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An American National Standard

Standard Test Method for dimer/trimer of chlorotrifluoroethylene (S-316) Recoverable Oil and Grease and Nonpolar Material by Infrared Determination[1]

This standard is issued under the fixed designation D7066; 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 oil and grease and nonpolar material in water and wastewater by an infrared (IR) determination of dimer/trimer of chlorotrifluoroethylene (S-316) extractable substances from an acidified sample. Included in this estimation of oil and grease are any other compounds soluble in the solvent.

1.2 The method is applicable to measurement of the light fuel although loss of some light ends during extraction can be expected.

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 at 2930 cm-[1] or 3.4 microns. Similarly, this test method defines nonpolar material in water and wastewater as that oil and grease which is not adsorbed by silica gel in the test method and measured by IR absorption at 2930 cm-[1].

1.4 This method covers the range of 5 to 100 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 problems, 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* (D3856 Guide for Good Laboratory Practices)*the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D3370 Practices for Sampling Water from Closed Conduits
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E168 Practices for General Techniques of Infrared Quantitative Analysis
E178 Practice for Dealing With Outlying Observations

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 *oil and grease*—the organic matter extracted from water or wastewater and measured by this test method.

3.2.2 *nonpolar material*—the oil and grease remaining in solution after contact with silica gel and measured by this test method.

3.2.3 *solvent*—dimer/trimer of chlorotrifluoroethylene (S-316)

4. Summary of Test Method

4.1 An acidified 250-mL sample of water or wastewater is extracted serially with three 15-mL volumes of dimer/trimer of

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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

chlorotrifluoroethylene (S-316). The extract is diluted to 50mL and a portion is examined by infrared spectroscopy (IR) for an oil and grease measurement.[3] A portion of the extract is contacted with silica gel to remove polar substances, thereby producing a solution containing nonpolar material. The nonpolar material is measured by infrared spectroscopy.

5. Significance and Use

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

5.2 Regulations and standards have been established that require monitoring of oil and grease in water and wastewater.

6. Interferences

6.1 Soaps, detergents, surfactants and other materials may form emulsions that may reduce the amount of oil and grease extracted from a sample. This test method contains procedures that can assist the analyst in breaking such emulsions.

6.2 Organic compounds and other materials not considered as oil and grease on the basis of chemical structure may be extracted and measured as oil and grease. Of those measured, certain ones may be adsorbed by silica gel while others may not. Those not adsorbed are measured as nonpolar material.

7. Apparatus

All glassware that will come in contact with the sample must be rinsed with dimer/trimer of chlorotrifluoroethylene (S-316) prior to beginning this procedure.

7.1 *Cell(s),* quartz, 10-mm path length (lower concentrations may require a longer pathlength), two required for double-beam operation, one required for single-beam operation, or built-in or drop-in cell for infrared filtometer analyzer operation.

7.2 *Filter Paper,* ashless, quantitative, general-purpose, 11-cm, Whatman #40 or equivalent.

7.3 *Glass Funnel.*

7.4 *Glass Wide Mouth Sample Bottle,* minimum 250-mL, with screw cap having a fluoropolymer liner.

7.5 *Glass Graduated Cylinder,* 100-mL

7.6 *Infrared Spectrometer,* double-beam dispersive, single-beam dispersive, Fourier transform, filtometers or other capable of making measurements at 2930 cm^{-1}.

7.7 *Magnetic Stirrer,* with small TFE-fluorocarbon stirring bar.

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

7.9 *Volumetric Flasks,* glass, various (10, 25, 50, 100, and 200-mL).

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

7.11 *Repeating pipetter,* glass, 15-mL, (optional).

7.12 *Volumetric Pipettes,* glass, various (0.50, 1.00, 5.00, 10.0 and 25.0-mL, including a 1.00 serological pipet graduated in 0.01-mL increments and a 5.00-mL serological pipet graduated in 0.1-mL increments, or equivalent).

7.13 *Benchtop shaker,* (optional).

7.14 *Glass Stirring Rod,* (optional).

7.15 *Analytical Balance.*

7.16 *Syringes,* 50 and 500 mL.

8. Reagents

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 *Isooctane (2,2,4-trimethylpentane)* 98 % minimum purity, for use in calibration.

8.4 *Octanoic Acid* 98 % minimum purity, for use in calibration.

8.5 *Silica Gel,* Anhydrous, 75 - 150 micrometers, Davisil Grade 923 (Supelco 21447-7A, or equivalent). Dry at 200–250°C for 24 hour minimum and store in a desiccator or tightly sealed container. Determine the dimer/trimer of chlorotrifluoroethylene (S-316) soluble material content of the silica gel by extracting 10 g of silica gel with 25 mL of dimer/trimer of chlorotrifluoroethylene (S-316) and collect the elute in a flask. Filter and fill a quartz cell for analysis by IR. The dimer/trimer of chlorotrifluoroethylene (S-316) soluble material must be less than 5 mg/L.

8.6 *Sodium Sulfate* (Na_2SO_4), ACS, granular anhydrous. Dry at 200-250 °C for 24 hours minimum and store in a tightly sealed container until use. (Note: Powdered sodium sulfate should not be used because water may cause it to solidify.)

8.7 Solvent - *dimer/trimer of chlorotrifluoroethylene* , IR spectroscopy grade, for example S-316 manufactured by Horiba Instruments, Irvine CA, 800-446-7422 (ASTM does not advocate the use of one vendor over another)

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 the addition (optional HCl replacement).

8.9 *Hydrochloric acid,* ACS, 1 + 1. Mix equal volumes of concentrated HCl and water

8.10 *Sodium Chloride (NaCl), crystalline, ACS*—or use in breaking emulsions, if needed. Wet thoroughly with solvent before using.

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

9. Sampling

9.1 Collect the sample in accordance with the principles described in Practices D3370, using a glass bottle equipped with a screw cap having a fluoropolymer liner. 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. Fill bottle with minimal headspace to prevent loss of volatile constituants. Do not allow the sample to overflow 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.

9.2 A sample of about 250mL is required for this test. Use the entire sample because removing a portion would not apportion the oil and grease that adheres to the bottle surfaces. The high probability that extractable matter may adhere to sampling equipment and result in measurements that are biased low precludes the collection of composite samples for determination of oil and grease. 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 four individual 63-mL samples over the course of a day. In the laboratory, pour each 63-mL sample into the separatory funnel, rinse each of the four bottles (and caps) sequentially with 10mL of solvent, and use the solvent for the extraction (Section 12.2.2). Do not exceed 50 mL of total solvent during the extraction and rinse procedure.

9.3 Preserve the sample with a sufficient quantity of either sulfuric (see Section 8.8) or hydrochloric acid (see Section 8.9) to a pH of 2 or lower and refrigerate at 0-4°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. To more accurately calculate the final oil concentration of the extract, the volume of acid added to each sample can be recorded, then subtracted from the final measured sample volume.

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 1.96 if HCl is used and 1.15 if H_2SO_4 is used (see 49 CFR part 172). Collect an additional 1 or 2 sample aliquots for the matrix spike and matrix spike duplicate (Section 14.5) and preserve with acid.

9.4 Refrigerate the sample at <4°C from the time of collection until extraction. Freezing the sample may break the bottle.

10. Preparation of Calibration and Spiking Solutions

NOTE 1—The calibration standard specified in this procedure reflects the objective of the test to detect recoverable oil and grease and nonpolar material in wastewater with an unknown composition of oil and grease. In a few cases, the composition of the oil and grease in a sample will be known. However, in order to obtain consistent results between sample sets and between laboratories with different wastewater matrices, calibration with the known oil and grease in a sample should not be used in this method.

10.1 *Calibration and Solvent Mixtures:*

NOTE 2—The calibration procedure below calls for transferring, by pipette or syringe, a volume of standard into a volumetric flask to obtain a desired concentration. Transfer volumes have been rounded for ease of measurement and calculation. It is highly recommended that calibration standards be prepared on a weight basis (that is, pipette a volume into a tared flask and weigh the amount pipetted), then converted to mg/mL by using the densities of octanoic acid (0.9100 g/mL) and isooctane (0.6920 g/mL). A solution containing equal volumes of isooctane and octanoic acid will have a density of 0.801 g/mL.To assure the most accurate concentrations, use the smallest serological pipet or syringe for measurements. The volume should always be greater than ½ the volume of the pipet or syringe.

Ideally, a linear calibration curve will be obtained from these standards. As discussed in Section 11, the concentrations of these standards can be adjusted to stay within the linear range of the IR instrument.

10.1.1 *Calibration Stock Solution*—Place 0.55 mL of octanoic acid and 0.72 mL of isooctane in a 10-mL volumetric flask and fill to the mark with solvent. Mix well. The resulting concentration is 50 mg/mL each octanoic acid and isooctane (100 mg/mL total oil and grease). This solution will be termed "Stock Solution".

10.1.2 *Diluted Stock Solution*—Place 2.5 mL of the Stock Solution to a 50-mL volumetric flask and fill to mark with solvent. Diluted Stock Solution = 5.0 mg/mL (5000 µg/mL).

10.1.3 *Calibration Solution A*—Place 1.0 mL of Diluted Stock Solution in a 10-mL volumetric flask and fill to the mark with solvent. Calibration Solution A = 0.5 mg/mL (500 µg/mL), equivalent to 100 mg/L oil and grease in a 250-mL water sample extracted into a 50-mL volume of solvent.

10.1.4 *Calibration Solution B*—Place 0.50 mL of Diluted Stock Solution in a 10-mL volumetric flask and fill to the mark with solvent. Calibration Solution B = 0.25 mg/mL (250 µg/mL), equivalent to 50 mg/L oil and grease in a 250-mL water sample extracted into a 50-mL volume of solvent.

10.1.5 *Calibration Solution C*—Place 0.20 mL of Diluted Stock Solution in a 10-mL volumetric flask and fill to the mark with solvent. Calibration Solution C = 0.1 mg/mL (100 µg/mL), equivalent to 20 mg/L of oil and grease in a 250-mL water sample extracted into a 50-mL solvent volume.

10.1.6 *Calibration Solution D*—Place 0.10 mL of Diluted Stock Solution in a 10-mL volumetric flask and fill to the mark with solvent. Calibration Solution D = 0.050 mg/mL (50 µg/mL), equivalent to 10 mg/L of oil and grease in a 250-mL water sample extracted into a 50-mL solvent volume.

10.1.7 *Calibration Solution E*—Place 0.05 mL of Diluted Stock Solution in a 10-mL volumetric flask and fill to the mark with solvent. Calibration Solution E = 0.025 mg/mL (25 µg/mL), equivalent to 5 mg/L of oil and grease in a 250-mL water sample extracted into a 50-mL solvent volume.

10.2 *Spiking Solution:*

10.2.1 Transfer equal volumes of octanoic acid and isooctane in a volumetric flask, beaker, or jar. Mix well.

10.2.2 Pour 220 to 250 mL of water into a sample bottle. Record the volume.

10.2.3 Using a syringe, dispense 15 µL of the octanoic acid/isooctane solution under the surface of the water. Cap the bottle and shake well.

10.2.4 Calculate the total oil and grease concentration by dividing 12.0 mg (mass of 15 µL for solution density of 0.801 g/mL assuming no loss of volume due to mixing) by the water volume in liters (0.220 to 0.250 L).

10.2.5 Calculate the isooctane concentration by dividing 5.80 mg (mass of 7.5 µL of isooctane) by the water volume in liters.

10.2.6 Calculate the octanoic acid concentration by dividing 6.83 mg (mass of 7.5 µL of octanoic acid) by the water volume in liters.

10.2.7 If necessary, this solution can be made more or less concentrated to suit the concentration needed for the matrix spike. A fresh spiking solution should be prepared weekly or bi-weekly.

11. Calibration

NOTE 3—The cell(s) used for calibration must be initially thoroughly cleaned with solvent and dried prior to beginning the calibration procedure. To reduce the solvent expense, it may be prudent to use methylene chloride or a solvent other than the solvent used for extraction. However, all traces of methylene chloride or other solvent must be removed so that they do not compromise the measurement. Baking the cell at an elevated temperature to remove all traces of solvent is recommended. Cool cell to room temperature before use.

The same cell or matched cells should be used throughout the calibration. 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 to prevent chemical reaction of solvent fumes with components of the instrument. For double-beam operation, either block the light beam from the reference cell containing solvent or remove the reference cell from the instrument during the intervals between scans in order to protect the solvent from unnecessary warming. However, place the reference cell in the reference beam during all scans. Rely upon recommendations of the manufacturer for single-beam and infrared filtometer analyzers because variations in design make it impractical to offer instructions for their use with this method. Also, in relation to infrared filtometer operation, reference to scanning or running, or both, should be interpreted to mean obtaining a reading or a plot at 2930-cm^{-1} or 3.4 microns.

In the procedure below, the IR instrument is calibrated from 0.025 to 0.5 mg/mL (25 to 500 µg/mL), equivalent to 5 to 100 mg/L of oil and grease in water, assuming a 250-mL sample extracted into 50 mL of solvent. If the IR instrument cannot be calibrated to 0.5 mg/mL (500 µg/mL), calibrate to a lesser range, but always use 5 calibration points if the IR instrument allows it. Ideally, the calibration curve obtained will be linear (refer to Section 11.11). If linearity cannot be achieved past a certain concentration, consider that concentration the upper bounds of the calibration and adjust the calibration standards accordingly. If a sample is encountered that exceeds the calibration range, dilute the sample extract to bring the concentration into the calibration range.

11.1 The calibration contains a minimum of 5 nonzero points and a solvent blank (Section 11.2).

11.2 For double-beam operation, fill the reference cell and the sample cell with solvent and scan from 3200 cm^{-1} (3.13 microns) to 2700 cm^{-1} (3.70 microns). A nearly horizontal, straight line should be obtained. If not, check cells for cleanliness, matching, etc. Drain and clean the sample cell. For single-beam and infrared filtometer analyzers, obtain spectral data for the solvent at this time. After running, drain, and clean the sample cell.

11.3 Fill the sample cell with Calibration Solution E. Scan as in 11.2; drain, and clean the sample cell.

11.4 Fill the sample cell with Calibration Solution D. Scan as in 11.2; drain, and clean the sample cell.

11.5 Fill the sample cell with Calibration Solution C. Scan as in 11.2; drain, and clean the sample cell.

11.6 Fill the sample cell with Calibration Solution B. Scan as in 11.2; drain, and clean the sample cell.

11.7 Fill the sample cell with Calibration Solution A. Scan as in 11.2; drain, and clean the sample cell.

11.8 For each double-beam spectrum obtained in 11.3 – 11.7, draw a baseline. Obtain the net absorbance for the peak that occurs near 2930 cm^{-1} (3.41 microns). Obtain net values for single-beam and infrared filtometer analyzer runs as recommended by IR manufacturer.

NOTE 4—For infrared instruments having computer capability, data may be obtained automatically or as described in 11.9. However, all data must be obtained consistently by one means or the other, not a combination of the two.

11.9 For each point, subtract the response of the reference blank (Section 11.2) from the response for the standard. Calculate the calibration factor (CF_x) in each of the five standards using the reference-blank-subtracted response and the following equation:

$$CF_x = (H_x - H_{RB})/C_x \quad (1)$$

where:

CF_x = calibration factor,
H_x = response of standard,
H_{RB} = response of reference blank, and
C_x = concentration of standard.

11.10 Calculate the mean calibration factor (CF_m), the standard deviation of the calibration factor (SD), and the relative standard deviation (RSD) of the calibration factor,

$$RSD = 100 \times SD/CF_m \quad (2)$$

where:

RSD = relative standard deviation of calibration factor,
SD = standard deviation of calibration factor, and
CF_m = average of calibration factors (CF_x).

11.11 If RSD ≤ 15 %, linearity through the origin can be assumed and CF_m may be used for calculations. If RSD > 15 %, a calibration curve must be used or the calibration standards must be adjusted to bound the linear range (see Section 11 note). Either the average calibration factor (CF_m) or the calibration curve is used, not both. Verification is done on the chosen calibration.

11.12 Verify calibration after each 10 analyses using calibration solution C or D, or alternating the calibration solutions. Calibration is verified if CF_X is within ±15 % of CF_m or its respective point on the calibration curve.

11.13 If calibration is not verified, prepare a fresh calibration solution and repeat the calibration verification test (Section 11.12). If calibration is not verified with the fresh calibration standard, recalibrate and reanalyze all extracts of all samples analyzed since the last calibration or verification, whichever is most recent.

12. Procedure

12.1 *Sample Pretreatment:*

12.1.1 Bring the sample and QC (that is, MS/MSD) aliquots to room temperature.

12.1.2 Either mark the sample bottle at the water meniscus or weigh the bottle for later determination of the sample volume. Weighing will be more accurate.

12.2 *Extraction:*

12.2.1 Transfer the sample from the sample bottle to a clean separatory funnel via a clean transfer funnel.

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

NOTE 5—Use of the sodium sulfate is necessary to prevent water from interfering in the determination. Because the sample is extracted three times, it is not necessary to remove all of the solvent from the separatory funnel; it is better to preclude water from reaching the sodium sulfate. If the sodium sulfate cakes when contacted with the extract, flush once with 2 mL of solvent into the 50-mL volumetric flask. Remove the solid with a clean spatula, and add about 1 g of fresh sodium sulfate to the filter. Rewet sodium sulfate with solvent before use.

12.2.3 Add 15 mL of solvent to the sample bottle. Cap with the original cap and shake the sample bottle to rinse all interior surfaces. Pour the solvent into the separatory funnel, rinsing down the sides of the transfer funnel.

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

12.2.5 Allow the phases to separate.

12.2.6 Drain the solvent (lower) layer from the separatory funnel through the sodium sulfate into a pre-cleaned 50-mL volumetric flask.

NOTE 6—Certain types of samples, such as those containing a large amount of detergent, may form an emulsion during the extraction. If emulsion forms between the phases and the emulsion is greater than one-third the volume of the solvent layer, the laboratory should employ emulsion-breaking techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, use of solvent phase separation paper, centrifugation, use of an ultrasonic bath with ice, addition of NaCl, increasing the temperature, lowering the pH, or other physical methods. Alternatively, solid-phase extraction (SPE), continuous liquid-liquid extraction, or other extraction techniques may be used to prevent emulsion formation. If such an emulsion cannot be broken by any attempted means, the test method is not applicable to the problem sample. Do not attempt to proceed since accurate, quantitative results for the test are not obtainable.

12.2.7 Repeat the extraction (Section 12.2.2 – 12.2.6) twice more with 15-mL portions of solvent. Rinse the tip of the separatory funnel, Na_2SO_4, filter paper, and filter funnel with a small (approximately 1-mL) portion of solvent and collect in the volumetric flask

NOTE 7—A milky extract indicates the presence of water. If the extract is milky, remove the Na_2SO_4 cake (Section 11.2.5), add approximately 1 g of fresh Na_2SO_4 to the filter funnel, and pass the extract through the Na_2SO_4 into a precleaned 50-mL volumetric flask.

12.2.8 Bring the solvent extract volume to 50 mL with solvent.

12.2.9 To verify the pH is correct, dip pH paper into the separatory funnel. Record the value.

12.2.10 Fill the sample bottle to the mark with water and determine the sample volume, or weigh the empty sample bottle and cap and determine the sample volume by difference, assuming a sample density of 1.00 g/mL. Alternatively, the actual sample density can be determined by weighing 100 mL of the sample water in a tared 100-mL flask. Subtract the volume of acid added to the sample, as recorded in 9.3.

12.3 *First Infrared Absorbance Measurement*—Measure and record the infrared absorbance of the extract in a manner identical to that used for the calibration standards. If the concentration of oil and grease exceeds the calibration range, dilute extract to bring sample within calibration range. Keep a record of each dilution for determination of the concentration in the sample in 13.2.

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

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

NOTE 8—The amount of silica gel needed has been estimated at 3 g for every 100 mg of polar material. However, this amount may be insufficient for some samples. If there is doubt about whether the amount of silica gel is adequate, the amount needed should be determined by test.

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

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

13. Calculation

13.1 Determine the concentration of oil and grease and/or nonpolar material in the extract (C_e) using the average calibration factor (CF_m), the calibration curve (Section 11.11), or as directed by the IR analyzer manufacturer.

13.2 Calculate the concentration of oil and grease or nonpolar material (C_s), or both, in the water sample as follows:

$$C_s = C_e \times D \times E/V \quad (3)$$

where:

C_s = concentration in the water sample in mg/L,
C_e = concentration in the extract in mg/mL,

D = dilution factor of extract from Sections 12.3 or 12.4, or both,
E = extract volume in mL, and
V = sample volume in L.

14. Quality Control (QC)

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

14.1 *Calibration and Calibration Verification*—See Section 11 of this test method for the calibration procedure and Sections 11.11 and 11.12 for the QC acceptance criteria for calibration and calibration verification.

14.2 *Initial Demonstration of Laboratory Capability*—If a laboratory has not performed the test before or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

14.2.1 Analyze seven replicates of a standard solution prepared from an aqueous independent reference material (IRM) containing 50 mg/L of oil and grease and/or nonpolar material. Spiking solution (10.2) may be used if it is from a separate batch than that used for calibration. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Be sure to record the concentration added to each replicate. This concentration is the "true value" used in the below calculation. 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.

14.2.2 Calculate the mean, standard deviation, relative precision, bias, and % recovery of the seven values using the below equations:

$$Relative\ Precision = 100*(\ std\ dev/mean) \quad (4)$$

$$Bias = 100*(mean - true\ value)/true\ value$$

$$\%\ Recovery = 100 + bias$$

The seven replicates must have an average % recovery of oil and grease in the range of 59 % - 100 % with a relative precision no grater than 8 %. If the relative precision and average percent recovery are outside of theses limits, the initial demonstration should be repeated.

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

14.3 *Laboratory Control Sample (LCS)*—To insure that the test method is in control, analyze an LCS containing 50 mg/L of oil and grease and/or nonpolar material for each batch of 20 samples. The LCS can be the standard spiking solution (10.2) adjusted for the midrange of analysis but it must be made independently from the standard spiking solution. Commercial verified standards are also acceptable. Be sure to record the concentration added to the LCS. This concentration is the "true value" used in the below calculation. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. Calculate the percent recovery of the LCS using the following equation:

$$\%\ recovery = 100 + [100*(concentration\ of\ LCS - true\ value)/true\ value] \quad (5)$$

The LCS shall have a percent recovery of oil and grease in the range of 59 % - 100 %.

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.

14.4 *Method Blank (Blank)*—Analyze a reagent water test blank with each batch. The test blank must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The concentration of oil and grease and/or nonpolar material found in the Blank must be less than 5 mg/L or 1/10 the concentration (which ever is lower) in the sample under test. If the concentration of oil and grease and/or nonpolar material 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.

14.5 *Matrix Spike (MS)*—To check for interferences in the specific matrix being tested, perform an MS on at least one sample from each batch of 20 samples. Spike an aliquot of the sample with a known concentration of oil and grease and/or nonpolar (Spiking solution, 10.2 may be used) and take it through the analytical method including preservation and pretreatment. Be sure to record the concentration of oil and grease and non-polar material added.

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

14.5.2 Calculate the percent recovery of both oil and grease (POG) and non-polar material (PNP) by using the appropriate values in the below formula.

$$P_{OG} = 100\,[(A_{OG}\ \ (V_s + V)) - B_{OG}V_s]/COGVs \quad (6)$$

where:

A_{OG} = concentration of oil and grease found in spiked sample,
B_{OG} = concentration of oil and grease found in unspiked sample,
C_{OG} = concentration of oil and grease analyte in spiking solution ,
P_{OG} = percent recovery of oil and grease of matrix spike,
V_s = volume of sample used, and
V = volume of spiking solution added.

$$P_{NP} = 100\,[(A_{NP}\ \ (V_s + V)\ -\ B_{NP}\,V_s]/C_{NP}V_s \quad (7)$$

where:

A_{NP} = concentration of non-polar material found in spiked sample,
B_{NP} = concentration of non-polar material found in unspiked sample,
C_{NP} = concentration of non-polar material analyte in spiking solution,
P_{NP} = percent recovery of non-polar material of matrix spike,
V_s = volume of sample used, and
V = volume of spiking solution added.

14.5.3 The percent recovery of the matrix spike sample shall be between 67 % and 100 % for oil and grease and between 35.5 % and 100 % for non-polar material.

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: (*1*) the matrix interference must be removed, (*2*) all samples in the batch must be analyzed by a test method not affected by the matrix interference, or (*3*) the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.6 *Duplicate:*

14.6.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

14.6.2 Calculate the Relative Percent Difference (RPD) between the matrix spike and matrix spike duplicate concentration using the below equation. The RPD shall be 8 % or less for oil and grease and 17 % or less for non-polar material:

$$RPD = 100^{*}(conc\ of\ MS - conc\ of\ MSD)/conc\ of\ MS \quad (8)$$

14.6.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.7 *Independent Reference Material (IRM)*—In order to verify the quantitative value produced by the test method, analyze an IRM submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the reference material should be in the range of 5 to 100 mg/L. The value obtained must fall within the control limits specified by the outside source. The spiking solution may be used as an IRM.

15. Precision and Bias[4]

15.1 The precision and bias data for this test method are based on an interlaboratory validation study.

15.2 The test design of the study meets the requirements of Practice D2777 for the analytes listed in this test method with one exception. Due to the cost of performing the analysis, each matrix tested contained only one set of Youden pair concentrations. In accordance with Section 1.5 of D2777, an exemption from the requirement for using three Youden pairs within each matrix was granted by the Technical Operations Committee of D19 on the recommendation of the Results Advisor in order to enable evaluation of the method based on more than one matrix. The exemption specified that a single Youden pair be used for each matrix and that the range of concentrations represented by all three Youden pairs thus formed cover the range of the test method.

15.3 The true values of the oil and grease concentrations were determined using Freon-113 as a solvent, then diluted to create the Youden pairs. Due to the nature of the sample preparation, the exact true values may vary from those reported, therefore the bias data presented here are “best estimates.” In this case, the average recovery of the matrix spike and matrix spike duplicate samples are a better estimate of matrix interference than bias.

15.4 All calculated statistical parameters are presented in Table 1. It is the user’s responsibility to ensure the validity of precision and bias outside of the interlaboratory validation study ranges and matrixes.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1176. Contact ASTM Customer Service at service@astm.org.

TABLE 1 Statistical Results of Interlaboratory Validation Study – S-316 Solvent

Analyte	Oil and Grease						Non-Polar Material					
Matrix	Site 1 – Can Producer		Site 2 – Meat Processor, Clarifier Effluent		Site 3 – Oil Reprocessor		Site 1 – Can Producer		Site 2 – Meat Processor, Clarifier Effluent		Site 3 – Oil Reprocessor	
True Value (mg/L)	55	40	5	7	350	470	55	40	5	7	350	470
No. Participating Labs	9	9	9	9	9	9	9	9	9	9	9	9
No. Labs Reported[A]	8	8	8	8	8	8	7	7	7	7	7	7
No. Values Retained	7	7	7	7	6[B]	6[B]	7	7	7	7	6[B]	6[B]
Mean (mg/L)	30.5	21.2	6.6	6.4	429.9	551.2	11.2	8.4	4.4	2.9	314.4	454.5
Overall Std Dev (mg/L)	14.4	10.6	4.4	3.2	159.8	136.4	3.9	4.3	4.56	2.5	93.0	124.7
Precision (%)	47.1	49.9	66.3	50.3	37.2	24.7	34.3	51.1	105.5	85.9	29.6	27.4
Bias (%)	–44.6	–47.0	32.7	–8.9	22.8	17.3	NA	NA	NA	NA	NA	NA
Single Operator Std Dev (mg/L)	3.7		2.6		69.7		1.1		2.7		73.4	
Avg Recovery of MS and MSD (%)	NA	72.4	NA	67.0	NA	79.2	NA	42.4	NA	70.3	NA	70.3
Relative % Difference of MS and MSD (%)	NA	8.26	NA	7.82	NA	4.74	NA	14.19	NA	17.4	NA	12.40

[A]One laboratory failed the initial demonstration of laboratory capability, and thus is not considered to have returned valid results for any of the samples. One laboratory disposed of its samples before performing the non-polar analysis.
[B]Values obtained for Site 3 samples from one lab were extraordinarily high - over twice the known concentration - in contrast to those from other labs, which generally were lower than the true concentration. Application of the single outlier procedure in Section 4 of ASTM Practice E178, "Standard Practice for Dealing With Outlying Observations," indicates that these results would be considered single outliers at a significance level of less than 0.5 %.

APPENDIX

(Nonmandatory Information)

X1. PRECISION AND BIAS

X1.1 The statistical parameters presented in Table X1.1 were derived from the interlaboratory method validation study, but did not meet the requirements of 7.2.3 of Practice D2777. The interlaboratory method validation study was designed to evaluate the performance of two solvents—dimer/trimer of chlorotrifluoroethylene (S-316) and dichloropentafluoropropane (AK-225) manufactured by AGC (www.ak-225.com). Several labs reported problems calibrating or detecting low levels of oil and grease using AK-225. Other labs used AK-225 with no issues, indicating the use of AK-225 is dependent on the type and model of IR instrument used. The data presented here is for reference or information only and may be useful if another interlaboratory method validation study is performed.

TABLE X1.1 Statistical Results of Interlaboratory Validation Study – AK-225

Analyte	Oil and Grease						Non-Polar Material					
Matrix	Site 1 – Can Producer		Site 2 – Meat Processor, Clarifier Effluent		Site 3 – Oil Reprocessor		Site 1 – Can Producer		Site 2 – Meat Processor, Clarifier Effluent		Site 3 – Oil Reprocessor	
True Value (mg/L)	55	40	5	7	350	470	55	40	5	7	350	470
No. Participating Labs	9	9	9	9	9	9	9	9	9	9	9	9
No. Labs Reported[A]	7	6	7	7	7	6	7	6	7	7	5	5
No. Values Retained[B]	6	5	6	6	6	4[C]	6	5	6	6	5	4[C]
Mean (mg/L)	33.5	22.6	12.6	12.4	458	629	19.5	13.2	5.0	3.6	333	375
Overall Std Dev (mg/L)	12.8	12.3	5.7	3.9	114	28.0	5.9	4.1	6.4	3.8	148	202
Precision (%)	38.2	54.5	45.3	31.4	24,9	4.4	30.4	31.0	130	104	44.5	53.9
Bias (%)	–39.1	–43.6	151	77.1	30.7	33.8	NA	NA	NA	NA	NA	NA
Single Operator Std Dev (mg/L)	6.0		3.7		99.2		2.1		2.3		76.4	
Avg Recovery of MS and MSD (%)	NA	72.4	NA	78.8	NA	87.4	NA	47.6	NA	29.4	NA	76.1
Relative % Difference of MS an MSD (%)	NA	16.5	NA	17.7	NA	54.2	NA	27.8	NA	192	NA	21.9

[A]Two laboratories failed the initial demonstration of laboratory capability, and thus are not considered to have returned valid results for any of the samples.
[B]One laboratory reported non-detects for 10 of the 12 samples; all data from this laboratory are subsequently excluded, even though their 2 detected values (for oil & grease at Site 3) did appear reasonable.
[C]One laboratory reported a result of 1832 for oil and grease, nearly 3 times the mean recovery among the other laboratories, and a value of zero for non-polar material, which are highly suspect results. Application of the single outlier procedure in Section 4 of ASTM Practice E178, "Standard Practice for Dealing With Outlying Observations," indicates that these results would be considered single outliers at a significance level of less than 0.1 %.