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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[1]

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 (ε) 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**).[2]

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.

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.

[1] 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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[2] The boldface numbers in parentheses refer to a list of references at the end of this standard.

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

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 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:*[3]

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)
~~D6304 Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration~~
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
~~E2412 Practice for Condition Monitoring of In-Service Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry~~

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

[3] 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.

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~~1800 cm^{-1} and 1670 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 ~~and D6304~~), base reserve (Test Method D2896 and D4739), acid number tests (Test Methods D664 and D974) and other FT-IR oil analysis methods for nitration ~~(Practice~~ (Test Method ~~E2412~~D7624), sulfate by-products (Test Method D7415), and additive depletion (Test Method D7412), ~~breakdown products and external contaminants (Practice E2412),~~ 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 pathlength 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.

~~11.2 *Sample Carryover*—To ensure the minimum amount of sample-to-sample cross-contamination or carryover, either a minimum volume of the subsequent sample or a solvent rinse should be used to flush out the previous sample. The efficacy of the flushing protocol may be assessed by consecutively analyzing an oil having a low (or zero) oxidation level (L1, for example, a fresh oil) and a used oil sample having a high oxidation level (H1) followed by a second run of the oil sample having a low oxidation level (L2) and then calculating the percent carryover (PC) as follows. The calculated PC should be less than 5 %.~~

$$PC = [(L2 - L1)/H1] \times 100 \quad (1)$$

~~*where:*~~

~~L1, H1, and L2 = the values measured for oxidation (using the parameters given in Table 1) for the samples run in the indicated sequence.~~

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:

$$\text{Oxidation in Abs/cm} = \text{Oxidation in Abs/0.100 mm} * 100 \quad (1)$$

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.

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

Method	Measurement, cm	Baseline Point(s), cm^{-1}
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