



# Standard Test Method for Comparison of Waterborne Petroleum Oils by Infrared Spectroscopy<sup>1</sup>

This standard is issued under the fixed designation D 3414; 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 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:<sup>2</sup>

D 1129 Terminology Relating to Water

D 1193 Specification for Reagent Water

D 3325 Practice for Preservation of Waterborne Oil Samples

D 3326 Practice for Preparation of Samples for Identification of Waterborne Oils

D 3415 Practice for Identification of Waterborne Oils

E 131 Terminology Relating to Molecular Spectroscopy

E 168 Practices for General Techniques of Infrared Quantitative Analysis

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers

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

## 3. Terminology

### 3.1 Definitions:

3.1.1 For definitions of terms used in this test method refer to Terminology E 131 and Terminology D 1129.

### 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  $\text{cm}^{-1}$  for KBr cells, and to 650  $\text{cm}^{-1}$  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 D 3326, Method D.)

**TABLE 1 Specifications for Infrared Spectrophotometers**

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

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 D 3415).

## 6. Apparatus

6.1 *Infrared Spectrophotometer*—An instrument<sup>3</sup> capable of recording in the spectral range from 4000 to 600  $\text{cm}^{-1}$  and meeting the specifications is shown in Table 1. Refer also to Practice E 275. 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.<sup>4</sup> Satisfactory oil spectra can be obtained with this cell with as little as 10  $\mu\text{L}$  of oil, compared to the nearly 100  $\mu\text{L}$  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 Attenuated 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*<sup>5</sup> 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.<sup>6</sup> 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 D 1193, 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 D 3325.

<sup>3</sup> Consult the manufacturer's operating manual for specific instructions on using this apparatus.

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

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

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

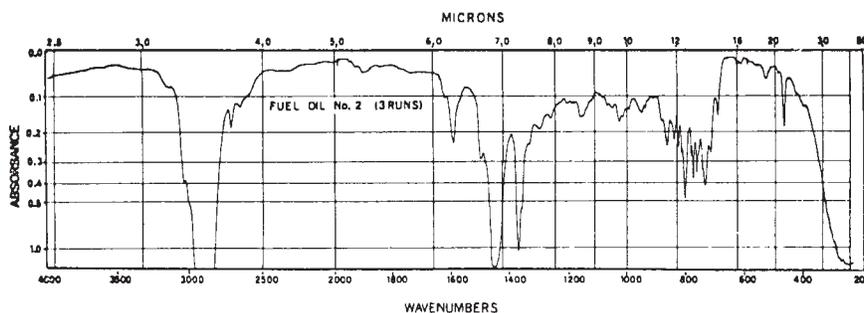


FIG. 1 Complete Spectrum of a No. 2 Fuel Oil, Analyzed in Triplicate

## 11. Analytical Procedures

### 11.1 Recording Spectra for Dispersive Instruments:

11.1.1 Operate the instrument in accordance with the manufacturer's instructions. Refer to Practices E 168 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 E 275. 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  $1583.1$   $\text{cm}^{-1}$  which should be distinct and well defined.<sup>7</sup> This is also true for the sideband at  $3100$   $\text{cm}^{-1}$  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  $1975 \pm 20$   $\text{cm}^{-1}$ .

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  $600$   $\text{cm}^{-1}$  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  $650$   $\text{cm}^{-1}$  for HATR cells with ZnSe, due to the spectral absorbance cutoff for ZnSe.

11.3 Preparation of Sample—Refer to Annex A1 and Practice D 3326 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 D 3326 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.)

## 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  $700$   $\text{cm}^{-1}$  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  $600$   $\text{cm}^{-1}$  for four oils weathered over 4 days. They show the general effects of weathering on baselines between  $1300$  and  $900$   $\text{cm}^{-1}$  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  $1975$   $\text{cm}^{-1}$ , that is, that they were set at an absorbance of 0.02 (95 % T).

12.3.1.2 Next, examine the absorbance at  $1377$   $\text{cm}^{-1}$  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  $600$   $\text{cm}^{-1}$ . For petroleum oils, the baseline

<sup>7</sup> Tables of Wavenumbers For The Calibration of Infrared Spectrometers, IUPAC, Commission on Molecular Structure and Spectroscopy, Butterworth and Co., Toronto, Canada, 1961.

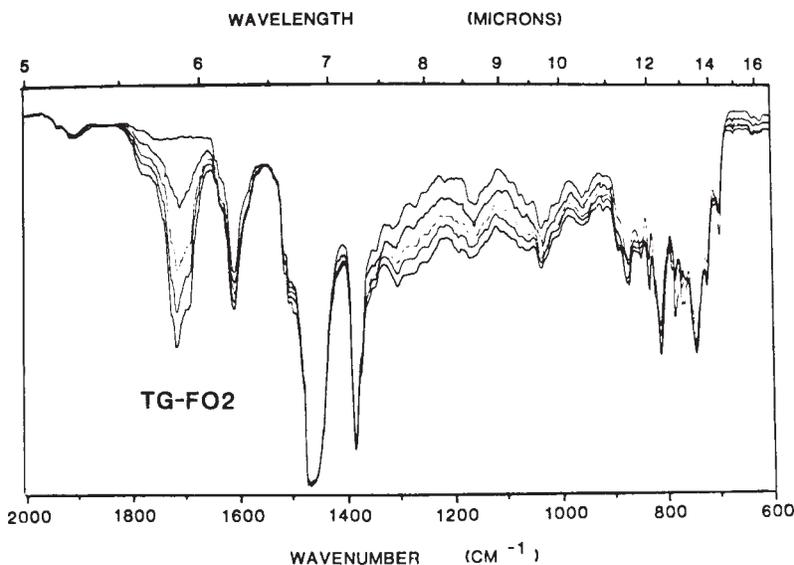


FIG. 2 No. 2 Fuel Oil Progressive Weathering Effects, 0 to 4 Days

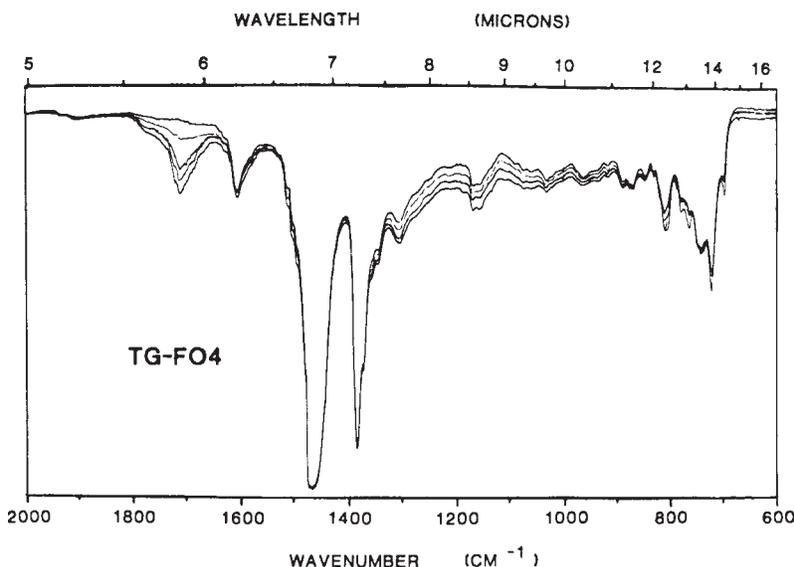


FIG. 3 No. 4 Fuel Oil Progressive Weathering Effects, 0 to 4 Days

will tend to move downward with weathering (to higher absorbance between 1350 to 900  $\text{cm}^{-1}$ ) but with little relative change of the peaks in that range.

12.3.1.4 Examine the 1770 to 1685  $\text{cm}^{-1}$  region to determine the extent of weathering—particularly in the 1708  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  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, re-dry the sample.

(b) (b) For residual  $\text{MgSO}_4$  from the drying procedure, check the 610  $\text{cm}^{-1}$  region for a small, sharp peak, and look for peak increases at 1075 and 1175  $\text{cm}^{-1}$ .

(c) (c) For residual pentane, if the sample has been deasphalted, look for the presence of small twin peaks at 910

and 920  $\text{cm}^{-1}$ . There also would be a corresponding increase in the peak at 722  $\text{cm}^{-1}$ .

12.3.1.6 Finally, scrutinize the “oil fingerprint” region (900 to 700  $\text{cm}^{-1}$ ) 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  $\text{cm}^{-1}$ . In that case, the spectra are compared directly in order to identify without consideration of weathering changes described as follows for petroleum oils.

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

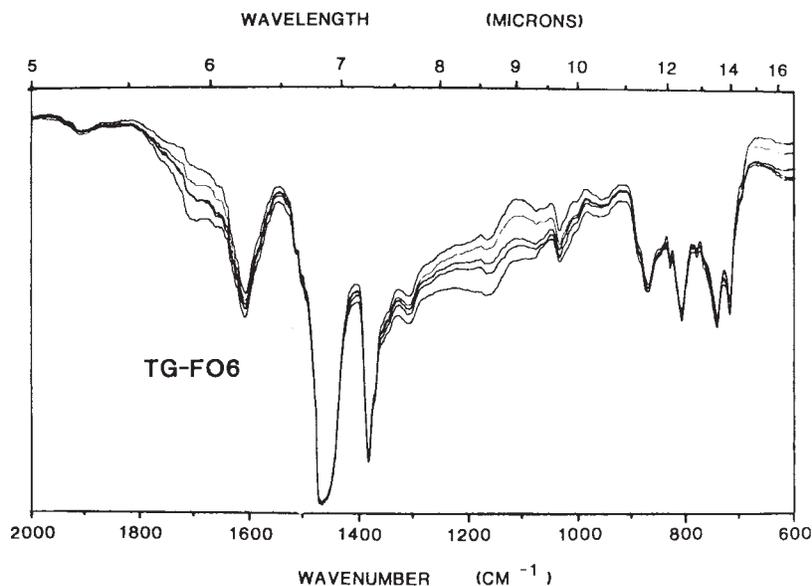


FIG. 4 No. 6 Fuel Oil Progressive Weathering Effects, 0 to 4 Days

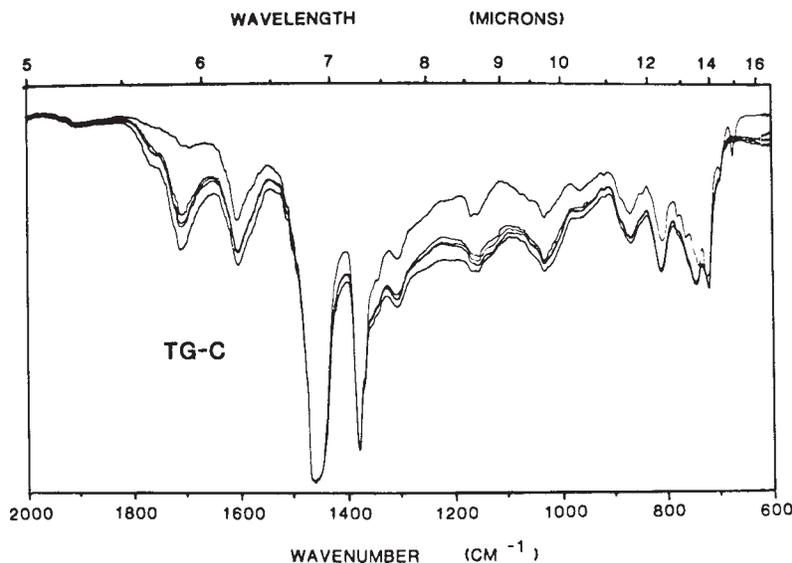


FIG. 5 Crude Oil Progressive Weathering Effects, 0 to 4 Days

12.3.3 If the spectra are of the same sample thickness, compare overall shapes over the entire curves. If obvious major differences (peaks or peak ratios) appear in the region between 2000 to 600  $\text{cm}^{-1}$ , then the spectrum of the suspect oil is designated a nonmatch (NM). If peak-for-peak similarities do exist in the overall shape of the entire curves, proceed to the next step.

NOTE 7—There are exceptions, namely in those cases when a contaminant is obviously present, for example, ester carbonyl compound. In some instances, the contaminant can be removed selectively by saponification. When it cannot, it may be indeterminate (I) whether or not the two oils being compared have a common origin.

12.3.4 Examine 1685, 1708, and 1770  $\text{cm}^{-1}$  for indications of weathering. Here, many weathered oils display well-defined carbonyl peaks, particularly at 1708 to 1710  $\text{cm}^{-1}$ . Even if the peaks are present in the carbonyl region in the spilled oil but not in the suspect oil, continue to the next step.

NOTE 8—If neither the spill nor suspect show signs of oxidative weathering, then any differences in the spectra are real and the oils do not match (NM).

12.3.5 Next, examine the region from 1350 to 900  $\text{cm}^{-1}$ , with special emphasis on the peaks at 1304, 1165, and 1032  $\text{cm}^{-1}$ . These peaks generally remain constant in shape and relative to each other in size with weathering except for a general shift of the baseline (between 1300 and 900  $\text{cm}^{-1}$ ) to higher absorbances (see Figs. 2-5). As the baseline shifts to higher absorbances the peak shapes tend to broaden, particularly with light oils—especially in the 1165  $\text{cm}^{-1}$  region. The 1165 unit also broadens with the presence of carbonyl impurities (likely ester C-O-C asymmetrical stretch). Taking these factors into account, if the curves are unlike, the oils do not match (NM).

12.3.6 The next area scrutinized is the critical “oil fingerprint” region which uniquely characterizes an oil (900 to 700

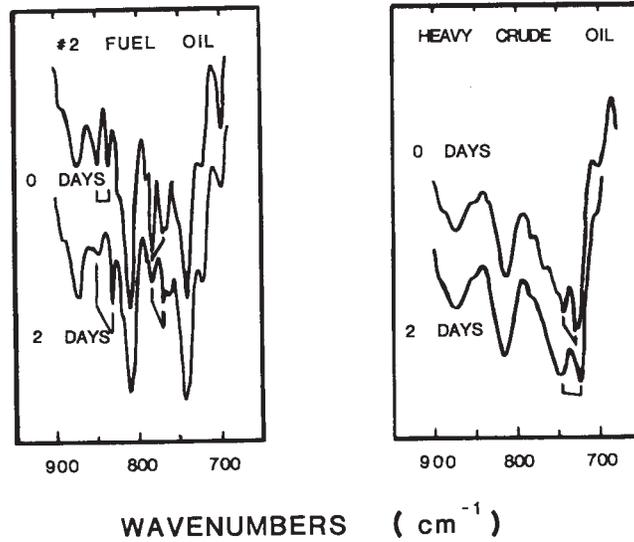


FIG. 6 Weathering Changes of Light and Heavy Oils

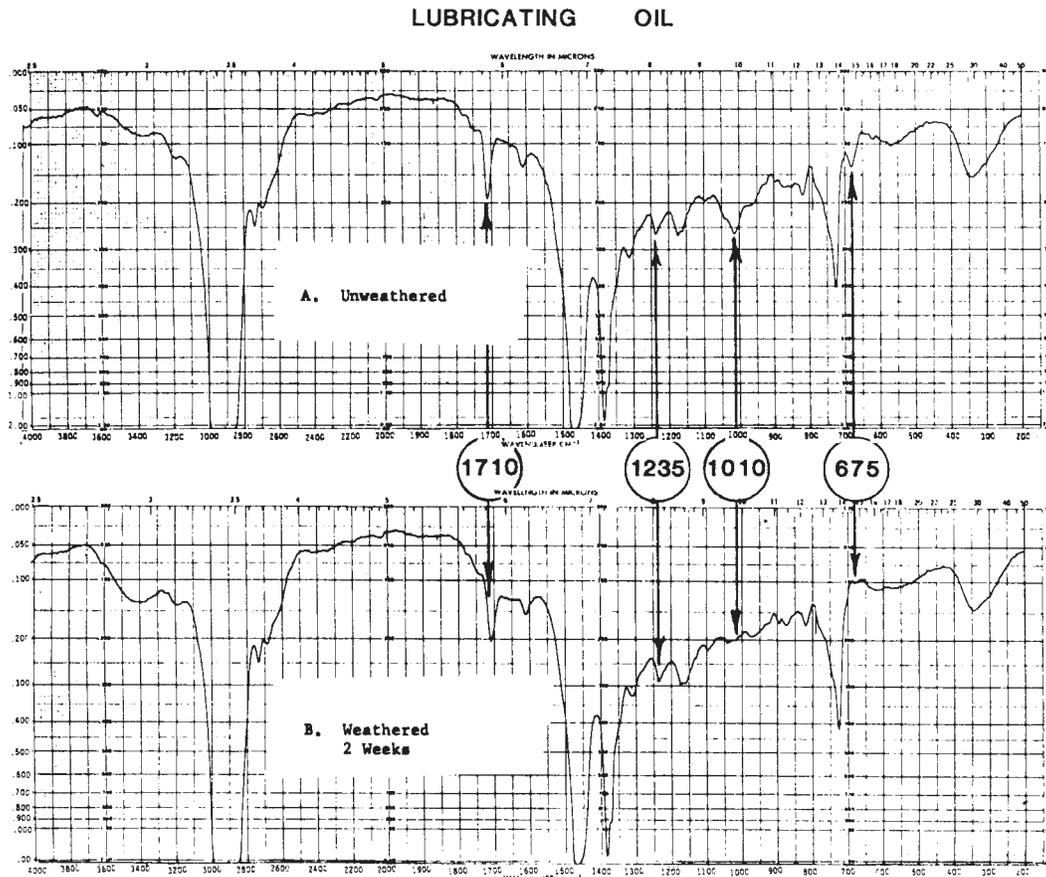


FIG. 7 Weathering of a Typical Lubricating Oil

cm<sup>-1</sup>). When the spilled oil is the same as the suspect oil, the peak shapes, amplitudes, and locations correspond, point for point, to each other. This spectral overlay is designated as a “match.” For detailed examination of this region, lay one curve over the other in such a way that the curve traces coincide at 875 cm<sup>-1</sup> prior to a peak-by-peak comparison.

NOTE 9—The 875 cm<sup>-1</sup> point was selected to give good overlays of the 900 to 700 cm<sup>-1</sup> region.

12.3.7 If an oil has been altered by weathering, the analyst must take such effects into consideration. If the effects are moderate, the analyst can account for them as outlined below. If the effects are severe, the best procedure is to weather

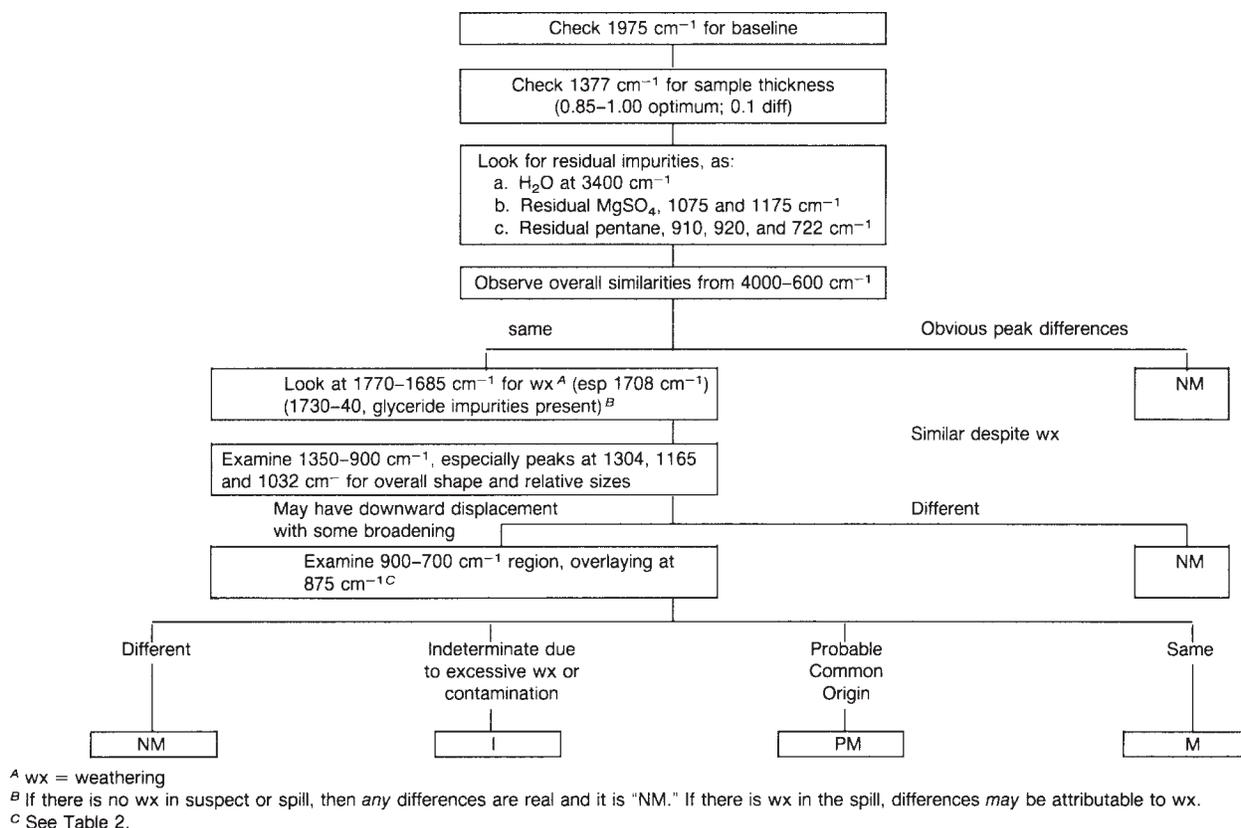


FIG. 8 Flow Chart for Infrared Spectral Comparisons of Oil

artificially a sample of the suspect to about the same degree as the spill (see Practices D 3326)<sup>8</sup>. For the shorter time frame, under 1 week, the weathering changes are qualitatively well known. The lighter oils weather faster during this period; the heavier oils progressively more slowly. The following describes the significant weathering effects for different oil classes:

12.3.7.1 Light distillate fuel oils and diesels display losses in band structure at 849, 810, 790, 782, 766, and 700 wave numbers ( $\text{cm}^{-1}$ ). There are apparent increases at 871, 832, and  $722 \text{ cm}^{-1}$  due in part to a downward shift of baseline (see Fig. 2 and Fig. 6).

12.3.7.2 No. 4 fuel oils show a decrease in the ratio of  $744/722 \text{ cm}^{-1}$  peaks. There is an apparent increase at  $722 \text{ cm}^{-1}$  with concomitant decreases at 700, 744, 766, 782, 790, and  $810 \text{ cm}^{-1}$  (see Fig. 3).

12.3.7.3 No. 5 and No. 6 fuel oils show minimal weathering effects, with slow development of the carbonyl peak at  $1708 \text{ cm}^{-1}$  and an apparent increase in absorbance at  $722 \text{ cm}^{-1}$  (see Fig. 4).

12.3.7.4 Crude oils weather differently depending on the nature of the crude oil. Light crude oils will weather like light fuel oils; heavy crude oils like heavy fuel oils (see Figs. 4–6.)

12.3.7.5 Lubricating oils may have additives with bands at 675, 1010, and  $1235 \text{ cm}^{-1}$ . The  $1235 \text{ cm}^{-1}$  additive peak, if

present, remains stable even with weathering and is an excellent indicator of a lubricating oil. The 1010 and  $675 \text{ cm}^{-1}$  bands lose structure on weathering (see Fig. 7). The  $722 \text{ cm}^{-1}$  band is very strong in paraffin-based lubricating oils and diminishes slightly with weathering. It is another excellent clue for the classification of lubricating oils. Some No. 2 or diesel oils weather to leave a residue with a large  $722 \text{ cm}^{-1}$  band and strongly resemble lubricating oils.

### 13. Report

13.1 Based upon the visual comparison of the spectra and after considering 12.2, report the sample of unknown origin as belonging to one of the categories below (see Table 2 for a summary of degrees of match):

13.1.1 *Match (M)*—Like one or more of the samples submitted for comparison. The spectra must be a virtual overlay with only minor differences permissible in the  $900$  to  $700 \text{ cm}^{-1}$  region (on the order of 0 to 2 mm (to 1.5 % transmittance) maximum for a spectrum approximately 15 cm from top to bottom).

13.1.2 *Probable Match (PM)*—Like one or more of the samples submitted for comparison except: differences attributable to specific contamination, differences in sample thickness, or changes that could be attributed to weathering (for example, carbonyl formation; baseline lowering from  $1375$  to  $900 \text{ cm}^{-1}$  with no marked peak ratio changes, that is, same general shape; moderate changes in the fingerprint,  $900$  to  $700 \text{ cm}^{-1}$  region—on the order of 2 to 7 mm (1.5–5 % *T*) displacement on peaks known to change).

<sup>8</sup> Anderson, C. P., Killeen, T. J., Taft, J. B., and Bentz, A. P., "Artificial Oil Weathering Techniques," Paper 527, 1979 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

**TABLE 2 Degree of Match**

Designation	Symbol	Characteristics
Match	M	Virtual overlay. Only minor differences in 900 to 700 $\text{cm}^{-1}$ region (0 to 2 mm to 1.5 % T).
Probable match	PM	Differences can all be attributed to weathering (carbonyl formation; baseline lowering from 1375 to 900 $\text{cm}^{-1}$ with no peak ratio changes; moderate differences in 900 to 700 $\text{cm}^{-1}$ region (2 to 7 mm; 1.5 to 5 % T) or differences due to specific contaminations.
Indeterminate <sup>A</sup>	I	Strong indications of a common origin, but weathering, contamination or thickness differences are greater than PM.
Nonmatch	NM	Spectra different; different peaks or peak ratios.

<sup>A</sup> Indeterminate spectra are similar. However, the differences are of such a nature that the analyst cannot say categorically (in a forensic sense) that the oils have different origins.

13.1.3 *Indeterminate (I)*—Like one or more of the samples submitted for comparison except for certain differences as described in 13.1.2. Such differences would be of increased magnitude over those for PM, but the overall similarity of the two oils suggests a common origin. Gross weathering, contamination or cell thickness differences may make it impossible to ascertain whether the unknown is the same oil or a totally different oil.

13.1.4 *Nonmatch (NM)*—Unlike the samples submitted for comparison. This includes presence or absence of peaks in one of the spectra, peak reversals, etc.

## 14. Precision and Bias

14.1 No statement is made about either the precision or bias of this test method for measuring waterborne oils, since the result merely states whether there is conformance to the criteria for success specified in the procedure.

## ANNEXES

### (Mandatory Information)

#### A1. LABORATORY SAMPLING

A1.1 Field samples are subsampled in the laboratory, taking approximately 1 g of oil, if available. The oil is withdrawn as free of water and debris as possible.

A1.1.1 *Thin Films*— For oil samples present as thin films on water, extract the film from the surface by placing a layer of spectroquality hexane (4 to 5 mm on the surface); stir and withdraw with a Pasteur pipet. Repeat, if necessary, to remove all the oil. Then evaporate the solvent under dry nitrogen.

A1.1.2 *Oil on Sand or Debris*—For oil samples on sand or debris, the oil is floated off with water, if possible; otherwise, it is extracted with pentane or hexane and dried (see Practices D 3326, Method B).

A1.1.3 *Emulsified Oil*— Oil emulsions can be broken by adding pentane or hexane and centrifuging. Sodium chloride will assist in breaking fresh-water emulsions. Separate layers and work up as in Practice D 3326, Method B.

#### A2. CELL LOADING PROCEDURE (LIQUID CELLS) (REFER TO PRACTICES E 168)

A2.1 Liquid cells (sealed or sealed-demountable cells) are generally used with potassium bromide (KBr) windows and a 0.05-mm TFE-fluorocarbon or lead spacer.

NOTE A2.1—If the sample is suspected of being wet, use AgBr windows which will resist reaction with water.

NOTE A2.2—For light oils (low viscosity) such as No. 2 fuel oil, the sealed cell should be used. It reduces evaporation losses and eliminates pathlength as a variable. DO NOT use a sealed cell if there is ANY chance that the sample is wet!

A2.2 Incline the cell with one port at top and the other below. Fill the cell from the bottom port using a Pasteur pipet.

NOTE A2.3—Use care to avoid forming bubbles.

A2.3 Stopper the cell with TFE-fluorocarbon plugs, taking care to avoid creating air bubbles or applying undue pressure. Insert the bottom plug first using a twisting motion. Gently insert the top plug.

NOTE A2.4—If an oil is too viscous to flow in a liquid cell, a transmission spectrum still can be obtained. A large drop of the oil is placed on the center of a KBr window. Another KBr window is placed over this with a 0.05-mm TFE-fluorocarbon or lead spacer forming a uniform oil smear. Always use the same spacer for obtaining spectra to be compared.

### A3. CELL LOADING PROCEDURE (LOW-CAPACITY SILVER HALIDE CELL)

A3.1 The low-capacity cell consists of two silver bromide (AgBr) or silver chloride (AgCl) windows with a 0.025-mm cavity pressed into the silver halide. The advantage of using this cell lies in the small amount of sample required for an analysis and the ease of cleaning the cell.

A3.1.1 Place a drop of oil sample into the cavity of one AgBr or AgCl window.

A3.1.2 Place the flat side of the second window over the sample and carefully press together to obtain a 0.025-mm pathlength.

A3.1.3 Slide the windows around on each other, with one edge up, to work out all air bubbles.

A3.1.4 Gently lay the windows in the TFE-fluorocarbon holder and screw in the retaining ring.

### A4. CELL AND CRYSTAL CLEANING PROCEDURES

A4.1 Thoroughly clean cell windows and crystals. Monitor the complete removal of residual hydrocarbon materials by examining the infrared absorption in the 3000 to 2900  $\text{cm}^{-1}$  region. A clean cell will show *no* absorption in this region.

A4.1.1 For sealed demountable cells: dismantle cells completely and thoroughly rinse each component. Rinse the windows with a solvent such as cyclohexane; the rest of the cell (spacers, end plates, parts, and plugs) rinse with another suitable solvent such as methylene chloride.

A4.1.2 Store cells and window components in a desiccator.

A4.2 *HATR With ZnSe Plate:*

A4.2.1 Clean the ZnSe plate thoroughly with cyclohexane. Soap and water may be used on this cell. It is critical that the crystal not be scratched. The window may be repolished by a commercial service which specializes in this process.

### A5. CARE OF CELL WINDOWS

A5.1 *Potassium Bromide (KBr)*—Keep potassium bromide windows in a desiccator when not in use, since moisture will fog them. If they become scratched, grind them on fine emery paper (600 grit). For deep scratches, first use a coarser grade emery paper (220 grit), then polish the windows on an optical lap using polishing rouge. (Detailed instructions are given by the manufacturers of the commercially available window-polishing kits.)<sup>9</sup>

A5.2 *Silver Bromide (AgBr)*—Handle AgBr windows carefully to avoid scratching since they are very soft. These windows may react with their aluminum containers; therefore, prevent their contact with the metal. Also, protect them from light as much as possible, since they darken on exposure to ultraviolet light. These limitations require occasional replacement of these windows. The replacement frequency is governed by the spectral baseline changes due to these factors. A new window will register about 43 % transmission at 4000  $\text{cm}^{-1}$ , when it drops to 33 %, it should be discarded.

<sup>9</sup> Application Notes: *How to Polish Crystals*, Barnes Engineering Co.

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