. The TOG precision and recovery standard (10.3) and the TPH precision and recovery standard (10.4) may also be used. The matrix and chemistry of the solutions should be equivalent to the solutions used in the collaborative study. Be sure to record the concentration added to each replicate. This concentration is the "true value" used in Eq 5. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

14.3.2 Calculate the mean, standard deviation, relative precision, bias, and % recovery of the seven values using Eq 4-6:

$$\text{Relative Precision} = 100 \times (\text{std dev/mean}) \quad (4)$$

$$\text{Bias} = 100 \times (\text{mean} - \text{true value})/\text{true value} \quad (5)$$

$$\%\ \text{Recovery} = 100 + \text{bias} \quad (6)$$

14.3.2.1 The seven replicates of the solution containing 50 mg/L of TOG must have an average % recovery of TOG in the range of 80 % to 124 % with a relative precision no greater than 8.4 %. If the relative precision and average percent recovery are outside of these limits, the initial demonstration should be repeated.

14.3.2.2 The seven replicates of the solution containing 50 mg/L of TPH must have an average % recovery of TPH in the range of 74 % to 117 % with a relative precision no greater than 10.2 %. If the relative precision and average percent recovery are outside of these limits, the initial demonstration should be repeated.

14.3.2.3 If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F-test and t-test in evaluating the acceptability of the mean and standard deviation.

[7] The statistics in this section were calculated according to Practice D5847 and are based on a single laboratory study. A full interlaboratory study will be completed within five years and this section will be updated accordingly.

14.4 *Laboratory Control Sample (LCS)*—To ensure that the test method is in control for TOG and TPH, analyze an LCS containing 50 mg/L of TOG and a separate LCS containing 50 mg/L of TPH for each batch of 20 samples. The LCS for TOG can be the TOG precision and recovery standard (10.3) but it must be made independently. The LCS for TPH can be the TPH precision and recovery standard (10.4) but it must be made independently. Commercial verified standards are also acceptable. Be sure to record the concentration added to each LCS. This concentration is the "true value" used in Eq 7. Each LCS must be taken through all of the steps of the analytical method, including sample preservation and pretreatment. Calculate the percent recovery of each LCS using Eq 7:

$$\%\ \text{recovery} = 100 + [100 \times (\text{concentration of LCS} - \text{true value})/\text{true value}] \quad (7)$$

14.4.1 The LCS for TOG shall have a percent recovery of TOG in the range of 78 % to 122 %. The LCS for TPH shall have a percent recovery of TPH in the range of 79 % to 121 %. If the results are 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.

14.5 *Method Blank (Blank)*—Analyze a reagent water test blank with each batch. The test blank must be taken through all of the steps of the analytical method including sample preservation and pretreatment. If measuring for TOG, the concentration of TOG found in the Blank must be less than 2.2 mg/L. If measuring for TPH, the concentration of TPH found in the Blank must be less than 3.7 mg/L. If the concentration of TOG or TPH, or both, is found above the stated level(s), analysis of samples is halted until the contamination is eliminated and a Blank shows no contamination at or above the stated level(s), or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.6 *Matrix Spike (MS)*—To check for interferences in the specific matrix being tested, perform an MS on at least one sample from each batch of 20 samples. Spike an aliquot of the sample with a known amount of total oil and grease and take it through the analytical method including preservation and pre-treatment. Be sure to record the concentration of total oil and grease added.

14.6.1 The spike concentration plus the background concentration must not exceed the calibration range of the analytical system. If the spike plus the background concentration exceeds the calibration range, perform an appropriate dilution so that the reading is within the calibration range. The spike must produce a concentration in the spiked sample that is 2 to 5 times the background concentration or 10 times the detection limit of the test method, whichever is greater.

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

$$P = 100 \times [(A \times V) - (B \times V)]/(C) \quad (8)$$

where:

100 = constant for converting from decimal to percent,
A = analyzed concentration of the spiked sample, in mg/L,
B = analyzed concentration of the unspiked sample, in mg/L,
C = known amount added during spike, in mg,
V = volume of sample (unspiked) used, in L, and
P = percent recovery.

14.6.3 The percent recovery of the spike shall fall within the limits of 70 % to 130 %. If the percent recovery is not within these limits, a matrix interference can be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: *(1)* the matrix interference must be removed, *(2)* all samples in the batch must be analyzed by a test method not affected by the matrix interference, or *(3)* the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

15. Precision and Bias

15.1 A single laboratory validation study was carried out with ocean substitute water, wastewater, and deionized water samples. The sample set included seven oils which are detailed in Table A1.3 of Annex A1. Each sample was prepared by spiking a given amount of oil into the water matrix and then extracted with n-hexane. For each extract, a measurement of TOG and TPH was carried out. For each concentration, the pooled mean, pooled standard deviation, and pooled recovery were calculated. The raw data are shown in Table A1.1 and Table A1.2 of Annex A1.

15.2 *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 by 2028 to update the repeatability and determine the reproducibility of the method. See Table 1 and Table 2.

15.3 *Method Detection Limit*—Eight samples of ocean substitute water were used to determine the method detection limit (MDL) according to 40 CFR Part 136, Appendix B. The raw data is shown in Table A1.5 and Table A1.6 in Annex A1. See Table 3 for TOG and Table 4 for TPH.

15.4 *Reproducibility*—A full interlaboratory study will be completed by 2028 to determine the reproducibility of this test method.

16. Keywords

16.1 dispersive infrared; filtometric infrared; FTIR; grease; HATR; hexane extraction; oil; spectroscopy; water