



Designation: D7414 – 21

# Standard Test Method for Condition Monitoring of Oxidation in In-Service Petroleum and Hydrocarbon Based Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry<sup>1</sup>

This standard is issued under the fixed designation D7414; 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 monitoring oxidation in in-service petroleum and hydrocarbon based lubricants such as in diesel crankcase, motor, hydraulic, gear and compressor oils, as well as other types of lubricants that are prone to oxidation.

1.2 This test method uses Fourier Transform Infrared (FT-IR) spectrometry for monitoring build-up of oxidation products in in-service petroleum and hydrocarbon based lubricants as a result of normal machinery operation. Petroleum and hydrocarbon based lubricants react with oxygen in the air to form a number of different chemical species, including aldehydes, ketones, esters, and carboxylic acids. This test method is designed as a fast, simple spectroscopic check for monitoring of oxidation in in-service petroleum and hydrocarbon based lubricants with the objective of helping diagnose the operational condition of the machine based on measuring the level of oxidation in the oil.

1.3 Acquisition of FT-IR spectral data for measuring oxidation in in-service oil and lubricant samples is described in Practice D7418. In this test method, measurement and data interpretation parameters for oxidation using both direct trend analysis and differential (spectral subtraction) trend analysis are presented.

1.4 This test method is based on trending of spectral changes associated with oxidation of in-service petroleum and hydrocarbon based lubricants. Warnings or alarm limits can be set on the basis of a fixed minimum value for a single measurement or, alternatively, can be based on a rate of change of the response measured, see Ref (1).<sup>2</sup>

1.4.1 For direct trend analysis, values are recorded directly from absorption spectra and reported in units of absorbance per 0.1 mm pathlength.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.96.03 on FTIR Testing Practices and Techniques Related to In-Service Lubricants.

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<sup>2</sup> The boldface numbers in parentheses refer to a list of references at the end of this standard.

1.4.2 For differential trend analysis, values are recorded from the differential spectra (spectrum obtained by subtraction of the absorption spectrum of the reference oil from that of the in-service oil) and reported in units of 100\*absorbance per 0.1 mm pathlength (or equivalently absorbance units per centimetre).

1.4.3 In either case, maintenance action limits should be determined through statistical analysis, history of the same or similar equipment, round robin tests, or other methods in conjunction with the correlation of oxidation changes to equipment performance.

NOTE 1—It is not the intent of this test method to establish or recommend normal, cautionary, warning, or alert limits for any machinery. Such limits should be established in conjunction with advice and guidance from the machinery manufacturer and maintenance group.

1.5 This test method is for petroleum and hydrocarbon based lubricants and is not applicable for ester based oils, including polyol esters or phosphate esters.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6.1 *Exception*—The unit for wave numbers is  $\text{cm}^{-1}$ .

1.7 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>3</sup>

<sup>3</sup> 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.

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

- D445** Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)
- D664** Test Method for Acid Number of Petroleum Products by Potentiometric Titration
- D974** Test Method for Acid and Base Number by Color-Indicator Titration
- D2896** Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration
- D4175** Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
- D4739** Test Method for Base Number Determination by Potentiometric Hydrochloric Acid Titration
- D5185** Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
- D7412** Test Method for Condition Monitoring of Phosphate Antiwear Additives in In-Service Petroleum and Hydrocarbon Based Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry
- D7415** Test Method for Condition Monitoring of Sulfate By-Products in In-Service Petroleum and Hydrocarbon Based Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry
- D7418** Practice for Set-Up and Operation of Fourier Transform Infrared (FT-IR) Spectrometers for In-Service Oil Condition Monitoring
- D7624** Test Method for Condition Monitoring of Nitration in In-Service Petroleum and Hydrocarbon-Based Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry
- E131** Terminology Relating to Molecular Spectroscopy
- E177** Practice for Use of the Terms Precision and Bias in ASTM Test Methods
- E691** Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

### 3. Terminology

3.1 *Definitions*—For definitions of terms relating to infrared spectroscopy used in this test method, refer to Terminology **E131**. For definitions of terms related to in-service oil condition monitoring, refer to Practice **D7418** and Terminology **D4175**.

3.2 *machinery health, n*—qualitative expression of the operational status of a machine subcomponent, component, or entire machine, used to communicate maintenance and operational recommendations or requirements in order to continue operation, schedule maintenance, or take immediate maintenance action.

### 4. Summary of Test Method

4.1 This test method uses FT-IR spectrometry to monitor oxidation levels in in-service petroleum and hydrocarbon based lubricants. The FT-IR spectra of in-service oil samples are collected according to the protocol for either direct trend analysis or differential trend analysis described in Practice **D7418**, and the levels of oxidation are measured using the peak height or area measurements described herein.

### 5. Significance and Use

5.1 A large number of compounds, such as aldehydes, ketones, esters, and carboxylic acids, are produced when oils react with atmospheric oxygen. Oxidation is measured using a common FT-IR spectral feature between  $1800\text{ cm}^{-1}$  and  $1670\text{ cm}^{-1}$  caused by the absorption of the carbonyl group present in most oxidation compounds. These oxidation products may lead to increased viscosity (causing oil thickening problems), acidity (causing acidic corrosion), and formation of sludge and varnish (leading to filter plugging, fouling of critical oil clearances and valve friction). Monitoring of oxidation products is therefore an important parameter in determining overall machinery health and should be considered in conjunction with data from other tests such as atomic emission (AE) and atomic absorption (AA) spectroscopy for wear metal analysis (Test Method **D5185**) and physical property tests (Test Methods **D445**), base reserve (Test Method **D2896** and **D4739**), acid number tests (Test Methods **D664** and **D974**) and other FT-IR oil analysis methods for nitration (Test Method **D7624**), sulfate by-products (Test Method **D7415**), and additive depletion (Test Method **D7412**), which also assess elements of the oil's condition, see Refs (**1-6**).

### 6. Interferences

6.1 Various additive packages, especially those containing esters and carboxylic acids, such as some viscosity index improvers, pour point depressants, and rust inhibitors, can give false positives for oxidation. In addition, oils mixed with any synthetic ester based oil products will also give very high values for oxidation. One should trend the in-service oil against the new oil to help identify these interferences. In some oils the contributions from additive packages and synthetic ester based oils may be so high that oxidation cannot be reliably measured.

6.2 High levels of water contamination and soot will also interfere with the measurement of oxidation.

### 7. Apparatus

7.1 Fourier transform infrared spectrometer equipped with sample cell, filter (optional) and pumping system (optional) as specified in Practice **D7418**.

7.2 *FT-IR Spectral Acquisition Parameters*—Set FT-IR spectral acquisition parameters according to instructions in Practice **D7418**.

### 8. Sampling

8.1 Obtain a sample of the in-service oil and a sample of the reference oil (required only for differential trend analysis) according to the protocol described in Practice **D7418**.

### 9. Preparation and Maintenance of Apparatus

9.1 Rinse, flush, and clean the sample cell, inlet lines, and inlet filter according to instructions in Practice **D7418**.

9.2 Monitor cell pathlength as specified in Practice **D7418**.

### 10. Procedure

10.1 Collect a background spectrum according to the procedure specified in Section 9 of Practice **D7418**.

10.2 *Differential Trend Analysis Only*—Collect the absorption spectrum of a reference oil sample according to the procedure specified in Section 9 of Practice D7418.

10.3 Collect the absorption spectrum of an in-service oil sample according to the procedure specified in Section 9 of Practice D7418.

10.3.1 Include the optional cell loading check as specified in Section 9 of Practice D7418 as appropriate.

10.4 Perform the required sample carryover procedure in Section 9 of Practice D7418 between all samples being scanned.

10.4.1 Refer to Section 9 of Practice D7418 for an optional procedure to determine the sample carryover efficacy.

10.5 *Data Processing*—All data are normalized to a path-length of 0.100 mm according to the procedure specified in Section 10 of Practice D7418.

## 11. Calculation

11.1 *Calculation of Oxidation Value:*

11.1.1 *Procedure A (Direct Trend Analysis)*—Oxidation by the direct trending method is calculated from the oil sample spectrum using the measurement area and baseline points listed in Table 1. Fig. 1 illustrates the area used in the measurement of oxidation in the spectrum of diesel crankcase oil.

11.1.2 *Procedure B (Differential Trend Analysis)*—Oxidation by the differential trending method is calculated from the differential spectrum using the measurement peak and baseline points listed in Table 1. Fig. 2 illustrates the band used in the measurement of oxidation in the differential spectrum of diesel crankcase oil.

## 12. Report

12.1 *Procedure A (Direct Trend Analysis)*—Values are reported in units of absorbance/0.100 mm.

12.2 *Procedure B (Differential Trend Analysis)*—Values are reported in units of absorbance per centimeter (Abs/cm), calculated as follows:

$$\begin{aligned} & \text{Oxidation in Abs/cm} & (1) \\ & = \text{Oxidation in Abs/0.100 mm} \times 100 \end{aligned}$$

12.3 *Trending*—Data shall be recorded and reported at selected time intervals during the lubricant’s life. Ideally, oxidation values would be compared to that of the newly formulated oil and plotted over time to visualize the relative changes in oxidation and to determine when there needs to be an oil change, albeit other parameters may dictate this change earlier. Sampling and reporting time intervals for oxidation are

based on the type of machinery and its previous history associated with this parameter.

12.4 *Effects of Oil Formulation*—The compositions of various oil formulations can have an effect on the results reported for oxidation value, and values from two different oil formulations should not be compared. Results should be interpreted relative to values measured for unused oils of the same formulation or trended directly from the sample history.

## 13. Precision and Bias<sup>4</sup>

13.1 The precision of this test method is based on an interlaboratory study conducted in 2016. Eleven laboratories tested 18 different materials. Every “test result” represents an individual determination. Each laboratory was asked to submit two replicate test results, from a single operator, for each material. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report RR:D02-1883.<sup>5</sup>

13.1.1 *Repeatability Limit (r)*—The value below which the absolute difference between two individual test results obtained under repeatability conditions may be expected to occur with a probability of approximately 0.95 (95 %).

13.1.1.1 Repeatability limits are estimated by the equation:

$$r = 0.0028x^2 - 0.014x + 0.6947 \quad (2)$$

where:

x = the average of two test results.

13.1.2 *Reproducibility Limit (R)*—The value below which the absolute difference between two test results obtained under reproducibility conditions may be expected to occur with a probability of approximately 0.95 (95 %).

13.1.2.1 Reproducibility limits are estimated by the equation:

$$R = 0.0074x^2 - 0.0571x + 3.0259 \quad (3)$$

where:

x = the average of two test results.

13.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

13.1.4 Any judgment in accordance with statements 13.1.1 and would have an approximate 95 % probability of being correct.

13.2 *Bias*—The procedure in this test method for measuring oxidation has no bias because the value for oxidation is defined only in terms of the test method.

## 14. Keywords

14.1 condition monitoring; differential trend analysis; direct trend analysis; Fourier transform infrared; FT-IR; hydrocarbon based lubricants; in-service petroleum lubricants; infrared; IR; lubricants; oils; oxidation

**TABLE 1 Parameters for Measuring Oxidation in In-Service Petroleum and Hydrocarbon Based Lubricants**

Method	Measurement, cm	Baseline Point(s), cm <sup>-1</sup>
Procedure A (Direct Trend Analysis)	Area from 1800 to 1670	Minima 2200 to 1900 and 650 to 550
Procedure B (Differential Trend Analysis)	Maximum height from 1800 to 1660	Single point at 1950

<sup>4</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1668. Contact ASTM Customer Service at service@astm.org.

<sup>5</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1883. Contact ASTM Customer Service at service@astm.org.