



Designation: D7678 – 11

Standard Test Method for Total Petroleum Hydrocarbons (TPH) in Water and Wastewater with Solvent Extraction using Mid-IR Laser Spectroscopy¹

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1. Scope

1.1 This test method covers the determination of total petroleum hydrocarbons (TPH) in water, and waste water, that are extractable from an acidified sample with a cyclic aliphatic hydrocarbon (for example cyclohexane), and measured by IR absorption in the region of $1370-1380\text{ cm}^{-1}$ (7.25–7.30 microns). Polar substances are removed by clean-up with Florisil.

1.2 The 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 oil and grease in water and wastewater as that which is extractable in the test method and measured by IR absorption in the region of $1370-1380\text{ cm}^{-1}$ (7.25–7.30 microns).

1.4 This method covers the range of 0.5 to 1000 mg/L and may be extended to a lower or higher level by extraction of a larger or smaller sample volume collected separately.

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 and health practices and determine the applicability of regulatory limitations prior to use.*

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. Referenced Documents

2.1 ASTM Standards:²

- D1129 Terminology Relating to Water
- D1141 Practice for the Preparation of Substitute Ocean Water
- D1193 Specification for Reagent Water
- D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)³
- 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
- D3921 Test Method For Oil and Grease and Petroleum Hydrocarbons in Water
- D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
- D7575 Test Method for Solvent-Free Membrane Recoverable Oil and Grease by Infrared Determination
- E168 Practices for General Techniques of Infrared Quantitative Analysis

2.2 ISO Standards:⁴

- ISO 9377-2 Determination of Hydrocarbon Oil Index

3. Terminology

3.1 *Definitions*—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 *Total petroleum hydrocarbons (TPH), n*—the extracted material which remains in the solvent after treatment with Na_2SO_4 and Florisil.

4. Summary of Test Method

4.1 An acidified 900 mL sample of water or wastewater is extracted with 50 mL of cyclohexane. The extract is treated

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

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

⁴ Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, Case postale 56, CH-1211, Geneva 20, Switzerland, http://www.iso.ch.

with sodium sulfate and Florisil to remove traces of water, as well as polar substances, thereby producing a solution containing nonpolar material. The nonpolar material is referred to as total petroleum hydrocarbons (TPH) and is measured by mid-infrared laser spectroscopy.

5. Significance and Use

5.1 The presence and concentration of total petroleum hydrocarbons, as well as 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 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 total 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 total petroleum hydrocarbons on the basis of chemical structure may be extracted, retained in the extract after filtration over Florisil and thus measured as total petroleum hydrocarbons (for example, halogenated hydrocarbons).

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.

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 at the measurement wavelengths. This will be 2-3 mm in case of quantum cascade laser based spectrometers. However, longer path lengths may be appropriate should more powerful lasers become available.

7.3 Mid-infrared laser spectrometer with an optical power >20 mW within the spectral region of 7.25-7.30 μm . Either double-beam or single-beam and capable of making measurements in the region from 7.25-7.30 μm or single beam instrument tunable from 7.14 – 7.30 μm .⁵

7.4 Glass Wide Mouth Sample Bottle, minimum 250 mL, 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.

7.5 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

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

7.8 Magnetic stirrer, with PTFE-fluorocarbon stirring bar.

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

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

7.11 Volumetric pipettes, glass, various (20, 30 and 40 mL).

7.12 Analytical balance.

7.13 Graduated glass syringes (for example Hamilton) 5 and 25 μL .

7.14 Benchtop shaker, (optional).

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, where 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.

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 use in 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, for example Fluka (mineral oil type A: Product No. 91975; mineral oil type B: Product No. 78473). Alternatively a readily prepared 1:1 (w:w) mixture of these oils may be used (for example, BAM K010 from the German Federal Institute for Materials Research and Testing).

8.6 *Florisil*—grain size 150 μm to 250 μm (60 mesh to 100 mesh), heated to 140°C for 16 h and stored in a desiccators. Florisil is a trade name for a prepared diatomaceous substance, mainly consisting of anhydrous magnesium silicate, available for example from Sigma Aldrich (Product Number 03286). Determine the cyclohexane soluble material content of the Florisil by extracting 10 g of Florisil with 25 mL of cyclohexane and collect the elute in a flask. Filter and fill a calcium fluoride cell for analysis by IR. The cyclohexane soluble material must be less than 0.5 mg/25mL.

8.7 *Sodium Sulfate (Na₂SO₄)*—anhydrous, granular.

⁵ For example: The ERACHECK from Eralytics GmbH has been found to meet these specifications.

8.8 *Sulfuric Acid (1+1)*—Slowly and carefully add 1 volume of sulfuric acid (H_2SO_4 , 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%)

9. Hazards

9.1 Normal laboratory safety applies to this 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 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 according to [7.4](#). Weigh the dried bottle before sample collection. Prerinse the sample bottle and cap with the solvent prior to 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 petroleum hydrocarbon that adheres 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 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 clean-up ([13.2](#)).

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 1-6 °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 can not 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 40CFR Part 136, Table II Footnote 3) of 1.15 if H_2SO_4 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 6 months at a temperature between 7 and 10°C.

11. Preparation of Apparatus

11.1 Mineral Oil A and B (1+1) for preparing the laboratory control sample (LCS) to be applied as matrix spike – Place 500 mg of Mineral Oil A and 500 mg of Mineral Oil B in a 2-10 mL glass vial with glass or fluoreopolymer stopper and mix thoroughly and store at 1-6 °C for a maximum period of 6 months.

12. Calibration and Standardization

12.1 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.

NOTE 1—This test method uses cyclohexane as solvent. 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 will be 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 best correlates 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 extractables (for example process monitoring of crude oil in 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 according to this test method. An appropriate correction factor can, however, be found to relate such values to the total petroleum hydrocarbon concentration according to this test method (see [12.4.6](#) and [14.3](#)). It lies within the sole responsibility of the user to assure comparability of the so obtained results.

12.2 Preparation of the Calibration Solutions:

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

12.2.2 *Calibration Solution G:* Place 50.0 mL of Stock Solution in a 100 mL volumetric flask and fill to mark with solvent. Calibration Solution G = 9000 mg/L.

12.2.3 *Calibration Solution F:* Place 10.0 mL of Stock Solution in a 100-mL volumetric flask and fill to mark with solvent. Calibration Solution F = 1800 mg/L.

12.2.4 Calibration Solution E—Place 10.0 mL of Calibration Solution G in a 100-mL volumetric flask and fill to mark with solvent. Calibration Solution E = 900 mg/L.

12.2.5 Calibration Solution D—Place 10.0 mL of Calibration Solution F in a 100-mL volumetric flask and fill to mark with solvent. Calibration Solution D = 180 mg/L.

12.2.6 Calibration Solution C—Place 10.0 mL of Calibration Solution E in a 100-mL volumetric flask and fill to mark with solvent. Calibration Solution C = 90 mg/L.

12.2.7 Calibration Solution B—Place 10.0 mL of Calibration Solution D in a 100-mL volumetric flask and fill to mark with solvent. Calibration Solution B = 18 mg/L.

12.2.8 Calibration Solution A—Place 10.0 mL of Calibration Solution C in a 100 mL volumetric flask and fill to mark with solvent. Calibration Solution A = 9 mg/L.

12.3 Preparation of the Laboratory Control Sample (LCS):

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

12.3.2 Using a micro-syringe add 9.0 mg of Mineral Oil A and B (1+1) to obtain a concentration of 10.0 mg/L. Obtain exact weight by difference weighing of the micro-syringe.

12.3.3 If necessary this solution can be made more or less concentrated to suit the concentration needed for the matrix spike.

12.4 Measurement of the Calibration Standards:

NOTE 3—Even though solvent of high grade is used for analysis, it will contain small (<0.5%) amounts of non-cyclic hydrocarbons. Furthermore, there will be a variation in this content between production batches (lot numbers), even from the same producer. To avoid that this unavoidable 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.

NOTE 4—During the calibration events which follow, the cell used for the calibration solutions must be thoroughly cleaned with fresh solvent prior to the addition of a new blend. Flow through cells as well as conventional cells with stoppers may be used. In the latter case take care to avoid insertion of the cell stopper so tightly that the cell could burst from expansion of its contents as it resides in the light beam. It is desirable to flush the cell compartment of the spectrometer with nitrogen or dry air. Use the same cell throughout the calibration procedure. Rely upon sole recommendations of the manufacturer of laser based spectrometers since variations in design make it impractical to offer instructions for their use with this method. Also, reference to scanning or running, or both, should be interpreted to mean obtaining an absorbance reading of the 1370-1380 cm^{-1} (7.25-7.30 μm) band. Calculation of the absorbance values of samples requires measurement of the solvent blank and measurement of the sample itself. These measurements may be carried out consecutively in a single beam instrument or quasi simultaneously using a double beam instrument. Alternatively, an IR laser spectrometer tunable from 1370 – 1400 cm^{-1} (7.30 – 7.14 μm) may be used for scanning the absorbance of the 1370 – 1380 cm^{-1} band measured with respect to an appropriate baseline point (for example 1400 cm^{-1} ; 7.14 μm). In either case solvent of the same lot has to be employed for blank and sample measurement.

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

12.4.2 For double-beam operation, fill the reference cell and the sample cell with solvent and record the intensities within the 1370-1380 cm^{-1} (7.25-7.30 μm) band. For single-beam analyzers, perform two measurements consecutively (I_0 and I_x). The standard deviation of the absorbance values (use equation 1 to calculate the absorbance values and use 10 such

values for calculation of the standard deviation) should be less than $\pm 0.5 \times 10^{-3}$ Absorbance (dimensionless quantity, referred to as absorbance value in the text). If not, check cells for cleanliness, matching, etc. Drain and clean the sample cell. For single beam instrument store spectral data for the solvent (I_0) at this time. For a tunable analyzer record I_x from the 1370 – 1380 cm^{-1} band and I_0 from 1400 cm^{-1} (7.14 μm) and subtract the thus calculated absorbance value of the blank from the one of the sample to obtain the absorbance value to be used in the calibration. After running, drain, and clean the sample cell.

12.4.3 For calibrating the instrument in the concentration range 9 - 18000 mg/L of tetradecane in solvent (corresponding to 0.5-1000 mg/L of tetradecane in water considering an enrichment factor of the solvent extraction of 18 which results when 900 mL of aqueous sample are extracted with 50 mL of solvent) repeat the following procedure for measurement of calibration samples A-G and S: Fill sample cell with Calibration Solution or the Stock Solution. Scan as in 12.4.2 and store I_x recorded for each sample; drain and clean the sample cell. In case of using a single beam instrument record spectral data for the solvent (I_0) prior to measurement of the next standard or follow instructions by the instrument manufacturer as sufficient instrument stability can prolong the intervals between recording the solvent blank.

12.4.4 Obtain the absorbance values within 1370-1380 cm^{-1} (7.25-7.30 μm) for every measured calibration standard and the Stock Solution as recommended by the instrument manufacturer. Alternatively, calculate the absorbance value for each standard (A_x) using the following equation:

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

NOTE 5—For infrared instruments having computer capability, data may be obtained automatically or as described in 12.4.4. However, all data must be obtained consistently by one means or the other, not a combination of the two.

12.4.5 On linear graph paper, plot the absorbance values, found in 12.4.4 or as permitted in Note 5, versus the respective mg/L values for each of the solutions examined. The points should lie close to a straight line. Draw the best-fitting straight line through the points and keep this calibration graph for use with the test samples. Preferably, determine the equation of the best-fitting straight line calculated 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.

12.4.6 When the oil awaiting analysis is used as calibration material a correction factor must be experimentally determined to calculate the total petroleum hydrocarbon value from the concentration values obtained (oil in water) (see also Note 2). For doing so, an additional calibration based on tetradecane as calibration material has to be carried out, following again 12.2 and 12.4. From the slopes of the obtained linear calibration graphs (k_{TD} and k_{Oil}) calculate the correction factor f according to:

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