



# Standard Test Method for Oil and Grease (Fluorocarbon Extractable Substances) by Gravimetric Determination <sup>1</sup>

This standard is issued under the fixed designation D 4281; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## INTRODUCTION

In the determination of oil and grease, an absolute quantity of a specific substance is not measured. Rather, groups of substances with similar physical characteristics are determined quantitatively on the basis of their common solubility in a specified fluorocarbon solvent. Oil and grease may therefore, be said to include hydrocarbons, fatty acids, soaps, fats, waxes, oil, and any other material that is extracted by the solvent from an acidified sample of the test. It is important that this limitation be clearly understood. Unlike some constituents—which represent distinct chemical elements, ions, compounds, or groups of compounds, oils and greases are defined by the method used for their determination.

## 1. Scope

1.1 These test methods cover the estimation of oil and grease in water and wastewater by a gravimetric determination of fluorocarbon extractable substances from an acidified sample. Also included in this estimation of oil and grease are any other compounds soluble in chlorofluorocarbon-113 and non-volatile under the conditions of test.

1.2 The following two test methods are included:

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1.3 These test methods are applicable to natural waters and domestic wastewaters. They are also suitable for most industrial wastewaters, although certain wastes may yield low results because of the presence of either excessive concentrations of natural greases or synthetic or modified compounds that are not well recovered by these test methods.

1.4 These test methods measure those groups of substance called oil and grease, whether soluble or insoluble, polar or non-polar, or biological or mineral in origin, to the extent these substances partition from the matrix into chlorofluorocarbon-113 and are not volatilized under conditions of the test. (See the Introduction and Section 3 of these test methods.)

1.5 Because these test methods include an acidification step prior to extraction, soluble metallic soaps are hydrolyzed and recovered as fatty acids in the extraction step.

1.6 These test methods were fully validated by collaborative testing in reagent Type IV water. The information on precision may not apply to other waters.

NOTE 1—Refer to companion procedures (Test Method D 3921).

1.7 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.8 *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.* For specific hazard statements, see 12.1, 13.2, 20.1, and 20.5.

## 2. Referenced Documents

### 2.1 ASTM Standards:

- D 1129 Terminology Relating to Water <sup>2</sup>
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits <sup>2</sup>
- D 1193 Specification for Reagent Water <sup>2</sup>
- D 3370 Practices for Sampling Water from Closed Conduits <sup>2</sup>
- D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water and Waste Water <sup>2</sup>
- D 3921 Test Method for Oil and Grease and Petroleum Hydrocarbons in Water <sup>3</sup>
- D 4210 Practice for Interlaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data <sup>2</sup>
- D 5789 Practice for Writing Quality Control Specifications

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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<sup>2</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 11.02.

for Standard Test Methods for Organic Constituents<sup>3</sup>

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *oil and grease*—the organic matter and other materials extracted by the solvent from water and wastewater and measured by these test methods.

### 4. Significance and Use

4.1 A knowledge of the quantity of oil and grease present in a waste is helpful in overcoming difficulties in wastewater treatment plant operation, in determining plant efficiencies, and in controlling the subsequent discharge of these materials to receiving streams.

4.2 When oils and greases are discharged in wastewater or treated effluents, they often cause surface films and shoreline deposits.

### 5. Interferences

5.1 This test method is entirely empirical, and duplicate results can be obtained only by strict adherence to all details. By definition, any material recovered is called oil and grease including such things as elemental sulfur and certain organic dyes. In addition, heavier residuals of petroleum may contain a significant portion of material insoluble in the solvent used.

5.2 The rate and time of extraction in the Soxhlet apparatus must be exactly as directed because of varying solubilities of different oils and greases. In addition, the length of time required for drying and cooling the extracted material cannot be varied. There may be a gradual increase in weight, presumably due to the absorption of oxygen, or a gradual loss of weight due to volatilization.

5.3 Modern industry uses a number of long-chain carbon compounds as lubricants and emulsifiers, as well as for other purposes. Often the composition of these materials differs from that of natural oils and greases, and may render them more soluble in water or more easily emulsified than the natural products. As a result, they behave as oils and greases in treatment processes and the receiving water. The procedures described here may fail to provide complete recovery of such products.<sup>4,5</sup>

5.4 Organic based boiler and cooling water chemicals such as polymeric dispersants and chelants, antifoams, filming and neutralizing amines, and oxygen scavengers may be recovered as oil and grease when these test methods are applied to such waters.

5.5 Low-boiling fractions are lost in the solvent-removal steps of the gravimetric procedures. Even lubrication oil fractions evaporate at a significant rate at the temperature necessary for removal of the last traces of the extraction solvent. Kerosine is still more volatile and gasoline cannot be determined with any reliability by a gravimetric method.

<sup>4</sup> Chanin, G., E. H. Chow, R. B. Alexander, and J. F. Powers, "Scum Analysis: A New Solution to a Difficult Problem," WWWEA-5,6-49-68.

<sup>5</sup> Taras, M. J. and K. A. Blum, "Determination of Emulsifying Oil in Industrial Wastewater," JWPEA-40-R404-68.

5.6 Suspended solids may interfere by contributing to emulsions.

### 6. Purity of Reagents

6.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>6</sup> 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type IV reagent water conforming to Specification D 1193.

### 7. Sampling

7.1 Collect the samples in accordance with Specification D 1192 or Practices D 3370, when applicable.

7.2 Collect grab samples only directly into the sample bottle. Oils and greases may be lost on any sampling equipment used. Do not rinse the sample bottles with the sample prior to filling as the oils may adhere to the inside of the bottle and lead to high results.

7.3 Because a portion of the collected oils and greases may adhere to the sample bottle, analyze all of the sample collected as one specimen. One-litre samples are normally specified, although larger or smaller samples may be taken depending on the concentration of extractables expected to be present.

7.4 Leave an air space above the liquid in the sample bottle to facilitate handling during analysis.

7.5 Collect all samples in glass bottles with nonorganic or insoluble caps, or both.

7.6 Acidify the sample to < pH 2 with HCl (1 + 1) or H<sub>2</sub>SO<sub>4</sub>(1 + 1) to maintain the integrity of the sample.

NOTE 2—For Clean Water Act purposes only H<sub>2</sub>SO<sub>4</sub> should be used and the sample should be cooled to 4°C and analyzed within 28 days.<sup>7</sup>

### TEST METHOD A—LIQUID-LIQUID EXTRACTION

#### 8. Scope

8.1 This test method covers the estimation of oil and grease from 4 to 100 mg/L in water and wastewater by a gravimetric determination of fluorocarbon extractable substances from an acidified sample.

8.2 This test method is generally applicable to samples containing extractable substances.

#### 9. Summary of Test Method

9.1 In this test method, an acidified water sample is extracted with fluorocarbon solvent in a separatory funnel.

<sup>6</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

<sup>7</sup> See Title 40, Code of Federal Regulations, Part 136 (40 CFR 136), Table 2, Required Containers, Preservation Techniques, and Holding Times, by the U.S. Environmental Protection Agency, available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20401.

9.2 In the gravimetric portion of the procedure, the fluorocarbon solvent containing the extracted materials is evaporated and the residue is determined gravimetrically.

## 10. Apparatus

10.1 *Drying Oven*, 103°C.

10.2 *Evaporating Flask*, 250-mL capacity. A flat-bottom boiling flask with standard taper fitting is recommended to facilitate solvent recycling.

10.3 *Distillation Apparatus*, water-cooled condenser, side arm, and receiver, all of appropriate standard taper fitting.

10.4 *Separatory Funnels*, 2-L funnels with TFE-fluorocarbon stopcocks.

10.5 *Steam Bath*.

10.6 *Desiccator*.

## 11. Reagents and Materials

11.1 *Acetone* ((CH<sub>3</sub>)<sub>2</sub>CO), technical grade.

11.2 *Filter Paper*, any high flow, low-retention grade, or optionally phase separating paper.<sup>8</sup>

11.3 *Fluorocarbon Solvent* (Chlorofluorocarbon-113 or 1,1,2-Trichloro-1,2,2-Trifluoroethane)<sup>9</sup> must be shown to contain no significant residue on evaporation. Redistill if necessary.

11.4 *Hydrochloric Acid* (HCl), sp gr 1.19.

11.5 *Sodium Bisulfate*—(NaHSO<sub>4</sub>·H<sub>2</sub>O).

11.6 *Sodium Chloride* (NaCl).

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

11.8 *Sulfuric Acid* (H<sub>2</sub>SO<sub>4</sub>), sp gr 1.84.

## 12. Procedure

12.1 Tare, to the nearest tenth of a milligram, a boiling flask that has been dried at 103°C in an oven for 1 h and cooled in a desiccator to room temperature. **Caution**—Always handle the flask with metal tongs or weighing gloves to avoid deposition of body oils.

NOTE 3—Run a reagent and materials blank to show that they contain no significant residue with respect to the precision of the test method at the level measured.

NOTE 4—Frequently, solvent will extract plasticizer from plastic tubing that is used to transfer from one container to another and from shipping container liner. Check for contamination by evaporating 180 mL of solvent on a steam bath and weighing the residue. The solvent should leave no measurable residue greater than 0.1 mg. If this value is exceeded, distill the solvent and check the distillate for residue.

12.2 Mark the sample bottle at the water meniscus for later determination of sample volume. Pour the acidified sample into a separatory funnel.

12.3 Add 60 mL of fluorocarbon solvent to the sample bottle, cap, and shake the bottle well. Pour the solvent into the separatory funnel and extract the sample by shaking vigorously for 2 min. Invert the separatory funnel and vent with stopcock

to relieve pressure buildup during the extraction. After the layers have separated, drain the solvent layer through filter paper held by a small funnel into the tared boiling flask. If emulsion problems are anticipated, add 1 g Na<sub>2</sub>SO<sub>4</sub> to the filter paper cone and slowly drain the solvent through the crystals. Add more Na<sub>2</sub>SO<sub>4</sub> if necessary.

NOTE 5—Solvent phase separation paper<sup>8</sup> helps to keep water out.

12.4 If a clear solvent layer cannot be obtained due to emulsion with water, add up to 100 g of NaCl to separatory funnel. Shake to dissolve the salt. Frequently this will break the emulsion. If the emulsion cannot be broken, this type of sample must be analyzed by the Soxhlet extraction test method.

12.5 Repeat the bottle rinse and extraction with two additional 60-mL portions of solvent, combining all solvent in the flask. Rinse the filter with 20 mL of solvent, into the flask.

12.6 Proceed to 13.1.

## 13. Procedure, Gravimetric for Test Methods A and B

13.1 Evaporate the solvent from the boiling flask (12.5, 20.8) on a hot water bath or steam bath. (Recovering solvent using a condenser system is recommended.)

13.2 When only a few millilitres of solvent remain (under 10 mL of solvent is not recommended), leave the flask on the steam bath and draw air through the flask using vacuum for 5 min to remove the last traces of solvent or residual water. Carefully wipe the exterior of the flask with a lint free cloth and a small amount of acetone to remove any water adhering to the flask. **Warning**—Wear protective gloves (polyethylene or similar solvent-resistant material) to prevent the acetone from coming in contact with the skin. Use acetone in a fume hood.

13.3 Place in a desiccator for 1 h, remove, and weigh immediately, to the nearest tenth of a milligram.

13.4 Measure the original sample volume by filling the sample bottle to the mark with water at 20°C and measure the volume of water with a graduated cylinder, to the nearest 5 mL.

NOTE 6—It is recommended that the chlorofluorocarbon-113 solvent be recycled to reduce costs and minimize discharges to the atmosphere. To recycle the solvent, attach a water cooled condenser with a side arm take off. The recovered solvent can usually be reused for this test without redistillation.

## 14. Calculation

14.1 Calculate the results of the determination, in milligrams per litre as follows:

$$\text{Extractable Residue, mg/L} = \frac{(B - A)}{C} \times 1000$$

where:

A = tare weight of boiling flask, mg,

B = weight of boiling flask after removal of extraction solvent, mg, and

C = volume of sample, L.

Report results to the nearest milligram per litre.

## 15. Precision and Bias<sup>10</sup>

15.1 Nine operators from nine laboratories determined four

<sup>8</sup> Whatman IPS Phase Separating Paper or an equivalent has been shown to be satisfactory; this material should be rinsed with solvent before use to eliminate silicone residue contamination.

<sup>9</sup> Freon 113 (E. I. DuPont de Nemours, Inc.) or equivalent has been shown to be satisfactory; this solvent is available as Freon TF, Freon PCA, Genetron 113, and Genesolve D.

<sup>10</sup> Supporting data for precision and bias statements are available from ASTM Headquarters. Request RR: D-19-1089.