



Standard Test Methods for Examination of Electrical Insulating Oils by Infrared Absorption¹

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1. Scope

1.1 These test methods cover the recording and interpretation of infrared absorption spectra of electrical insulating oils from 2.5 to 25 μm (4000 to 400 cm^{-1}).

NOTE 1—While these test methods are specific to ratio recording double-beam dispersive spectrophotometers, recent developments have made available single-beam Fourier-transform rapid scan infrared spectrophotometers. By computerized subtraction techniques, ratio methods can be used. This equipment may be suitable if it complies with the specifications described in Table 1.

1.2 Two test methods are covered, a Reference Standard Test Method and a Differential Test Method.

1.3 These test methods are designed primarily for use as rapid continuity tests for identifying a shipment of oil from a supplier by comparing its spectrogram with that obtained from previous shipments, or with the sample on which approval tests were made. They also may be used for the detection of certain types of contamination in oils, and for the identification of oils in storage or service, by comparison of the spectra of the unknown and known oils. The test methods are not intended for the determination of the various constituents of an oil.

1.4 **Caution**—Infrared absorption is a tool of high resolving power. Conclusions as to continuity of oil quality should not be drawn until sufficient data have been accumulated so that the batch-to-batch variation is clearly established.

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.*

2. Referenced Documents

2.1 ASTM Standards:

D 923 Test Method for Sampling Electrical Insulating Liquids²

E 131 Terminology Relating to Molecular Spectroscopy³

E 168 Practices for General Techniques of Infrared Quantitative Analysis³

¹ These test methods are under the jurisdiction of ASTM Committee D-27 on Electrical Insulating Liquids and Gases and are the direct responsibility of Subcommittee D27.03 on Analytical Tests.

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² Annual Book of ASTM Standards, Vol 10.03.

³ Annual Book of ASTM Standards, Vol 03.06.

E 932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrophotometers³

3. Terminology

3.1 *Definitions*—For definitions of terms and symbols, refer to Terminology E 131.

4. Summary of Test Methods

4.1 The infrared absorption spectrum may be recorded on the spectrophotometer by either of the two test methods outlined below. In both test methods differences in wavelength or frequency and intensity of the absorption bands are observed and measured.

4.1.1 *Reference Standard Test Method*—An infrared cell filled with the insulating oil sample is placed in the sample beam of the spectrophotometer. With the shutter of the reference beam open, the infrared absorption spectrum is recorded over the entire range of the instrument. The absorption spectrum of the sample oil is compared with a reference spectrum obtained with oil from a previous sample or the qualification oil.

4.1.2 *Differential Test Method*—Two cells having the same sample path length are filled, one with sample oil and the other with the reference oil. The filled cells are then placed in the paths of the sample and reference beams, respectively, and the differential absorption spectrum recorded. This spectrum is then compared with the reference differential spectrum obtained in a similar manner with the same cells filled with the reference oil.

5. Significance and Use

5.1 The infrared spectrum of an electrical insulating oil is a record of the absorption of infrared energy over a range of wavelengths. The spectrum indicates the general chemical composition of the sample.

NOTE 2—The infrared spectrum of a pure chemical compound is probably the most characteristic property of that compound. However, in the case of oils, multicomponent systems are being examined whose spectra are the sum total of all the spectra of the individual components. Because the absorption bands of the components may overlap, the spectrum of the oil is not as sharply defined as that for a single compound. For these reasons, these test methods may not in every case be suitable for the quantitative estimation of the components of such a complex mixture as mineral oil.

TABLE 1 Specifications for Spectrophotometer

Property	Part	Section	Specification
Wavelength repeatability	I	2, 3(a), 3(c)	$\pm 0.02 \mu\text{m}$
Wavelength accuracy	II	4, 8	$\pm 0.03 \mu\text{m}$
Spectral resolution	III	9, 10, 13	Condition C
Photometric repeatability and linearity	IV	14, 15, 16, 17	Not yet established
Stray radiant energy	V	18, 19, 20	The scattered light as measured with a CaF_2 shutter shall not exceed 0.5 % transmission at $14 \mu\text{m}$ (714 cm^{-1})

6. Apparatus

6.1 *Infrared Spectrophotometer*—An infrared spectrophotometer capable of meeting the specifications outlined in the sections indicated in Table 1 in the 2.5 to 25- μm (4000 to 400-cm^{-1}) range when measured in accordance with Practice E 932.

6.2 *Absorption Cells*—Three types of cells may be used for measuring the absorbance of electrical insulating oils, namely (1) the sealed or fixed liquid cell, (2) the variable space cell, and (3) the demountable liquid cell. The use of the demountable cell is not recommended for quantitative analysis. Use sealed fixed liquid and demountable liquid cells that meet the requirements of Practices E 168. When measuring the absorbance of an oil by the Reference Standard Test Method, a sealed or fixed cell having a sample path length of 0.1 ± 0.014 mm is recommended. Cells having a fixed path length of 0.2 ± 0.028 mm have been found to be acceptable. When the Differential Test Method is used, two matched sealed or fixed cells each having a sample path length of 0.050 ± 0.007 mm is recommended. Where two matched cells are not available, a variable space cell may be adjusted and used in place of one fixed cell. With spectrophotometers having a range up to $16.7 \mu\text{m}$ (600 cm^{-1}), liquid cells may be provided with sodium chloride (NaCl) windows. With instruments having a range up to $25 \mu\text{m}$ (400 cm^{-1}), use liquid cells with potassium bromide (KBr) windows.

6.3 *Cell Filling Device*—Use a hypodermic syringe of 5-mL capacity or other apparatus suitable for filling the liquid cells, which are constructed of glass, stainless steel, or other inert material.

7. Sampling

7.1 Obtain the sample in accordance with Test Methods D 923.

8. Calibration

8.1 Adjust and calibrate the spectrophotometer in accordance with Practice E 932.

9. Conditioning

9.1 Store the sample in its original container and shield it from light. Allow the sealed container to stand undisturbed in the room in which the test is to be made for a sufficient period of time to permit the sample to attain room temperature before it is opened.

9.2 Prior to taking specimens of transformer oil or light cable oil, shake the sample container thoroughly and allow it to stand undisturbed for 15 min in order for all air bubbles to be dissipated from the sample. For heavy cable oils, gently tilt or invert the sample container and swirl the fluid several times and then permit it to stand undisturbed for 15 min.

10. Cleaning, Storing, and Filling the Cell

10.1 After the cells have been used, thoroughly rinse them with a suitable reagent grade or functionally equivalent organic solvent such as 1,1,1-trichloroethane, isopropanol, or chloroform, followed by rinsing with a reagent grade or functionally equivalent hydrocarbon solution, such as heptane or petroleum naphtha and store in a desiccator until they are to be used.

10.2 When a cell is to be used, clean it again as described in 10.1 followed by two rinsings with the sample obtained from the middle portion of the fluid. Rinse the cell with the sample with the use of the hypodermic syringe, which shall also be cleaned prior to use in accordance with 10.1.

10.3 When filling the cell, fill the cleaned and rinsed syringe with about 2 mL of the sample. With the cell in the upright position and the TFE-fluorocarbon plugs removed from the ports in the cell, insert the syringe in the lower port and slowly fill the cell by exerting gradual pressure on the syringe plunger. When oil is observed flowing from the top port, lay the cell flat, remove the syringe, and plug the lower port.

NOTE 3—**Caution:** A pocket in some cells may secrete minute quantities of a previous sample which may contaminate the current sample and cause erroneous results. Where this is suspected, dry the cell out after cleaning and rinsing with a reagent grade or functionally equivalent hydrocarbon solvent, such as heptane or petroleum naphtha, by sweeping it with dry nitrogen applied at a pressure not exceeding 20 mm Hg.

11. Procedure—Reference Standard Test Method

11.1 Fill a clean sealed or fixed cell having a sample path length of 0.10 ± 0.014 mm (or 0.20 ± 0.028 mm) with the sample as outlined in Section 10 and place the filled cell in the sample beam. Leave the shutter in the reference beam in the open position. Adjust the scanning speed, gain, and other variable controls to the values established for the particular spectrophotometer to provide the desired resolution. Where the instrument is provided with a scale changer, it is recommended that it be used with the 2.5 to 1 ratio in preference to the linear mode in obtaining recordings of the spectra. Record the infrared spectrum over the entire range of the instrument in accordance with Practices E 168, using nonlinear absorbance charts.

11.2 Compare the infrared spectrum of the sample with the reference spectrum of a sample from a previous shipment, or the approved qualification oil, recorded by the same procedure, using the same cell and with the same instrument settings. Comparison can be made by superimposing the two spectra over a viewing light or by testing both samples and recording the infraspectrum on the same chart using different colored inks. Note and record any differences in the wavelengths or frequencies of absorption bands and in apparent intensity of

these bands. Differences between these spectra can be amplified considerably by using an expanded ordinate scale during the scanning.

11.3 Measurements of the absorbance at specific absorption bands, if required, are made by the base-line method described in Practices E 168 and corrected for thickness by expressing the results as absorbance per millimetre.

12. Procedure—Differential Test Method

12.1 Fill with the reference oil two matched cells, each having a path length of 0.050 ± 0.007 mm; insert one cell in the reference beam and the other in the sample beam. Adjust the spectrophotometer as described in 10.1, set the pen position at approximately 50 % transmission at $2.5 \mu\text{m}$ (4000 cm^{-1}), and record the differential infrared spectrum over the entire range of the instrument, in accordance with Practices E 168. Evidences of peaks (positive or negative) will be an indication that the cells are not matched or that the amplifier balance is not properly adjusted.

NOTE 4—Peaks that are below the base line are considered “positive” and those above the base line are “negative.”

12.2 Where two fixed matched cells having a sample path length of 0.050 ± 0.007 mm are not available, a variable cell whose sample path length can be adjusted to equal the path length of the fixed cell may be used. The procedure for adjusting the sample path length of the variable cell is as follows:

12.2.1 Set the variable path length cell to the nominal thickness of the fixed path length liquid cell.

12.2.2 Place the variable and fixed path length cells, both filled with the reference oil, in the paths of the reference and sample beams, respectively.

12.2.3 Close both beams of the spectrophotometer and adjust the electrical balance on the amplifier to no drift on the recorder pen.

12.2.4 Set the pen position to approximately 90 % transmission at $2.5 \mu\text{m}$ (4000 cm^{-1}).

12.2.5 Record the differential infrared spectrum over the entire range of the instrument in accordance with Practices E 168.

12.2.6 Adjust the path length of the variable cell until absorptions due to differences in sample path length are no longer present; then repeat as in 12.2.5.

12.3 With the same two matched cells with which the reference/reference differential spectrum was recorded, fill one with the reference oil and the other with the sample oil and insert them in the paths of the reference and sample beams, respectively. Record the differential infrared spectrum over the entire range of the instrument in accordance with Practices E 168, using a nonlinear absorbance chart. Compare the reference/reference differential infrared spectrum obtained in accordance with either 12.1 or 12.2 with the sample/reference differential infrared spectrum of this paragraph. Comparison can be made by recording on the same chart with a different colored ink or by superimposing the two spectra over a viewing light. Note and record any differences in the wavelengths or frequencies of absorption bands and in apparent intensity of these bands.

NOTE 5—This procedure is recommended to ensure that the recording of spurious absorptions due to amplifier drift at zero energy null points are not erroneously assumed to be absorptions induced by differences in composition.

12.4 Measurements of the absorbance per millimetre, if required, shall be made as described in 11.3.

13. Calculation

13.1 Convert measured absorbances and differences in absorbance and report as absorbance per millimetre in order to correct for variations in the sample path length, within the tolerances prescribed for the cells. Absorbance may not be a linear function of sample path length over a wide range of cell lengths; therefore strictly adhere to the cell sizes and make comparison of absorbance per millimetre measured with different path lengths only with caution. Calculate absorbance per millimetre using the equations given in this section for measurements obtained by either the Reference Standard Test Method or the Differential Test Method.

13.2 *Reference Standard Test Method*—Differences in the absorbance per millimetre at specific absorption bands of spectra obtained from two samples of oil shall be expressed as the difference in absorbance, calculated as follows:

$$\begin{aligned} &\text{Difference between absorbance per millimetre} \\ &\text{of sample } S \text{ and sample } R \text{ at } X \mu\text{m} \\ & (10,000/X \text{ cm}^{-1}) = (A_S - A_R)/T \end{aligned}$$

where:

A_S = absorbance of the sample oil at $X \mu\text{m}$ ($10,000/X \text{ cm}^{-1}$) as calculated by the base-line method Practices E 168) at λ_1 and λ_2 boundary points,

A_R = absorbance of the reference oil at $X \mu\text{m}$ ($10,000/X \text{ cm}^{-1}$) as calculated by the base-line method (Practices E 168) at λ_1 and λ_2 boundary points,

X = wavelength of wavenumber of absorption band, and

T = sample path length of cell used, mm.

13.3 *Differential Test Method*—The absorbance per millimetre at specific absorption bands of the differential spectrum obtained from two samples of oil shall be expressed as follows:

$$\begin{aligned} &\text{Difference between differential absorbance per millimetre} \\ &\text{of sample } S \text{ and sample } R \text{ at } X \mu\text{m} \\ & (10,000/X \text{ cm}^{-1}) = (A_d - A_b)/T_S \end{aligned}$$

where:

A_b = differential absorbance at $X \mu\text{m}$ ($10,000/X \text{ cm}^{-1}$) when both reference and sample cells contain reference oil as calculated by the base-line method (Practices E 168) at λ_1 and λ_2 boundary points,

A_d = differential absorbance at $X \mu\text{m}$ ($10,000/X \text{ cm}^{-1}$) when both reference and sample cells contain reference and sample oils, respectively, as calculated by the base-line method (Practices E 168) at λ_1 and λ_2 boundary points,

X = wavelength of wave number of absorption band, and

T_S = sample path length of sample cell, mm.

NOTE 6—To indicate the direction of the peak from the base line, a

positive and negative notation shall be used to express the value of A_b and A_d . A positive value shall signify that the sample oil has greater absorbance than the reference oil whereas a negative sign shall indicate a lesser absorbance.

14. Report

14.1 When comparing the spectrum of a sample oil S with that of a reference oil R and there is no significant difference between them, report that the apparent infrared absorbance per millimetre of the two samples is the same. However, where the spectra of these oils differ at any band or points that may be considered significant, report that the apparent infrared absorbance per millimetre of sample S is significantly higher or lower than that of sample R in the band between $Y \mu\text{m}$ ($10,000/Y \text{ cm}^{-1}$) and $Z \mu\text{m}$ ($10,000/Z \text{ cm}^{-1}$) or at a point of $X \mu\text{m}$ ($10,000/X \text{ cm}^{-1}$).

14.2 Where the difference in absorbance per millimetre has been calculated as outlined in 12.2 report that:

The infrared absorbance per millimetre of sample S is higher or lower than that of sample R at $X \mu\text{m}$ ($10,000/X \text{ cm}^{-1}$) by _____ absorbance per millimetre.

14.3 Report when the differential spectrum of two oils (R and S) obtained on one instrument does not show any significant difference over the entire range of the instrument. Also report where the difference is significant at any points or bands.

15. Precision and Bias

15.1 It is not practical to specify the precision or bias of these test methods, as they are meant to be qualitative or semiquantitative determinations.

16. Keywords

16.1 electrical insulating oils; infrared; oil; spectrophotometer

APPENDIX

(Nonmandatory Information)

X1. SIGNIFICANCE OF ABSORPTION BANDS

X1.1 Some reference tests may be used to determine the significance of specific absorption bands and of changes in their absorption.^{4,5,6} The following are some of the absorption bands commonly observed in electrical insulating oil spectra:

2.8 μm (3571 cm^{-1})

This region is assigned to O—H and N—H stretching vibrations and is useful for the determination of certain phenol-type oxidation inhibitors. Minor amounts or minor changes in amount will not be detected with the cell thickness specified in this method. A cell with 1 mm or more sample path length is required to detect such changes. This region is also an absorption wavelength for moisture content.

3.4, 6.9, 7.3 μm (2941, 1449, 1370 cm^{-1})

Paraffinic methyl and methylene absorptions. Changes in concentration are not usually detected with the sample path length specified.

5.7 to 6.0 μm (1754 to 1667 cm^{-1})

The region of carbonyl (C = O) stretching vibrations. The specific locations of absorptions in this region permit generalizations as to the type of compound present, that is, ester, acid, anhydride, ketone, etc. These absorptions serve to indicate oxidation products or contaminants.

6.23 μm (1605 cm^{-1})

Aromatic structure absorptions indicative of the aromaticity of the oil. This region also is an absorption wavelength for moisture content.

8 to 15 μm (1250 to 667 cm^{-1})

Region of bending or deformation vibrations generally subject to interaction with other vibrations in the molecule. This is known as the finger print region. These effects are found over wide frequency ranges, which become useful as an identifying characteristic of a compound. The contour of the curve in this region is a unique characteristic of an oil and changes in the refining process or crude source may be reflected in the contour.

13.8 μm (725 cm^{-1})

Methylene skeletal rocking vibration, from four or more adjacent methylene groups, which provides an indication of long chain paraffinic structure present in the oil.

⁴ Colthup, N. B., "Spectra Structure Correlations in the Infrared Region," *Journal of the Optical Society of America*, Vol 40, No. 6, June 1950, p. 397.

⁵ Jones, R. N., and Sandorfy, C., *Chemical Applications of Spectroscopy*, Vol 9, Interscience Publishers, Inc., New York, N. Y., Chapter IV, 1956, p. 247.

⁶ Bellamy, L. S., *The Infrared Spectra of Complex Molecules*, Methuen and Co., Ltd., London, England, 1958.

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