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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.

ε[1] NOTE—Added research report reference to Section 15 editorially in March 2008.

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 *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[2]) *the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D3370 Practices for Sampling Water from Closed Conduits
D3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and 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 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.

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

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

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

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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.

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

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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.

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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 (i.e. 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
C_x = concentration of standard

11.10 Calculate the mean calibration factor (CFm), 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
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 (i.e., MS/MSD) aliquots to room temperature.

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