



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

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 (ϵ) indicates an editorial change since the last revision or reapproval.

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.

Current edition approved Feb. 1, 2011. Published March 2011. DOI: 10.1520/D7678-11.

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 (Withdrawn 2013)³
- 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:

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

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.

12.5 Calibration Verification:

12.5.1 Verify instrument calibration by analyzing a standard at the concentration of one of the calibration standards. Analysis of a single calibration standard to verify an existing calibration curve may suffice. The instrument calibration is verified when 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 ± 12 mg/L.

12.5.2 If calibration cannot be verified, recalibrate the instrument.

12.6 Initial Demonstration of Laboratory Capability:

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

12.6.2 Analyze four replicates of a standard solution prepared each by weighing in 9.00 mg of a mixture of a mineral oil type A and B (see 8.5) in 900 ml of reagent water. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps. The replicates may be interspersed with samples.

12.6.3 Calculate the mean and standard deviation of the four values and compare to the acceptable ranges of precision and bias obtained through the single laboratory validation study. The found mean value shall lie between 12.5 and 13.9 mg/L whereas the precision shall be smaller than 7.3 %. These limits have been calculated applying a significance level of $\alpha = 0.01$.

NOTE 6—A mixture of a mineral oil type A and 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. It is therefore suited to verify the correct performance of the test method despite of its different chemical composition to most crude and condensate oil types.

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

12.7 Laboratory Control Sample (LCS):

12.7.1 To ensure that the test method is in control, analyze the LCS containing 10 mg/L of a synthetic 1:1 (w:w) mixture of an mineral oil type A and B (see 8.5) with each batch of 20 samples. The selected LCS follows recommendation of Practice D5847 to use an independent reference material as the LCS. If large numbers of samples are analyzed in the batch, analyze the LCS after every 50 samples. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within the limits 12.2 - 14.1

mg/L calculated on basis of the results from the single laboratory validation study.

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

12.8 Method Blank:

12.8.1 Analyze a reagent water test blank with each batch. The concentration of total petroleum hydrocarbons found in the blank must be less than 0.5 mg/L. If the concentration of total petroleum hydrocarbons is found above this level, analysis of samples is halted until the contamination is eliminated and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

12.9 Matrix Spike (MS)

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

12.9.2 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 the test method, whichever is greater.

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

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

where:

- A = concentration found in spiked sample (mg/L),
- B = concentration found in unspiked sample (mg/L),
- C = amount added during spiking (mg),
- V = volume of sample used (L).

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

13. Procedure

13.1 Extraction:

13.1.1 Mix the sample by shaking the original sample bottle. Check the pH of the liquid by touching pH-sensitive

paper to the cap. If necessary, add sufficient sulfuric acid to attain a pH of 2 or less.

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

13.1.3 Add 50 mL of solvent and a magnetic stirrer bar to the sample in the original sample bottle. Recap immediately and stir vigorously for 30 min on the magnetic stirrer. After turning off the magnetic stirrer allow contents settle and bubbles disappear. Extraction by shaking may be adequate, but verify efficiency.

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

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 extracting agent layer from the microseparator.

13.1.7 When not using a micro separator for phase separation, add water to facilitate withdrawing the organic phase using a glass pipette or similar.

13.1.8 When transferring the organic phase to the clean-up column (Fig. X1.2) in 13.2, 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 using a glass pipette, or, when using the micro separator (Fig. X1.1), to position the meniscus below the cock.

13.2 Clean-Up Procedure:

13.2.1 Transfer the organic phase to a small column (see Fig. X1.2) filled with 2 g of Florisil (8.6) and covered with a layer of 2 g of sodium sulfate (8.7).

13.2.2 Let the organic phase run through the column into a glass bottle (7.3) and cap immediately.

NOTE 7—Other procedures using the same amount of Florisil for cleaning the extract may be used as an alternative, provided the results are equivalent to the column testing of Florisil. Such alternatives may include shaking the total extract with 2 g of Florisil and 2 g sodium sulfate per 50 mL of extract during 30 min on a shaking apparatus. Another alternative consists in using a filter stack containing 2 g of Florisil and 2 g sodium sulfate per 50 mL of extract and pushing the extract through this filter stack using a glass syringe.⁶

13.3 Measurement:

13.3.1 Measure and record the infrared absorbance of the extract in a manner identical to that used for the calibration standards. If the concentration of total petroleum hydrocarbons

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

14. Calculation of Results

14.1 Determine the concentration of total petroleum hydrocarbons (TPH) in the extract using the linear calibration graph (12.4.5), or as directed by the infrared laser spectrometer manufacturer.

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

$$\text{total petroleum hydrocarbons mg/L} = \frac{R \times D}{E} \quad (4)$$

R = measured concentration of total petroleum hydrocarbons in mg/L in treated extract

D = dilution factor, if any, as utilized in 13.3

D = volume of diluted extract/volume of undiluted extract

E = enrichment factor due to the preformed solvent extraction

E = V /volume of solvent used in mL

V = volume of extracted water found in 10.2. A sample density of 1g/mL is assumed.

14.3 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 formula:

$$\text{total petroleum hydrocarbons mg/L} = c_{oil} \times f \quad (5)$$

where:

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

f = correction factor calculated according to Eq 2.

15. Precision and Bias

15.1 A single laboratory validation study was carried out. Tetradecane standards were prepared as described in 12 and every standard analyzed in triplicate. Table 1 summarizes the obtained results. The reproducibility of this test method is being determined by an interlaboratory study and will be available before 2016.

15.2 Within the single laboratory validation study two types of water matrixes namely reagent water (Guide D1192, Type 2)

TABLE 1 Single laboratory study Calibration with tetradecane

Calibration Standard	mg/L (TD in CH) ^A	mg/L (TD in water) ^A	1st det. [A.U.]	2nd det. [A.U.]	3rd det. [A.U.]	Mean value	Rel. std. dev. (%)
A	9	0.5	0.90	0.78	0.85	0.84	7.15
B	18	1	1.46	1.52	1.43	1.47	3.12
C	90	5	4.51	4.28	4.34	4.38	2.66
D	180	10	8.16	7.80	7.97	7.98	2.26
E	900	50	36.82	36.03	34.45	36.43	1.08
F	1800	100	72.02	71.23	71.67	71.64	0.55
G	9000	500	360.45	362.15	361.12	361.24	0.24
S	18000	1000	739.12	793.63	740.80	739.85	0.12

^A Example of a calibration obtained for tetradecane (TD) in cyclohexane (CH) according to this test method. Due to enrichment during extraction 18 times higher concentration are found in cyclohexane than in water.

TABLE 2 Single laboratory study Samples in ocean substitute water (OSW)

mg/L oil added to OSW	type of target oil	1 det. mg/L	2 det. mg/L	3 det. mg/L	4 det. mg/L	5 det. mg/L	6 det. mg/L	7 det. mg/L	Mean Value mg/L	Rel. Std. Dev. %	Recovery %
0	none	0.03	-0.15	0.33	-0.09	-0.11	0	-0.01	0	0.16 ^A	-
5	BAM	5.97	8.15	6.8	7.44	7.49	7.54	7.31	7.24	9.47	144.8
5	A-oil	4.44	4.95	3.54	5.2	4.7	4.59	5.3	4.67	12.6	93.4
5	P-oil	5.84	5.5	5.14	4.3	4.63	4.35	4.35	4.87	12.86	97.4
10	BAM	12.96	13.77	12.48	13.61	13.04	12.94	13.62	13.2	3.59	132
10	A-oil	9.11	8.68	8.76	9.46	9.31	9.62	8.93	9.12	9.91	91.2
10	P-oil	9.09	9.04	8.45	9.6	8.88	9.33	9.14	9.07	3.94	90.7
50	BAM	65.27	65.79	64.94	64.54	65.31	65.57	65.6	65.29	0.66	130.6
50	A-oil	46.92	46.61	47.3	49.31	47.55	46.41	48.89	47.57	2.35	95.14
50	P-oil	49.32	49.98	49.63	51.14	50.7	48.95	53.36	50.44	2.97	100.9

^A Due to a mean equal to zero this value is the standard deviation not the relative standard deviation.

Recoveries obtained with this test method when spiking ocean substitute water (Practice D1141) with different types of petroleum hydrocarbons (crude oils).

OSW = ocean substitute water.

BAM = BAM K010 (used as calibration material substance by ISO9377-2): 1:1 mixture of Diesel (mineral oil type A) and Lubrication Oil (mineral oil type B)

A-oil = Crude Oil, asphaltic-base type

P-oil = Crude Oil, paraffin-base type.

Planned reporting range = 0.5 – 1000 mg/L.

TABLE 3 Single laboratory study Samples in reagent water

mg/L oil added to reagent water	type of target oil	1 det. mg/L	2 det. mg/L	3 det. mg/L	4 det. mg/L	Mean Value mg/L	Rel. Std. Dev %	Recovery %
0	none	-0.06	0.14	-0.02	-0.06	0	0.1 ^A	-
10	BAM	13.59	13.25	12.82	13.11	13.19	2.41	131.9

^A Due to a mean equal to zero this value is the standard deviation not the relative standard deviation.

and ocean substitute water (Practice D1141) were used. Analysis of three different types of petroleum hydrocarbons, present in these waters was investigated. For this purpose these types of petroleum hydrocarbons were spiked into the different water matrixes at three different concentration levels. Table 2 and Table 3 summarize the obtained results and demonstrate the

capability of this test method for measuring total petroleum hydrocarbons in water and waste water.

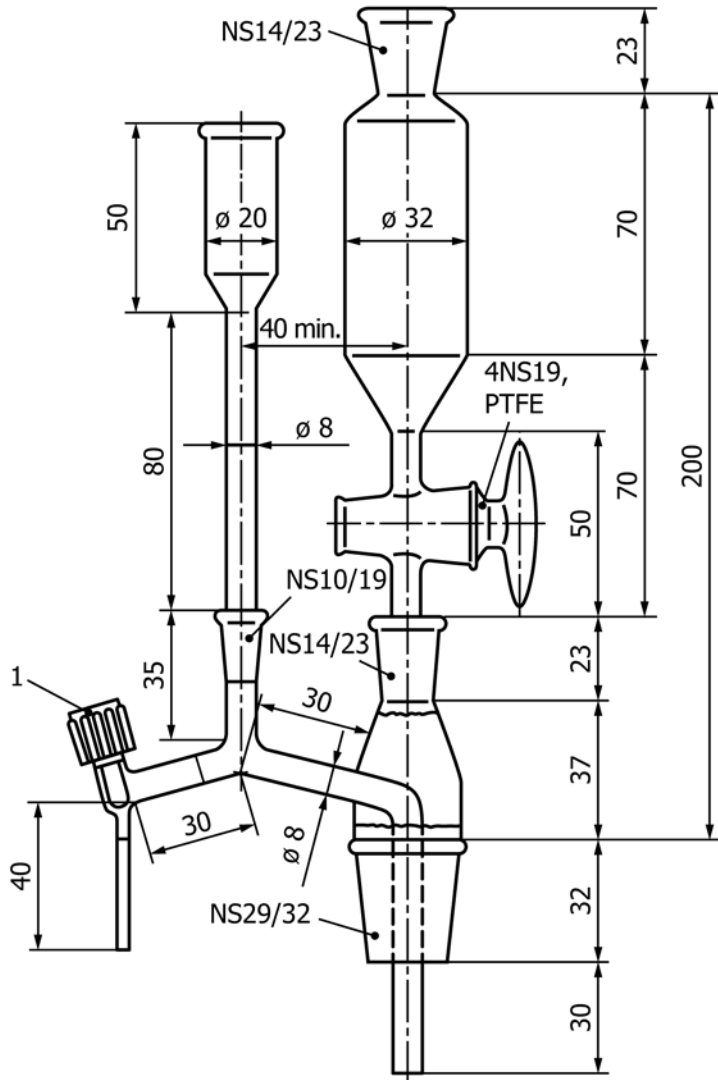
16. Keywords

16.1 total petroleum hydrocarbons (TPH); oil

APPENDIX

(Nonmandatory Information)

X1. APPENDIX

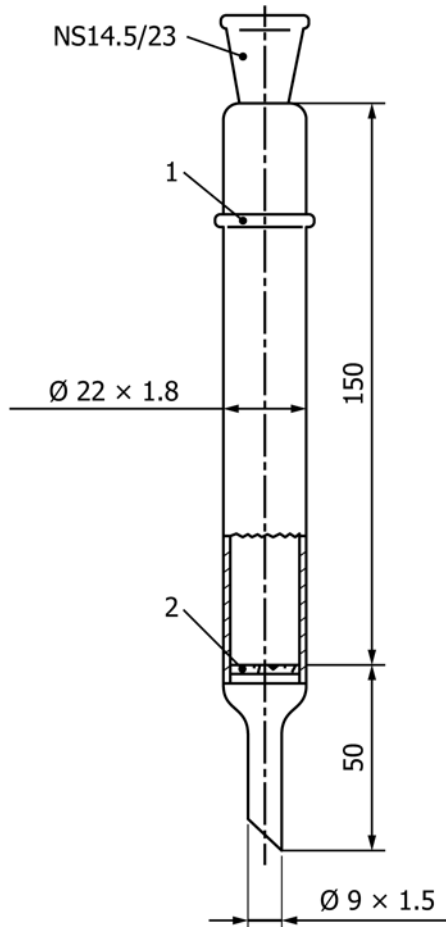


Dimensions in mm

Key

1 Spindle stopcock, PTFE

FIG. X1.1 Example of a micro-separator



Dimensions in mm

Key

- 1 Glass bulb
- 2 Fritted glass filter

FIG. X1.2 Example of a clean-up column

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/