



Designation: D7678 – 17 (Reapproved 2022)

# Standard 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<sup>1</sup>

This standard is issued under the fixed designation D7678; 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 ( $\epsilon$ ) 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 (TOG) and total petroleum hydrocarbons (TPH) in water and waste water that are extractable by this test method from an acidified sample with a cyclic aliphatic hydrocarbon (for example cyclohexane, cyclopentane) and measured by IR absorption in the region from  $1370\text{ cm}^{-1}$  to  $1380\text{ cm}^{-1}$  ( $7.25\text{ }\mu\text{m}$  to  $7.30\text{ }\mu\text{m}$ ) using a mid-IR laser spectrometer. Polar substances are removed by clean-up with Florisil.<sup>2</sup>

1.2 This test 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 solvent-less IR methods that require drying of the employed solid phase material prior to measurement. Similarly, a more complete fraction of extracted petroleum hydrocarbons are accessible by this test method as compared to GC methods that use a time window for quantification, as petroleum hydrocarbons eluting outside these windows are quantified too.

1.3 This test method covers the range of  $0.1\text{ mg/L}$  to  $1000\text{ mg/L}$  and may be extended to a lower or higher level by extraction of a larger or smaller sample volume collected separately.

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

1.5 *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.*

1.6 *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:<sup>3</sup>

- 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
- D3921 Test Method For Oil and Grease and Petroleum Hydrocarbons in Water (Withdrawn 2013)<sup>4</sup>
- 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 ISO Standards:<sup>5</sup>

- ISO 9377-2 Determination of Hydrocarbon Oil Index

### 2.3 Code of Federal Regulations (CFR) Publications:<sup>6</sup>

- 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

<sup>1</sup> 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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<sup>2</sup> Florisil is a trademark by U.S. Silica Company, Frederick, MD.

<sup>3</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>4</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

<sup>5</sup> 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>.

<sup>6</sup> Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, <http://www.access.gpo.gov>.

### 3. Terminology

#### 3.1 Definitions:

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

#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *grease, n*—difference between measured value for TOG and TPH of a sample.

3.2.2 *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  $\text{cm}^{-1}$  to 1380  $\text{cm}^{-1}$ .

3.2.3 *total petroleum hydrocarbons (TPH), n*—material that can be extracted from water or wastewater by this test method, which remains in the extract after treatment with  $\text{Na}_2\text{SO}_4$  and Florisil, and which can be measured by infrared absorption in the region from 1370  $\text{cm}^{-1}$  to 1380  $\text{cm}^{-1}$ .

### 4. Summary of Test Method

4.1 Hydrocarbons from an acidified 900-mL sample of water or wastewater are extracted with 50 mL of solvent. The material, which is measured directly after extraction by mid-infrared laser spectroscopy is referred to as total oil and grease (TOG). The material, which is measured after the extract is treated with sodium sulfate and Florisil to remove traces of water as well as polar substances, and thereby producing a solution containing non-polar material, and which is measured by mid-infrared laser spectroscopy is referred to as total petroleum hydrocarbons (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 oil and grease as well as total petroleum hydrocarbons, 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 oil and grease as well as total petroleum hydrocarbons in water and wastewater.

### 6. Interferences

6.1 Soaps, detergents, surfactants, and other materials may form emulsions that could reduce the amount of TOG and TPH 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 on the basis of chemical structure (for example, halogenated hydrocarbons) may be extracted and measured by this test 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. Prior to starting this procedure, the glassware shall be rinsed with solvent and dried.

7.2 *Cell(s)*, calcium fluoride, two required for double-beam operation, one required for single-beam operation. The path

length of the cells should be chosen for optimum signal to noise ratio at the measurement wavelengths. This will be 2 mm to 3 mm in case of quantum cascade laser based spectrometers. Longer path lengths may be appropriate, if more powerful lasers become available.

7.3 *Mid-infrared laser spectrometer* with an optical power >20 mW within the spectral region from 1370  $\text{cm}^{-1}$  to 1380  $\text{cm}^{-1}$  (7.25  $\mu\text{m}$  to 7.30  $\mu\text{m}$ ). Either double-beam or single-beam and capable of measuring in the spectral region from 1370  $\text{cm}^{-1}$  to 1380  $\text{cm}^{-1}$  (7.25  $\mu\text{m}$  to 7.30  $\mu\text{m}$ ) or single-beam instrument tunable from 1370  $\text{cm}^{-1}$  to 1400  $\text{cm}^{-1}$  (7.14  $\mu\text{m}$  to 7.30  $\mu\text{m}$ ).<sup>7</sup>

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

7.5 *Micro-separator* (for example, see **Fig. X1.1**), or other suitable device for phase separation.

7.6 *Clean-up columns*, made from glass, with frit of sinter porosity 2 (for example, see **Fig. X1.2**) or equivalent ready-made clean-up column containing  $\text{Na}_2\text{SO}_4$  and Florisil (for TPH measurements).

7.7 *Glass bottle*, 50 mL to 100 mL, with glass or fluoropolymer stopper, or crimped cap with lined PTFE septum.

7.8 *Magnetic stirrer*, with PTFE stir bar (optional).

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

7.10 *PTFE wash bottle*.

7.11 *Volumetric pipettes*, glass, various (10 mL, 20 mL, and 50 mL).

7.12 *Analytical balance*.<sup>109c/astm-d7678-172022</sup>

7.13 *Graduated glass syringes*, 5  $\mu\text{L}$  and 25  $\mu\text{L}$ .

7.14 *Benchtop shaker*.

7.15 *Glass stirring rod* (optional).

7.16 A 1.00-mL serological glass pipet graduated in 0.01-mL increments and a 5.00-mL serological glass pipet graduated in 0.1-mL increments, or equivalent (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, if such specifications are available. 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.

<sup>7</sup> The sole source of supply of the Oil in Water analyzers known to the committee at this time is QuantaRed Technologies GmbH. 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,<sup>1</sup> which you may attend.

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 *Tetradecane*—99.0 % minimum purity, for calibration.

8.4 *Petroleum Hydrocarbons*, similar in composition to petroleum hydrocarbons determined by this test method for possible use as calibration material.

8.5 *Mineral Oil Type A (Diesel Oil without Additives) and Mineral Oil Type B (Lubricating Oil without Additives)*—These oil types may be obtained from suppliers of fine chemicals and mixed 1:1 (w:w). The mixture can be stored at 1 °C to 6 °C for up to six months. Alternatively, a readily prepared 1:1 (w:w) mixture of these oils may be used (for example, BAM K010<sup>8</sup>).

8.6 *Florisil*—grain size 150 µm to 250 µm (60 mesh to 100 mesh), activated by heating to 140 °C for 16 h and stored in a desiccator. Florisil is a trademark name for a prepared diatomaceous substance, mainly consisting of anhydrous magnesium silicate.

8.7 *Sodium Sulfate (Na<sub>2</sub>SO<sub>4</sub>)*—anhydrous, granular.

8.8 *Sulfuric Acid (1+1)*—Slowly and carefully add 1 volume of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, sp gr 1.84) to 1 volume of water, stirring and cooling the solution during addition.

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

8.10 *Solvent*—Cyclohexane (minimum purity 99.5 %) or cyclopentane (minimum purity 98.5 %).

8.11 *Stearic Acid (C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>)*, minimum purity 98 %.

## 9. Hazards

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

## 10. Sampling

10.1 Collect the sample in accordance with the principles described in Practices **D3370**, using a glass bottle in accordance with **7.4**. Pre-rinse the sample bottle and cap with the solvent and weigh the dried bottle before sample collection. Do not rinse the sample bottle with the sample to be analyzed. Do not allow the sample to overflow from the bottle during collection. Preventing overflow may not be possible in all sampling situations, however, measures should be taken to minimize overflow at all times.

10.2 A sample volume of about 900 mL is required 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 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. 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 of solvent and combine the extracts. Be sure to determine the correct ratio of solvent volumes taken from each sample prior to measurement.

10.3 Preserve the sample with a sufficient quantity of sulfuric acid (see **8.8**) or hydrochloric acid (see **8.9**) to a pH of 2 or lower and refrigerate at 1 °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, perform 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, 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 (see 40 CFR Part 136, Table II, Footnote 3) of 1.15 if H<sub>2</sub>SO<sub>4</sub> is used and 1.96 if HCl is used (see 49 CFR Part 172).

10.4 Samples shall be extracted and analyzed within one week. Once extracted, the extract can be stored up to two weeks at a temperature between 7 °C and 10 °C.

## 11. Calibration

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 while performing this test method.

NOTE 1—This test method uses cyclohexane as standard solvent as it is widely available. However, other cyclic aliphatic hydrocarbons such as cyclopentane may be used instead with very similar figures of merit in terms of precision and dynamic range. It is the responsibility of the user to demonstrate equivalent performance when using solvents other than cyclohexane.

NOTE 2—For calibration of the instrument, standards prepared by weighing tetradecane in solvent shall be used. This is different to former test methods (for example, Test Method **D3921**), which allow calibration either with the type of petroleum hydrocarbon that is known to be present in the sample of water or wastewater or, alternatively, using a defined calibration material (for example, mixture of isooctane and cetane). The purpose of defining one calibration material is to facilitate comparability of results obtained by different laboratories. Tetradecane was selected as calibration material, as it correlates best with different types of petroleum hydrocarbons including heavy crude oil and condensate. In case the concentration of petroleum hydrocarbon in a constant matrix void of other extractable materials (for example process monitoring of crude oil in

<sup>8</sup> The sole source of supply of the prepared mixture BAM K010 known to the committee at this time is the German Federal Institute for Materials Research and Testing. 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,<sup>1</sup> which you may attend.



water) is to be determined, calibration of the instrument may be done with the type of petroleum hydrocarbon awaiting analysis. In this special case, the clean-up step may be omitted and the extract measured directly after solvent extraction. However, measurement of the calibration standards and the samples must be done in the same way. The thus obtained values (oil in water) are, however, not to be considered as the total petroleum hydrocarbon (TPH) concentration of the sample in accordance with this test method. An appropriate correction factor can be found to relate such values to the total petroleum hydrocarbon concentration in accordance with this test method (see 11.4.6 and 14.4). It lies within the sole responsibility of the user to assure comparability of the results.

## 11.2 Preparation of the Calibration Solutions:

**11.2.1 Calibration Stock Solution S**—Weigh a 100-mL volumetric flask including stopper. Draw about 1.800 g of tetradecane or the type of the petroleum hydrocarbon awaiting analysis (if available) and transfer it to this flask. Obtain its exact weight by difference weighing. Fill to the mark with solvent and mix the liquid well by shaking the flask. Calculate the exact concentration of the calibration material in solution in terms of mg/L.

**11.2.2 Calibration Solution G**—Draw 50.0 mL of Stock Solution, transfer it to a 100 mL volumetric flask and fill the flask to the mark with solvent. Calibration Solution G = 9000 mg/L.

**11.2.3 Calibration Solution F**—Draw 10.0 mL of Stock Solution, transfer it to a 100 mL volumetric flask and fill to mark with solvent. Calibration Solution F = 1800 mg/L.

**11.2.4 Calibration Solution E**—Draw 10.0 mL of Calibration Solution G, transfer it to a 100 mL volumetric flask and fill to mark with solvent. Calibration Solution E = 900 mg/L.

**11.2.5 Calibration Solution D**—Draw 10.0 mL of Calibration Solution F, transfer it to a 100 mL volumetric flask and fill to mark with solvent. Calibration Solution D = 180 mg/L.

**11.2.6 Calibration Solution C**—Draw 10.0 mL of Calibration Solution E, transfer it to a 100 mL volumetric flask and fill to mark with solvent. Calibration Solution C = 90 mg/L.

**11.2.7 Calibration Solution B**—Draw 10.0 mL of Calibration Solution D, transfer it to a 100 mL volumetric flask and fill to mark with solvent. Calibration Solution B = 18 mg/L.

**11.2.8 Calibration Solution A**—Draw 10.0 mL of Calibration Solution C, transfer it to a 100 mL volumetric flask and fill to mark with solvent. Calibration Solution A = 9 mg/L.

## 11.3 Preparation of the Laboratory Control Sample (LCS):

**11.3.1** Pour 900 mL reagent water into a sample bottle. Record exact volume or weight.

**11.3.2** Using a micro-syringe, add 9.0 mg of a mixture of mineral oil Type A and Type B (8.5) to obtain a concentration of 10.0 mg/L. Obtain exact weight by difference weighing of the micro-syringe.

## 11.4 Measurement of the Calibration Solutions:

**NOTE 3**—Even though solvent of high grade is used for analysis, it will contain small (<0.5 %) amounts of non-cyclic hydrocarbons and other residue. Furthermore, there will be a variation in this content between production batches (lot numbers), even from the same producer. To avoid that this inevitable variation in product quality affects the results of this test method, solvent from the same bottle must be used for reference and sample measurement.

**NOTE 4**—During calibration, the cell must be thoroughly cleaned with solvent prior to filling with a new calibration solution. Flow-through cells as well as conventional cells with stoppers may be used. Use the same cell throughout the calibration procedure and subsequent measurements.

Follow recommendations of the manufacturer of laser based spectrometers, since variations in design make it impractical to offer instructions for their use with this test method.

**11.4.1** The calibration contains a minimum of 6 non-zero points.

**11.4.2 Check Cell for Cleanliness**—For double-beam analyzers, fill the reference cell and the sample cell with solvent and record the intensities within the 1370 cm<sup>-1</sup> to 1380 cm<sup>-1</sup> (7.25 μm to 7.30 μm) band. For single-beam analyzers, perform two consecutive measurements (I<sub>0</sub> and I<sub>x</sub>). For a tunable analyzer, record I<sub>x</sub> from the 1370 cm<sup>-1</sup> to 1380 cm<sup>-1</sup> band and I<sub>0</sub> from 1400 cm<sup>-1</sup> (7.14 μm) and subtract the thus calculated absorbance value. The standard deviation of 3 absorbance values (see Eq 1) should be less than ± 0.2 × 10<sup>-3</sup> Absorbance (dimensionless quantity, referred to as absorbance value). If higher, check cells for cleanliness, matching, alignment, etc., and repeat the procedure.

**11.4.3** Use solvent from the same bottle used for preparation of the calibration solutions for background measurements (I<sub>0</sub>) and, in case of a single beam analyzer, perform a background measurement (I<sub>0</sub>) before every measurement of a calibration solution, unless otherwise instructed by the instrument manufacturer.

**11.4.4** For calibrating the instrument in the concentration range between 9 mg/L and 18 000 mg/L tetradecane in solvent (corresponding to 0.5 mg/L to 1000 mg/L tetradecane in water, considering an enrichment factor of the solvent extraction of 18, which results, if 900 mL of aqueous sample is extracted with 50 mL of solvent), repeat the following procedure for measurement of Calibration Solutions A–G and S: Fill sample cell with calibration solution or stock solution, respectively, and obtain the absorbance values within the 1370 cm<sup>-1</sup> to 1380 cm<sup>-1</sup> band (7.25 μm to 7.30 μm) for every solution as recommended by the instrument manufacturer. Alternatively, calculate the absorbance value for each standard (A<sub>x</sub>) using the following equation:

$$A_x = \log \frac{I_0}{I_x} \quad (1)$$

**11.4.5** Plot the absorbance values found in 11.4.4 versus the respective concentration values (in mg/L) for each of the solutions examined. The points should lie close to a straight line. Determine the equation of the best-fitting straight line by a linear regression technique. Record this equation for use with the test samples. For infrared laser instruments with built-in data evaluation capability use this software for data evaluation.

**11.4.6** If the oil awaiting analysis is used as calibration material, a correction factor must be experimentally determined to calculate the TOG or TPH value from the concentration value obtained (oil in water). For doing so, an additional calibration based on tetradecane as calibration material has to be carried out, following 11.2 and 11.4. From the slopes of the obtained linear calibration graphs (k<sub>TD</sub> and k<sub>Oil</sub>) calculate the correction factor f according to:

$$f = \frac{k_{TD}}{k_{Oil}} \quad (2)$$

where:

$k_{TD}$  = slope of the linear calibration graph using tetradecane as calibration material, and

$k_{oil}$  = slope of the linear calibration graph using the oil awaiting analysis as calibration material.

## 12. Quality Control

### 12.1 Calibration Verification:

12.1.1 Verify instrument calibration by analyzing a standard at the concentration of one of the calibration solutions. Analysis of a single calibration standard to verify an existing calibration curve may suffice due to the high linearity of the calibration curve. The instrument calibration is verified, if the obtained concentration value falls within three standard deviations of the mean value of this standard found in the single laboratory validation study. It is recommended to use a standard of 900 mg/L tetradecane in cyclohexane for verification of the calibration. In this case the obtained concentration shall fall within  $900 \pm 12$  mg/L.

12.1.2 If calibration cannot be verified, recalibrate the instrument.

### 12.2 Qualification of Sample Clean-Up:

12.2.1 The sample clean-up, required for the measurement of TPH, uses Florisil to absorb polar substances in the extract. Clean-up columns can be prepared in the lab by filling small glass columns (7.6) with 2-g Florisil (8.6) and covering it with 2 g of sodium sulfate (8.7). Ready-made clean-up columns can be purchased and used as delivered, if qualified by the manufacturer. Other procedures using the same aliquot of Florisil per volume of extract may be used alternatively, provided that results are equivalent.

NOTE 5—The use of ready-made cartridges filled with Florisil and covered with  $\text{Na}_2\text{SO}_4$  (for example, LiquiSpec TPH cartridges)<sup>9</sup> was found to be suitable for clean-up of samples.

12.2.2 For each batch of Florisil or ready-made clean-up columns, the suitability shall be tested.

12.2.3 Prepare a test solution by mixing 130-mg stearic acid (8.11) with solvent in a 200-mL volumetric flask. Fill flask to the mark with solvent.

12.2.4 Determine the concentration of the solution in accordance with the calibration obtained in 11.4 and record the result.

12.2.5 Draw the solution through the clean-up column and determine the concentration of the treated solution in accordance with the same calibration. The ratio of the two results shall be less than 1/30.

12.2.6 If the ratio is higher, activate the Florisil in accordance with 8.6 and repeat the procedure.

12.2.7 Prepare a solution by mixing 360 mg of a mixture (1:1) of mineral oil Type A and Type B (8.5) with solvent in a 200 mL volumetric flask. Fill flask to the mark with solvent.

12.2.8 Determine the concentration of the solution in accordance with the calibration obtained in 11.4 and record the result.

12.2.9 Draw the solution through the clean-up column and determine the concentration of the treated solution in accordance with the same calibration. The recovery (result for the treated extract/result for the untreated extract) shall be at least 95 %.

12.2.10 If the value is lower, the sample is diluted by the cartridge and a larger sample volume must be passed through the cartridge.

### 12.3 Initial Demonstration of Laboratory Capability:

12.3.1 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.

12.3.2 Analyze four samples, prepared by weighing 9.00 mg of a mixture of mineral oil Type A and Type B (see 8.5) in 900 ml reagent water. Each sample must be taken through the complete analytical test method including any sample preservation and pretreatment steps. Determine TOG and TPH parameters for each sample.

12.3.3 Calculate the mean and standard deviation for TOG and TPH of the four measurements and compare them to the acceptable ranges of precision and bias obtained through the interlaboratory validation study. For TOG, the mean value shall be between 12.1 mg/L and 13.9 mg/L, whereas the precision shall be less than 8.4 %. For TPH, the mean value shall be between 11.1 mg/L and 12.5 mg/L, whereas the precision shall be less than 7.0 %. These limits have been calculated applying a significance level of  $\alpha = 0.01$ .

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. Therefore, it is suited to verify the correct performance of this test method despite of its different chemical composition compared to most crude and condensate oil types.

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

### 12.4 Laboratory Control Sample (LCS):

12.4.1 Periodic verification of the correct implementation of this test method shall be performed by analyzing the LCS, containing 10 mg/L of a mixture of mineral oil Type A and Type B (see 8.5), with every batch of 20 samples. The selected analyte 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 a LCS after every 50 samples. The LCS must be taken through all steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within the range between 11.4 mg/L and 14.6 mg/L for TOG and between 10.5 mg/L and 13.1 mg/L for TPH. These limits are calculated on basis of results from the interlaboratory validation study at a significance level of  $\alpha = 0.01$ .

<sup>9</sup> The sole source of supply of the LiquiSpec TPH cartridges known to the committee at this time is QuantaRed Technologies GmbH. 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,<sup>1</sup> which you may attend.

12.4.2 If the result is not within these limits, analysis of samples is halted until the problem is identified and corrected. Either all samples in the batch must be re-analyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of this test method.

#### 12.5 Method Blank:

12.5.1 Analyze a reagent water test blank with each batch. The concentration of TOG found in the blank must be less than 0.2 mg/L. If the concentration of TOG is found above this level, analysis of samples is halted until the contamination is eliminated and a blank sample shows no contamination at or above this level. All samples in the batch must be re-analyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of this test method.

#### 12.6 Matrix Spike (MS):

12.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known amount of tetradecane and taking it through the analytical method. Addition of tetradecane shall be carried out using a glass syringe and by difference weighing.

12.6.2 The spike concentration plus the background concentration of total petroleum hydrocarbons 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 this test method, whichever is higher.

12.6.3 Calculate the percent recovery of the spike (P) using the following equation:

$$P = 100 \frac{AV - BV}{C} \quad (3)$$

where:

A = concentration found in spiked sample (mg/L),

B = concentration found in unspiked sample (mg/L),

C = amount added during spiking (mg), and

V = volume of sample used (L).

12.6.4 The recovery of the spike shall fall within the limits 70 % to 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 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 this test method.

### 13. Procedure

#### 13.1 Extraction:

13.1.1 Mix the sample by shaking the original sample bottle.

13.1.2 Bring temperature of the sample to 22 °C ± 3 °C.

13.1.3 Add 50 mL of solvent to the sample and recap immediately. Shake vigorously for 2 min. Allow contents to settle and bubbles to disappear. Extraction by stirring for 30

min may be adequate, but make sure that the solvent wets all surfaces of the sample bottle and cap.

13.1.4 In the case of formation of emulsions, add MgSO<sub>4</sub> \* 7 H<sub>2</sub>O during the liquid-liquid extraction step. Typically, an amount of 5 g to 10 g will be sufficient.

13.1.5 If using a glass flask with a ground neck, remove the stopper and replace it by the micro separator (Fig. X1.1).

13.1.6 Add enough water to allow withdrawal of the organic phase layer from the microseparator and collect the sample in a glass beaker.

13.1.7 If no micro separator is used for phase separation, add water to the sample bottle to facilitate withdrawal of the organic phase using a glass pipette, glass syringe or similar and collect the organic phase in a glass beaker.

13.1.8 Take care to avoid the transfer of water, as this will incrust the surface of the sodium sulfate. It is recommended to transfer the organic layer in several steps while using a glass pipette or glass syringe. If a micro separator Fig. X1.1 is used, position the meniscus below the cock.

#### 13.2 Measurement of Total Oil and Grease (TOG):

13.2.1 Use solvent from the same bottle as for the extraction to obtain a reference measurement (I<sub>0</sub>) and measure and record the infrared absorbance of the extract (A<sub>X</sub>) in a manner identical to that used for the calibration standards (11.4.3 and 11.4.4).

13.2.2 If the concentration of total oil and grease exceeds the calibration range, dilute the extract to bring the concentration within the calibration range. Use cyclohexane of the same lot as used for extraction. If dilution is necessary, step 13.2 is to be repeated with the diluted extract.

13.2.3 If the sample is turbid or water droplets have been transferred to the glass beaker, the use of a small drying column filled with Na<sub>2</sub>SO<sub>4</sub> prevents water from interfering with the measurement.

NOTE 7—A drying step can be recommended for TOG measurements at low analyte concentrations to avoid influence of the inevitable residue in the solvent.<sup>10</sup>

#### 13.3 Measurement of Total Petroleum Hydrocarbons (TPH):

13.3.1 Use a new column or cartridge for every measurement. If the clean-up column is prepared in the laboratory, fill the clean column with 2-g Florisil and cover it with 2 g of Na<sub>2</sub>SO<sub>4</sub>. If ready-made clean-up columns are used refer to the instructions of the manufacturer.<sup>10</sup>

13.3.2 Draw solvent from the same bottle used for extraction through the clean-up cartridge and determine a reference (I<sub>0</sub>).

13.3.3 Draw the extract through the clean-up cartridge, measure and record the absorbance of the treated extract (A<sub>X</sub>) in a manner identical to that used for the calibration standards (11.4.3 and 11.4.4).

<sup>10</sup> Ready-made drying and clean-up columns (LiquiSpec TOG and LiquiSpec TPH, respectively), have been found to be suitable. The sole source of supply of these columns known to the committee at this time is QuantaRed Technologies GmbH. 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,<sup>1</sup> which you may attend.



13.3.4 If the concentration of total petroleum hydrocarbons exceeds the calibration range, dilute the extract to bring the concentration within the calibration range. Use cyclohexane of the same lot as used for extraction. If dilution is necessary, step 13.3 is to be repeated with the diluted extract.

13.3.5 If the difference between TOG and TPH (grease) is higher than the expected adsorption capability of the clean-up column, dilute the extract using cyclohexane of the same lot as used for extraction. Alternatively, increase the amount of Florisil in the clean-up column. If dilution is necessary, step 13.3 is to be repeated with the diluted extract.

#### 14. Calculation of Results

14.1 Determine the concentration of TOG and TPH in the extract by applying the calibration curve (11.4.5), or as directed by the infrared laser spectrometer manufacturer.

14.2 To the nearest 0.1 mg/L, calculate the concentration of total oil and grease (TOG) in the original water or waste water sample as follows:

$$\text{Total Oil and Grease (TOG)} = \frac{R_{TOG}D}{E} \quad (4)$$

where:

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

$D$  = dilution factor (volume of diluted extract/volume of undiluted extract), if any, as utilized in 13.3.2, and

$E$  = enrichment factor (volume of water/volume of solvent) due to extraction.

14.3 To the nearest 0.1 mg/L, calculate the concentration of total petroleum hydrocarbons (TPH) in the original water or waste water sample as follows:

$$\text{Total Petroleum Hydrocarbons (TPH)} = \frac{R_{TPH}D}{E} \quad (5)$$

where:

$R_{TPH}$  = measured concentration of total petroleum hydrocarbons in mg/L in the treated extract,

$D$  = dilution factor (volume of diluted extract/volume of undiluted extract), if any, as utilized in 13.3.4, and

$E$  = enrichment factor (volume of water/volume of solvent) due to extraction.

14.4 In case calibration and analysis was performed with the oil awaiting analysis omitting the clean-up step (Note 2) the

obtained values (oil in water,  $c_{Oil}$ ) can be converted to total petroleum hydrocarbons values using the following equation:

$$\text{total petroleum hydrocarbons mg/L} = c_{Oil} \times f \quad (6)$$

where:

$c_{Oil}$  = concentration of oil in water, mg/L, and

$f$  = correction factor calculated in accordance with Eq 2.

#### 15. Precision and Bias<sup>11</sup>

15.1 The precision and bias of this test method is based on an interlaboratory study conducted in 2017. The results are shown in Tables 1 and 2 for TOG and TPH parameters, respectively.

15.2 Each of 11 participating laboratories tested 8 different samples. All 11 laboratories reported values for TPH, 6 laboratories reported values for TOG.

15.3 The test design of the study meets the criteria of Practice D2777 – 13 with two exemptions. Due to the considerable effort and cost of logistics of the study, only one matrix was tested at three Youden pair concentrations, another matrix was tested with only one Youden pair of concentrations. Additional single laboratory validation studies were performed for calibration verification (Table 3), method detection limit (Table 4) and high concentrations (Table 5). These exemptions have been granted by the Technical Operations Committee and the results advisor of the D19 Committee on Water.

15.4 Details are given in ASTM Research Report No. RR:D19-1196.

15.5 Ready-made Na<sub>2</sub>SO<sub>4</sub>/Florisil cartridges (LiquiSpec TPH cartridges) have been used for clean-up by all laboratories.

15.6 It is the user's responsibility to ensure the validity of precision and bias outside of the interlaboratory validation study ranges and matrices.

#### 16. Keywords

16.1 oil; total oil and grease (TOG); total petroleum hydrocarbons (TPH)

<sup>11</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1196. Contact ASTM Customer Service at service@astm.org.

**TABLE 1 Statistical Summary for Total Oil and Grease (TOG)**

Sample	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
Analyte	BAM	BAM	BAM	BAM	A-Oil	A-Oil	BAM	BAM
Nominal concentration (mg/L)	9	10	48	50	104	100	50	52
Number of results reported	6	6	6	6	6	6	6	6
Number of usable results	6	6	6	6	6	6	6	6
Average recovery (mg/L)	11.6	12.6	62.0	64.4	117.1	110.4	64.8	67.6
Average recovery (%)	128.6	125.5	129.1	128.7	112.6	110.4	129.6	130.1
Overall RSD (mg/L)	0.5	0.8	0.5	0.9	6.5	6.4	1.1	0.7
Overall RSD (%)	4.6	6.3	0.8	1.4	5.6	5.8	1.6	1.0
Number of usable pairs	6			6		6		6
Single analyst RSD (%)	4.5			0.5		1.4		0.5