



# Standard Test Method for Comparison of Waterborne Petroleum Oils By Fluorescence Analysis<sup>1</sup>

This standard is issued under the fixed designation D 3650; 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.

## 1. Scope\*

1.1 This test method covers the comparison of waterborne petroleum oils with oils from possible sources by means of fluorescence spectroscopy (1).<sup>2</sup> Useful references for this test method include: (2) and (3) for fluorescence analysis in general and (4), (5), and (6) for oil spill identification including fluorescence.

1.2 This test method is applicable to crude or refined petroleum products, for any sample of neat oil, waterborne oil, or sample of oil-soaked material. Unless the samples are collected soon after the spill occurs, it is not recommended that volatile fuels such as gasoline, kerosine, and No. 1 fuel oils be analyzed by this test method, because their fluorescence signatures change rapidly with weathering. Some No. 2 fuel oils and light crude oils may only be identifiable up to 2 days weathering, or less, depending on the severity of weathering. In general, samples weathered up to 1 week may be identified, although longer periods of weathering may be tolerated for heavy residual oils, oil weathered under Arctic conditions, or oil that has been protected from weathering by collecting in a thick layer.

1.3 *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 the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 1129 Terminology Relating to Water<sup>3</sup>

D 1193 Specification for Reagent Water<sup>3</sup>

D 1796 Test Method for Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure)<sup>4</sup>

<sup>1</sup> 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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<sup>2</sup> The boldface numbers in parentheses refer to the references at the end of this test method.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 05.01.

D 3325 Practice for Preservation of Waterborne Oil Samples<sup>5</sup>

D 3326 Practices for Preparation of Samples for Identification of Waterborne Oils<sup>5</sup>

D 3328 Test Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography<sup>5</sup>

D 3414 Test Method for Comparison of Waterborne Petroleum Oils by Infrared Spectroscopy<sup>5</sup>

D 3415 Practice for Identification of Waterborne Oils<sup>5</sup>

D 4489 Practices for Sampling of Waterborne Oils<sup>5</sup>

E 131 Terminology Relating to Molecular Spectroscopy<sup>6</sup>

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers<sup>6</sup>

E 520 Practice for Describing Detectors in Emission and Absorption Spectroscopy<sup>7</sup>

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method refer to Terminology D 1129, Practice D 3415, and Terminology E 131.

## 4. Summary of Test Method

4.1 This test method consists of fluorescence analyses of dilute solutions of oil in spectroquality cyclohexane. In most cases the emission spectra, with excitation at 254 nm, over the spectral range from 280 to 500 nm, are adequate for matching.

4.2 Identification of the sample is made by direct visual comparison of the sample's spectrum with the spectra from possible source samples.

NOTE 1—When weathering has occurred, it may be necessary to consider known weathering trends when matching spectra (Fig. 1 and Fig. 2).

## 5. Significance and Use

5.1 This test method is useful for rapid identification of waterborne petroleum oil samples as well as oil samples

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 11.02.

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 14.01.

<sup>7</sup> *Annual Book of ASTM Standards*, Vol 03.06.

\*A Summary of Changes section appears at the end of this standard.

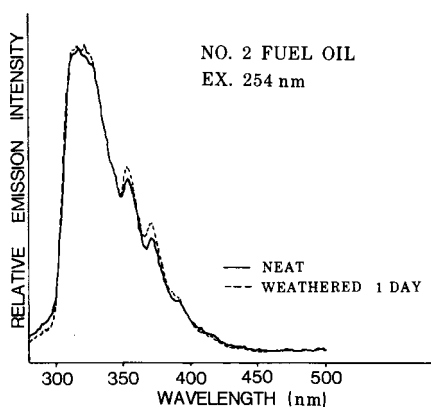


FIG. 1 Fluorescence Spectra for a Typical No. 2 Fuel Oil (Unweathered and Weathered One Day)

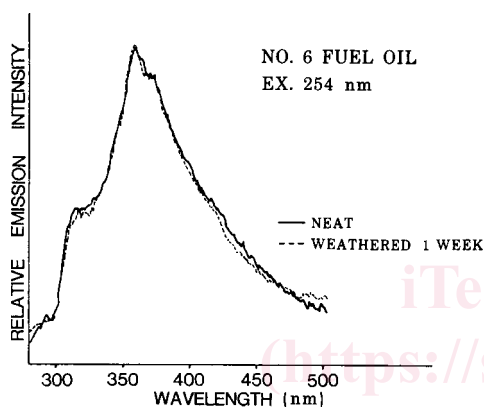


FIG. 2 Fluorescence Spectra for a Typical No. 6 Fuel Oil (Unweathered and Weathered One Day)

obtained from fuel or storage tanks, or from sand, vegetation, or other substrates. This test method is applicable to weathered and unweathered neat oil samples.

5.2 The unknown oil is identified through the comparison of the fluorescence spectrum of the oil with the spectra (obtained at similar instrumental settings on the same instrument) of possible source samples. A match of the entire spectrum between the unknown and possible source sample indicates a common source.

## 6. Interferences

6.1 The fluorescence spectrum will be distorted if an oil sample has been contaminated by an appreciable amount, for example, 1 % of common chemical impurities such as other oils that are fluorescent on excitation at 254 nm.

NOTE 2—Storage of samples in improper containers (for example, plastics) may result in contamination. This interference can be eliminated by observing proper procedures for collection and preservation of samples. Refer to Practice D 3325.

NOTE 3—“Spectroquality” cyclohexane may not have a low enough fluorescence solvent blank. Lots vary in the content of fluorescent impurities, which may increase with storage time even if the bottle is unopened.

6.2 Oil residues may build up in fluorescence cells particularly after prolonged usage with heavy oils. In such a case, follow the procedure using nitric acid for cleaning glassware (10.1.3).

6.3 Possible interferences from Raman or RayleighTyndall scattering are not observed in the emission scan ranges selected.

## 7. Apparatus

7.1 *Fluorescence Spectrophotometer (or Spectrofluorometer)*—An instrument recording in the spectral range of 220 nm to at least 600 nm for both excitation and emission responses and capable of meeting the specifications stated in Table 1.

7.2 *Excitation Source*—A high-pressure xenon lamp (a 150-W xenon lamp has proven acceptable). Other continuum sources, such as deuterium or high-pressure xenon-mercury, which have sufficient intensity in the ultraviolet region, could be used as excitation sources.

NOTE 4—Line sources such as a low-pressure mercury lamp may also be used for excitation at 254 nm, if the flexibility of using arbitrary excitation wavelengths or excitation spectra is not desired and if source intensity is adequate.

7.3 *Fluorescence Cells*—Standard cells, made from fluorescence-free fused silica with a pathlength of 10 mm and a height of 45 mm.

7.4 *Recorder or Computer*—Strip chart or X-Y recorder, with a response time less than 1 s for full-scale deflection, or a computer capable of digitizing the data at a rate of 1 data point per nanometre.

7.5 *Cell-Filling Device*—Disposable Pasteur capillary pipet.

7.6 *Volumetric Flasks*—Low-actinic glass, ground-glass stoppered volumetric flasks (100-mL).

7.7 *Micropipet*, 10 to 50- $\mu$ L capacity.

7.8 *Analytical Balance*, with a precision of at least  $\pm 0.1$  mg.

7.9 *Weighing Pans*, 5 to 7-mm diameter, 18 mm deep, made of aluminum or equivalent.

7.10 *Test Tubes*, disposable 15-mL glass test tubes.

TABLE 1 Specifications for Fluorescence Spectrophotometers

Wavelength Reproducibility	
Excitation monochromator	better than $\pm 2$ nm
Emission monochromator	better than $\pm 2$ nm
Gratings (Typical Values)	
Excitation monochromator	minimum of 600 lines/mm blazed at 300 nm <sup>A</sup>
Emission monochromator	minimum of 600 lines/mm blazed at 300 nm or 500 nm <sup>A</sup>
Photomultiplier Tube <sup>B</sup>	
Either S-20 <sup>C</sup> or S-5 <sup>D</sup> Response <sup>E</sup>	
Resolution	
Excitation monochromator	better than 2 nm
Emission monochromator	better than 2 nm
Time Constant	
not to exceed one second	

<sup>A</sup> Or designed to have a good efficiency in this spectral region.

<sup>B</sup> See Practice E 520.

<sup>C</sup> Photomultiplier tubes such as Hamamatsu R-446-UR.

<sup>D</sup> Photomultiplier tubes such as RCA 1P28 or Hamamatsu R-106.

<sup>E</sup> Or equivalent having a good spectral response in the spectral region from 280 to 600 nm.