Designation: D3414 – 98 (Reapproved 2004)

Standard Test Method for Comparison of Waterborne Petroleum Oils by Infrared Spectroscopy[1]

This standard is issued under the fixed designation D3414; 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 provides a means for the identification of waterborne oil samples by the comparison of their infrared spectra with those of potential source oils.

1.2 This test method is applicable to weathered or unweathered samples, as well as to samples subjected to simulated weathering.

1.3 This test method is written primarily for petroleum oils.

1.4 This test method is written for linear transmission, but could be readily adapted for linear absorbance outputs.

1.5 *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.* Specific precautionary statements are given in Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D3325 Practice for Preservation of Waterborne Oil Samples
D3326 Practice for Preparation of Samples for Identification of Waterborne Oils
D3415 Practice for Identification of Waterborne Oils
E131 Terminology Relating to Molecular Spectroscopy
E168 Practices for General Techniques of Infrared Quantitative Analysis
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method refer to Terminology E131 and Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *weathering of waterborne oil*—the combined effects of evaporation, solution, emulsification, oxidation, biological decomposition, etc.

4. Summary of Test Method

4.1 The spill sample and potential source oil(s) are treated identically to put them in an appropriate form for analysis by infrared spectrophotometry. The oils are transferred to suitable infrared cells and the spectra are recorded from 4000 to 600 cm^{-1} for KBr cells, and to 650 cm-1 for HATR cells with ZnSe crystals. All analyses are performed on the same instrument using the same sample cell, which is cleaned between samples. The spectra of the sample and the potential source oil(s) are then compared by superimposing one upon the other, looking at particular portions of the spectra. A high degree of coincidence between the spectra of the sample and a potential source oil indicates a common origin. This test method is recommended for use by spectroscopists experienced in infrared oil identification or under close supervision of such qualified persons.

5. Significance and Use

5.1 This test method provides a means for the comparison of waterborne oil samples with potential sources. The waterborne samples may be emulsified in water or obtained from beaches, boats, oil-soaked debris, and so forth.

5.2 The unknown oil is identified by the similarity of its infrared spectrum with that of a potential source oil obtained from a known source, selected because of its possible relationship to the unknown oil.

5.3 The analysis is capable of comparing most oils. Difficulties may be encountered if a spill occurs in an already polluted area, that is, the spilled-oil mixes with another oil.

5.4 In certain cases, there may be interfering substances which require modification of the infrared test method or the use of other test methods (see Practice D3326, Method D.)

5.5 It is desirable, whenever possible, to apply other independent analytical test methods to reinforce the findings of the infrared test method (see Practice D3415).

[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.

TABLE 1 Specifications for Infrared Spectrophotometers

Abscissa accuracy	Better than ± 5 cm^{-1} from 4000 to 2000 cm^{-1} range; better than ± 3 cm^{-1} from 2000 to 600 cm^{-1}(or below).
Abscissa repeatability	2.5 cm^{-1} from 4000 to 2000 cm^{-1}; 1.5 cm^{-1} from 2000 to 600 cm^{-1}(or below).
Ordinate accuracy	± 1 % of full scale.
Ordinate repeatability	within 1 % of full scale.

6. Apparatus

6.1 *Infrared Spectrophotometer*—An instrument[3] capable of recording in the spectral range from 4000 to 600 cm^{-1} and meeting the specifications is shown in Table 1. Refer also to Practice E275. Fourier transform infrared spectrophotometers meet these specifications.

NOTE 1—Although this test method is written for the use of dispersive infrared spectroscopy, Fourier transform infrared spectroscopy can also be used for oil comparison.

6.2 *Sample Cells*:

6.2.1 *Demountable Cells*—The cell generally used is a demountable liquid cell using a 0.05-mm spacer. This cell is usable for all oil types, the heavy oils being analyzed as smears. For light oils, a sealed cell can be used, provided that the sample is known to be dry. Another type used is a low-capacity demountable cell using a silver halide window with a 0.025-mm depression.[4] Satisfactory oil spectra can be obtained with this cell with as little as 10 µL of oil, compared to the nearly 100 µL required for the standard cells. This cell can also be used to screen for the presence of water in oil samples.

6.2.2 *Horizontal Attentuated Reflectance Apparatus (HATR)*, may be used instead of demountable cells. If so, all analyses must be performed with the same HATR apparatus.

6.3 *Cell Windows*:

6.3.1 Potassium or silver bromide should be used for demountable cells. Silver chloride may be substituted for the bromide.

NOTE 2—Sodium chloride should not be used; results obtained using this window material, although consistent with each other, are not directly comparable to those from the other window materials. Sodium chloride was shown by Brown, *et al* [5] to give results significantly different from those obtained with potassium bromide or silver chloride, based on quantitative comparisons.

6.3.2 Zinc selenide is the material of choice for the HATR apparatus.

6.4 *Accessories*:

6.4.1 *Reference Beam Attenuator*, for setting baseline with the low-capacity silver halide cell.

6.4.2 *Disposable Pasteur Pipets and Hypodermic Syringes*.

6.4.3 *Window-Polishing Kit*.

6.4.4 *Centrifuge*.

6.4.5 *Vortex Mixer*.

6.4.6 *Hot Plate*.

6.4.7 *Light-Box*, for viewing spectra.

7. Reagents

7.1 *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 specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] For sample treatment and for cleaning cells, special spectroquality reagents are required. Other grades may be used, provided it is first established that the reagent is of sufficiently high purity to permit its use without decreasing the accuracy of the determination.

7.2 *Purity of Water*— Unless otherwise indicated references to water shall be understood to mean reagent water conforming to Specification D1193, Type II.

7.3 *Magnesium Sulfate*—anhydrous, reagent grade, for drying samples.

7.4 *Solvents*—Spectroquality solvents for sample treatment and cleaning cells include cyclohexane, pentane, hexane, methylene chloride, and methanol.

8. Precautions

8.1 Take normal safety precautions when handling organic solvents. Take precautions to ensure that wet oil samples do not come in contact with water-soluble cell window materials. Most spectrophotometers require humidity control (to about 45 %), particularly if they have humidity-sensitive detectors such as those with cesium iodide optics. The primary precaution which must be taken to provide the best possible results is that all samples analyzed should be treated in an identical fashion, run in the same cell, on the same instrument and preferably on the same day by the same operator.

NOTE 3—If the samples cannot be analyzed the same day, one of the first samples must be repeated to ensure that the spectra are not significantly different.

9. Sampling

9.1 *On-Scene*—A representative sample of the waterborne oil is collected in a glass jar (precleaned with cyclohexane and dried) having a TFE-fluorocarbon-lined cap. In the same time frame, samples are collected of potential source samples that are to be compared to the waterborne sample.

9.2 *Laboratory*—See Annex A1.

10. Preservation of Sample

10.1 Refer to Practice D3325.

11. Analytical Procedures

11.1 *Recording Spectra for Dispersive Instruments*:

[3] Consult the manufacturer's operating manual for specific instructions on using this apparatus.

[4] The Mini-cell made by Wilks Scientific Corp., S. Norwalk, CT, has been found to be satisfactory for this purpose.

[5] Brown, C. W., Lynch, P. F., and Ahmadjian, M. "Identification of Oil Slicks by Infrared Spectroscopy," NTIS Accession No. ADA 040975, 1976.

[6] "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 Rosin, J.," Reagent Chemicals and Standards," D. Van Nostrand Co., New York, NY, and the "United States Pharmacopeia".

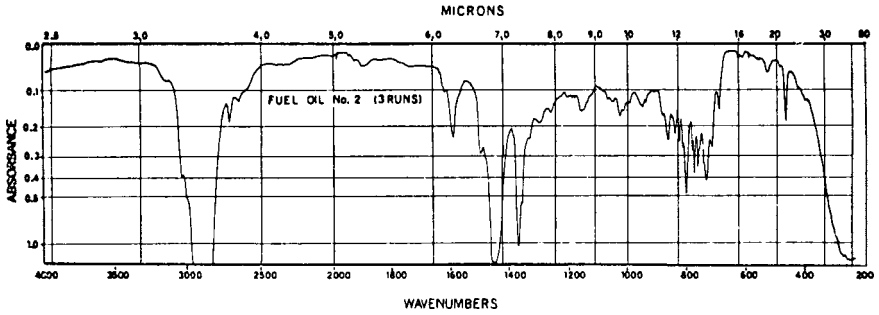

FIG. 1 Complete Spectrum of a No. 2 Fuel Oil, Analyzed in Triplicate

11.1.1 Operate the instrument in accordance with the manufacturer's instructions. Refer to Practices E168 for more information on handling cells.

11.1.2 Check the calibration daily by scanning a 0.05-mm polystyrene film in accordance with Practice E275. Observe whether the test spectra are within the limits of the instrument specifications. This calibration check should be performed before every oil spill set and the spectrum retained with spectra from the spill and suspects as part of the case record.

11.1.3 Test the resolution by observing the sidebands in the polystyrene spectrum at 2850.7 and 1583.1 cm^{-1} which should be distinct and well defined.[7] This is also true for the sideband at 3100 cm^{-1} which should have a clear inflection with a displacement of at least 1 to 3 % T where T = transmittance.

11.1.4 Place the sample in a liquid cell (see Annex A2 or Annex A3) and insert cell into the infrared beam. Set the absorbance to read 0.02 A (95 % T) at 1975 ± 20 cm^{-1}.

NOTE 4—The absorbance is set at a fixed value so that the resultant spectra can be compared from a common baseline.

11.1.5 Scan the spectrum from 4000 to 600 cm^{-1} using normal operating conditions and slit settings.

11.2 *FTIR Instruments*:

11.2.1 Collect data from a background scan (air only) under conditions identical to those under which the sample will be run, that is, with the cell in the instrument and all instrument parameters the same.

11.2.2 Normalize the absorbance before comparing the spectra.

11.2.3 Collect data from 650 cm-1 for HATR cells with ZnSe, due to the sprectral absorbance cutoff for ZnSe.

11.3 *Preparation of Sample*—Refer to Annex A1 and Practice D3326 for sample preparation.

NOTE 5—The primary objective in sample preparation is the removal of water to protect the sample cells and get a "clean" spectrum of the oil. If at all possible, the use of solvent should be avoided. It is sometimes necessary to use solvent in order to break refractory emulsions or to extract the oil from solid substrates. It must be remembered that for valid comparisons of spectra, both oils being compared must have been prepared the same way, that is, if one is deasphalted with pentane, the other must be also (see Practices D3326 for the deasphalting procedure. It should be noted that 15 parts of solvent (versus 40) is all that is necessary for quantitative precipitation of the asphaltene fraction.)

[7] *Tables of Wavenumbers For The Calibration of Infrared Spectrometers*, IUPAC, Commission on Molecular Structure and Spectroscopy, Butterworth and Co., Toronto, Canada, 1961.

12. Interpretation of Spectra

12.1 Ultimately, oil identification is based on a peak-by-peak comparison of the spill spectrum with those of the various potential sources. A light-box is convenient for superimposing these spectra. When the results are to be used for forensic purposes, comparisons *must* be made on spectra obtained by using the same sample preparation, sample cell, and the same instrumental conditions, preferably with the same operator on the same day.

12.2 *Sample Spectra*

12.2.1 Fig. 1 shows the infrared spectrum of a No. 2 fuel oil to illustrate the general spectral characteristics of an oil analyzed by infrared transmission through KBr windows. This particular illustration is actually a superposition of three independent spectra which graphically show how reproducible the triplicates are, even with a demountable cell, if proper techniques are used. The "oil fingerprint" region between 900 to 700 cm^{-1} can be seen to have a large amount of fine detail characteristic of a light oil.

12.2.2 Figs. 2-5 show spectra from 2000 to 600 cm^{-1} for four oils weathered over 4 days. They show the general effects of weathering on baselines between 1300 and 900 cm^{-1} and relative changes of individual peaks in the" fingerprint" region. The figures are, respectively: No. 2, No. 4, No. 6 fuel oils, and a Louisiana crude with curves at 0, 1, 2, 3, and 4 days outdoor weathering.

12.2.3 Fig. 6 and Fig. 7 show details of weathering of various oil types as described in 12.3.7.

12.3 *Overlay Method*:

12.3.1 The overlay method consists of a visual comparison of the spectrum of a spill with that of a potential source in the sequence as follows and outlined in Fig. 8. This may be accomplished using a light-box or even recording two spectra on the same chart.

12.3.1.1 First ensure that the spectra have comparable baselines at 1975 cm^{-1}, that is, that they were set at an absorbance of 0.02 (95 % T).

12.3.1.2 Next, examine the absorbance at 1377 cm^{-1} to obtain qualitative assurance that the samples were analyzed at the same thickness, that is, same cell path length (see 12.3.2).

12.3.1.3 Then examine the curve for overall similarities in shape from 4000 to 600 cm^{-1}. For petroleum oils, the baseline will tend to move downward with weathering (to higher absorbance between 1350 to 900 cm^{-1}) but with little relative change of the peaks in that range.

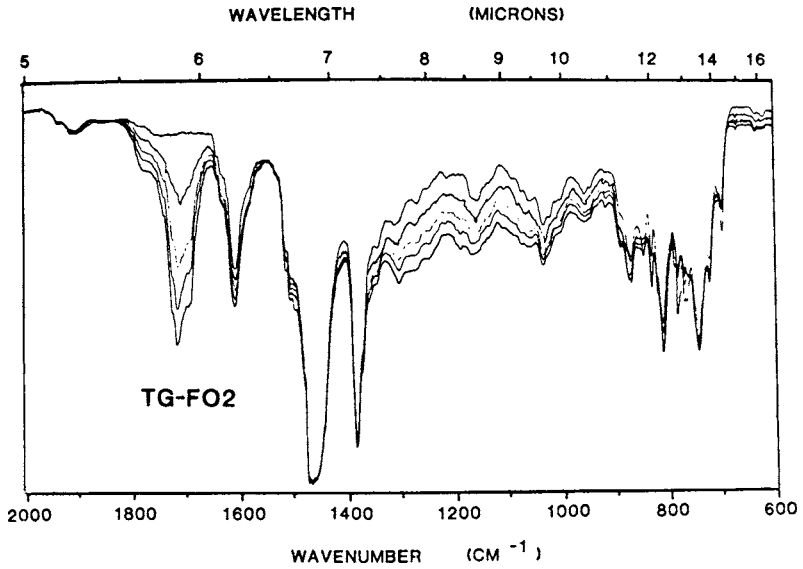

FIG. 2 No. 2 Fuel Oil Progressive Weathering Effects, 0 to 4 Days

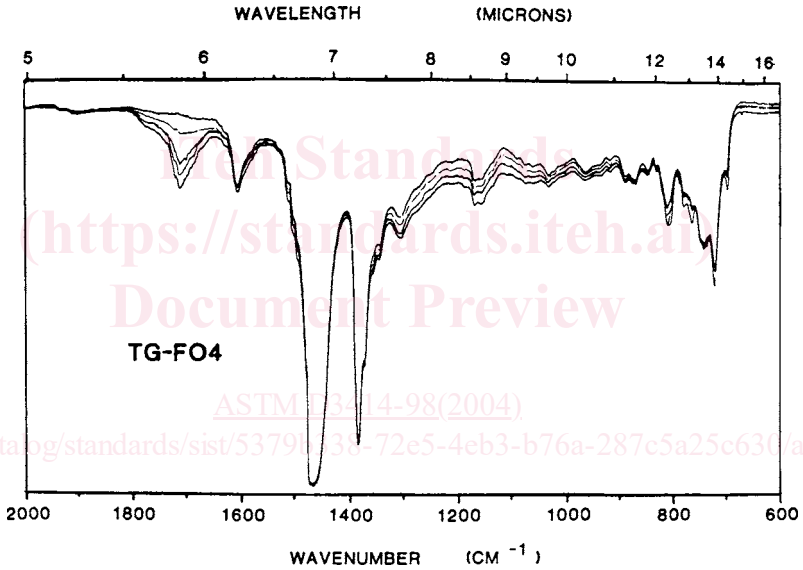

FIG. 3 No. 4 Fuel Oil Progressive Weathering Effects, 0 to 4 Days

12.3.1.4 Examine the 1770 to 1685 cm^{-1} region to determine the extent of weathering—particularly in the 1708 cm^{-1} region where carbonyls from oxidative weathering first appear.

12.3.1.5 Before making a detailed comparison, make sure there are no interferences from residual foreign materials:

(a) (*a*) For water in the spill sample, check in the 3400 cm^{-1} region for a broad peak. (If water is suspected to be present, check first in a low-capacity silver halide cell). If an appreciable amount of water is present, redry the sample.

(b) (*b*) For residual $MgSO_4$ from the drying procedure, check the 610 cm^{-1} region for a small, sharp peak, and look for peak increases at 1075 and 1175 cm^{-1}.

(c) (*c*) For residual pentane, if the sample has been deasphalted, look for the presence of small twin peaks at 910 and 920 cm^{-1}. There also would be a corresponding increase in the peak at 722 cm^{-1}.

12.3.1.6 Finally, scrutinize the "oil fingerprint" region (900 to 700 cm^{-1}) for similarities. If slight variations do occur in this region, the peaks are examined for possible changes induced by weathering. The sequential steps are outlined in 12.3.2 through 12.3.7.

NOTE 6—Animal or vegetable oils would have a pronounced ester carbonyl at 1730 to 1740 cm^{-1}. In that case, the spectra are compared directly in order to identity without consideration of weathering changes described as follows for petroleum oils.

12.3.2 Examine the intensity of the 1377 cm^{-1} peak since it is a good indicator of the sample thickness. An absorbance value between 0.85 and 1.00 at 1377 cm^{-1} gives the optimum spectrum. The matching of oil spectra from a common source is considerably easier when samples are of the same thickness.

12.3.3 If the spectra are of the same sample thickness, compare overall shapes over the entire curves. If obvious major