Designation: D 3921 – 96 (Reapproved 2003)ε1

An American National Standard

Standard Test Method for Oil and Grease and Petroleum Hydrocarbons in Water[1]

This standard is issued under the fixed designation D 3921; 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.

This standard has been approved for use by agencies of the Department of Defense.

ε[1] NOTE—Editorial changes were made throughout in January 2003.

1. Scope

1.1 This test method covers the determination of fluorocarbon-extractable substances as an estimation of the combined oil and grease and the petroleum hydrocarbon contents of a sample of water or waste water in the range from 0.5 to 100 mg/L. It is the user's responsibility to assume the validity of the standard for untested types of water.

1.2 This test method defines oil and grease in water and waste water as that matter which is extractable in the test method and measured by infrared absorption. Similarly, this test method defines petroleum hydrocarbons in water and waste water as that oil and grease which is not adsorbed by silica gel in the test method and that is measured by infrared absorption.

1.3 Low-boiling organic materials are lost by evaporation during the manipulative transfers. However, these evaporative losses are generally much lower than those experienced with gravimetric procedures that require solvent evaporation before the residue is weighed.

1.4 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[2]

D 1193 Specification for Reagent Water[2]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water[2]

D 3325 Practice for Preservation of Waterborne Oil Samples[3]

D 3370 Practices for Sampling Water from Closed Conduits[2]

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[2]

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[3]

E 168 Practices for General Techniques of Infrared Quantitative Analysis[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129 and Practices E 168.

3.2 *Definitions of Terms Specific to This Standard:*

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

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

4. Summary of Test Method

4.1 The acidified sample of water or waste water is extracted serially with three 30-mL volumes of 1, 1, 2-trichloro-1, 2, 2-trifluoroethane (referred to in this test method as solvent). [5] The extract is diluted to 100 mL and a portion is examined by infrared spectroscopy [6] to measure the amount of oil and grease removed from the original sample. A major portion of the remaining extract is contacted with silica gel to remove polar substances, thereby providing a solution of petroleum hydrocarbons. This treated extract is then similarly examined by infrared spectroscopy.

5. Significance and Use

5.1 The presence of oil and grease in domestic and industrial waste water is of concern to the public because of its deleterious aesthetic effect and its impact on aquatic life. Regulations and standards have been established that require monitoring of oil and grease in water and waste water. This test

[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 Jan. 10, 2003. Published January 2003. Originally approved in 1980. Last previous edition approved in 1996 as D 3921 – 96.

[2] *Annual Book of ASTM Standards,* Vol 11.01.

[3] *Annual Book of ASTM Standards,* Vol 11.02.

[4] *Annual Book of ASTM Standards,* Vol 03.06.

[5] Gruenfeld, M., "Extraction of Dispersed Oils from Water for Quantitative Analysis by Infrared Spectrophotometry," *Environmental Science and Technology,* Vol 7, 1973, pp. 636–639.

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

method provides an analytical procedure to measure oil and grease in water and waste water.

6. Interferences

6.1 Since the constituents oil and grease and petroleum hydrocarbons are defined as the results of the test procedure, interferences are precluded by definition. Interpretation of test results on the basis of chemical structure, pollution potential, or treatability should be approached with caution, however, because of the diversity of substances measured by this procedure.

6.2 Organic solvents and certain other organic compounds 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 which are not adsorbed are measured as petroleum hydrocarbons.

7. Apparatus

7.1 *Cell(s)*, quartz, 10-mm path length, two required for double-beam operation, one required for single-beam operation, or built-in cell for nondispersive infrared analyzer operation.

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

7.3 *Glass Bottle*, approximately 1000-mL, with screw cap having a TFE-fluorocarbon liner.

7.4 *Graduated Cylinder*, 1000-mL.

7.5 *Infrared Spectrometer*, double-beam dispersive, single-beam dispersive, Fourier transform, or nondispersive infrared analyzer.

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

7.7 *Separatory Funnel*, 2000-mL, with TFE-fluorocarbon stopcock (one for each sample analyzed during any one period of time).

7.8 *Volumetric Flask*, 100-mL (minimum of six required for calibration plus one for each sample analyzed during any one period of time).

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, [7] 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 water (not sample water) shall be understood to mean reagent water conforming to Specification D 1193, Type II.

8.3 *Calibration Oil and Grease*, similar in composition to oil and grease determined by this test method for possible use as calibration material.

8.4 *Cetane (n-Hexadecane)*, 99 % minimum purity, for possible use in calibration mixture.

8.5 *Isooctane (2,2,4-Trimethylpentane)*, 99 % minimum purity, for possible use in calibration mixture.

8.6 *Silica Gel* [8], 100 to 200 mesh, which has been deactivated with 2 % water.

8.7 *Sodium Bisulfate* ($NaHSO_4$), monohydrate.

8.8 *Sodium Sulfate* (Na_2SO_4), anhydrous, granular.

8.9 *Solvent* —1, 1, 2-trichloro-1, 2, 2- trifluoroethane. [9]

NOTE 1—Frequently, this solvent will extract plasticizer from the liner of its shipping container. Check for such contamination by evaporating 100 mL of solvent in a steam bath and weighing its residue. If this value exceeds 0.1 mg, purify the solvent by distillation and check the overhead material for residue. Store the purified solvent in clean, glass bottles having TFE-Fluorocarbon cap liners. Purification of this solvent as a matter of course is highly desirable.

8.10 *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.

9. Sampling

9.1 Collect the sample in accordance with the principles described in Practices D 3370, using a glass bottle equipped with a screw cap having a TFE-fluorocarbon liner.

9.2 A sample of about 750 mL is required for this test. Use the entire sample since no portion should be removed for other tests.

9.3 Preserve the sample with a sufficient quantity of either sulfuric acid (see 8.10) or sodium bisulfate (see 8.7) to attain a pH of 2 or lower. The amount of reagent required will be dependent upon the pH of the sample at the time of collection and upon its buffer capacity.

10. Calibration

NOTE 2—A choice of two calibration species is available to the analyst. The preferred material is a sample of the same oil and grease that is known to be present in the sample of water or waste water awaiting analysis. The other material is a mixture of *iso*octane and cetane. This latter blend is to be used when the same (as described) material is not available.

10.1 If the blend of *iso*octane and cetane is to be used for calibration, prepare a calibration mixture by pipetting 15 mL of *iso*octane and 15 mL of cetane into a glass-stoppered bottle. Mix the contents well and maintain the integrity of the mixture by keeping the container tightly sealed except when a portion is withdrawn for blending.

10.2 *Calibration Solution Blend A*—Place about 20 mL of solvent into a 100-mL volumetric flask, stopper, and weigh. To this flask quickly add about 1 mL of either the calibration oil and grease or the calibration mixture of *iso*octane and cetane. Obtain its exact weight by difference. Fill to the mark with

[7] *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 Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[8] Silica Gel, Davison Chemical Grade 923 has been found to be satisfactory for this purpose. Other available types from the same or different suppliers may be suitable.

[9] This solvent is available also as Freon 113, Freon TF, Freon PCA, Genetron 113, Genesolve D, and as other names.

solvent and mix the liquid well by shaking the flask. Calculate the exact concentration of the calibrating material in solution in terms of mg/100 mL. If the calibration oil and grease is used, proceed to 10.3. If the calibration mixture is used, multiply this calculated concentration (about 730 mg/100 mL) by 1.4 (refer to Note 3). This new concentration value (about 1022 mg/100 mL) is to be used for Blend A throughout the remainder of this test method.

NOTE 3—Dating back to at least 1951,[10] for many years a mixture of *iso*octane, cetane, and benzene was accepted as a standard for calibration. Concern regarding the hazards of exposure to benzene, which acts here only as a diluent having no contribution at 2930 cm^{-1} (3.41 μm), has prompted elimination of this chemical as a component for calibration. To maintain relevance between current and future analytical data with those of the past, it is necessary to compensate for differences in concentration and in density between the former and the present calibration standards. The factor of 1.4 accomplishes this because the weight ratio of combined *iso*octane plus cetane in the new two-way mixture to that in the older three-way mixture is 1.000 to 0.714, or 1.40. Henceforth, all concentrations involving the calibration mixture will be based upon the converted value obtained in 10.2.

10.3 *Calibration Solution Blend B*—Dilute 4 mL of Blend A with solvent in a 100-mL volumetric flask (about 41 mg/100 mL).

10.4 *Calibration Solution Blend C*—Dilute 3 mL of Blend A with solvent in a 100-mL volumetric flask (about 31 mg/100 mL).

10.5 *Calibration Solution Blend D*—Dilute 50 mL of Blend B with solvent in a 100-mL volumetric flask (about 20 mg/100 mL).

10.6 *Calibration Solution Blend E*—Dilute 30 mL of Blend C with solvent in a 100-mL volumetric flask (about 9 mg/100 mL).

10.7 *Calibration Solution Blend F*—Dilute 10 mL of Blend E with solvent in a 100-mL volumetric flask (about 0.9 mg/100 mL).

NOTE 4—During the calibration events which follow, the cell used for the blends must be thoroughly cleaned with fresh solvent and then dried prior to the addition of a new blend. 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. For single-beam operation, use the same cell throughout the calibration procedure. Rely upon sole recommendations of the manufacturer for single-beam and nondispersive infrared analyzers since variations in design make it impractical to offer instructions for their use with this method. Also, in relation to nondispersive infrared operation, reference to scanning or running, or both, should be interpreted to mean obtaining a reading or a plot of the 2930-cm^{-1} (3.41-μm) band.

10.8 Fill the reference cell (for double-beam operation) and the sample cell with solvent and scan from 3200 cm^{-1} (3.13 μm) to 2700 cm^{-1} (3.70 μm). A nearly horizontal, straight line should be obtained. If it is not, check cells for cleanliness, matching, etc. Drain and clean the sample cell. Obtain spectral data for the solvent at this time for single-beam and nondispersive infrared instruments, also. After running, drain, and clean the sample cell.

10.9 Fill the sample cell with Blend B. Scan as in 10.8; drain, and clean the sample cell.

10.10 Fill the sample cell with Blend C. Scan as in 10.8; drain, and clean the sample cell.

10.11 Fill the sample cell with Blend D. Scan as in 10.8; drain, and clean the sample cell.

10.12 Fill the sample cell with Blend E. Scan as in 10.8; drain, and clean the sample cell.

10.13 Fill the sample cell with Blend F. Scan as in 10.8; drain, and clean the sample cell.

10.14 For each double-beam spectrum obtained in 10.9 through 10.13, draw a baseline similar to that found in Fig. 1. Obtain the net absorbance for the peak that occurs near 2930 cm^{-1} (3.41 μm). Obtain net values for single-beam and nondispersive infrared runs as recommended.

NOTE 5—For infrared instruments having computer capability, data may be obtained automatically or as described in 10.14. However, all data must be obtained consistently by one means or the other, not a combination of the two.

10.15 On linear graph paper, plot the new absorbance values, found in 10.14 or as permitted in Note 5, versus the respective mg/100 mL values for each of the blends examined. The points should lie very nearly in a straight line. Draw the best-fitting straight line through the points and keep this calibration graph for use with the test samples. Alternatively, determine the equation of the best-fitting straight line calculated by a linear regression technique. Record this equation for use with the test samples.

11. Procedure

NOTE 6—This procedure applies to all samples regardless of the type of infrared instrumentation used for measurement. Thus, to comply with this test method, no extraction is to be attempted in a nondispersive infrared analyzer or any other instrument capable of automatic or semiautomatic extraction.

11.1 *Extraction*:

11.1.1 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 or sodium bisulfate to attain a pH of 2 or less.

11.1.2 Add 30 mL of solvent to the sample in the original sample bottle. Recap immediately and shake the bottle vigorously for 2 min. Allow the bottle to stand until the contents settle and bubbles disappear. Remove the cap carefully to release any pressure build-up and immediately transfer the contents of the bottle to a clean separatory funnel. Wash down the transfer funnel with clean solvent, stopper the separatory funnel, and recap the bottle. Allow the contents of the separatory funnel to settle. Transfer the bottom layer into a clean 100-mL volumetric flask through filter paper and about 1 g of sodium sulfate that have been prewetted with solvent to remove any organic material which could contaminate the sample.

[10] Simard, R. G., Hasegawa, I., Bandaruk, W., and Headington, C. E., "Infrared Spectrophotometric Determination of Oil and Phenols in Water", *Analytical Chemistry*, Vol 23, 1951, pp. 1384–1387.