Designation: D7412 – 22

# Standard 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[1]

This standard is issued under the fixed designation D7412; 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 phosphate antiwear additives in in-service petroleum and hydrocarbon based lubricants such as various types of engine oils, hydraulic oils, and other lubricants that are formulated for protection against wear. Typical phosphate antiwear additives include zinc dialkyldithiophosphates, trialkyl phosphates, and triaryl phosphates.

1.2 This test method uses Fourier Transform Infrared (FT-IR) spectrometry for monitoring of phosphate antiwear additive depletion in in-service petroleum and hydrocarbon based lubricants as a result of normal machinery operation. Monitoring the depletion of phosphate antiwear additives in in-service lubricants can indicate unusual wear or severe operating conditions of the machine. This test method is designed as a fast, simple spectroscopic check for monitoring of phosphate antiwear additives 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 phosphate antiwear additives in the oil.

1.3 Acquisition of FT-IR spectral data for measuring phosphate antiwear additives in in-service oil and lubricant samples is described in Practice D7418. In this test method, measurement and data interpretation parameters for phosphate antiwear additives 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 phosphate antiwear additives in 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 centimeter).

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 changes in the level of phosphate antiwear additives 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 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*

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

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

*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)

D2896 Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D5185 Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

D7414 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

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 definition 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 levels of phosphate antiwear additives 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 phosphate antiwear additives are measured using the peak height or area measurements described herein.

## 5. Significance and Use

5.1 Antiwear additives are commonly used in petroleum and hydrocarbon based lubricants to prevent machinery wear by forming a chemical barrier activated by frictional heat. Antiwear additives that are phosphate based can be measured by FT-IR spectroscopy using the phosphate absorption band. Initially, phosphate antiwear additives will decompose and form a protective film by binding to metal surfaces and through oxidative mechanisms, and so a decrease in the level of phosphate antiwear additive relative to that in the new oil is expected during normal machinery operation. Subsequently, significant depletion of phosphate antiwear additives due to oxidation or hydrolysis can occur when the lubricant is subjected to high temperatures and high levels of moisture. This usually occurs prior to the point where the oxidation of the lubricant begins to accelerate, making trending of phosphate antiwear additives a useful indicator of the lubricant's remaining in-service life. Monitoring of phosphate antiwear additive depletion 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), physical property tests (Test Methods D445 and D2896) and other FT-IR oil analysis methods for oxidation (Test Method D7414), sulfate by-products (Test Method D7415), and nitration (Test Method D7624), which also assess elements of the oil's condition, see Refs **(1-6)**.

## 6. Interferences

6.1 Refer to Practice D7418 for a list of common interferents affecting the quality of all FTIR generated spectra.

6.2 When the sample has increased baseline (soot >2.5 %) or interferent peak present, follow the optional procedure in Practice D7418 Section 11 depending on measurement accuracy needs.

## 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.

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[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.

## 9. Preparation and Maintenance of Apparatus

9.1 Rinse, flush, and clean the sample cell, 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 Phosphate Antiwear Value:*

11.1.1 *Procedure A (Direct Trend Analysis)*—Phosphate antiwear value 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 phosphate antiwear additives in the spectrum of diesel crankcase oil.

11.1.2 *Procedure B (Differential Trend Analysis)*—Phosphate antiwear value by the differential trending method is calculated from the differential spectrum using a minimum peak height and a two-point baseline (Table 1), giving negative values as the amount of phosphate antiwear additives in the in-service oil relative to that in the reference oil progressively decreases. Fig. 2 illustrates the band used in the measurement of phosphate antiwear additives 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.

**TABLE 1 Parameters for Measuring Phosphate Antiwear Additives in In-Service Petroleum and Hydrocarbon Based Lubricants**

| Method | Measurement, cm$^{-1}$ | Baseline Point(s), cm$^{-1}$ |
|---|---|---|
| Procedure A (Direct Trend Analysis) | Area from 1025 to 960 | Minima 2200 to 1900 and 650 to 550 |
| Procedure B (Differential Trend Analysis) | Minimum height from 1020 to 930 | Two points at 1020 and 930 |

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

$$\text{Phosphate Antiwear in Abs/cm} \tag{1}$$

$$= \text{Phosphate Antiwear in Abs}/0.100 \text{ mm} * 100$$

12.3 *Trending*—Data shall be recorded and reported at selected time intervals during the lubricant's life. Ideally, phosphate antiwear values would be compared to that of the newly formulated oil and plotted over time to visualize the relative changes in phosphate antiwear additives 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 phosphate antiwear additives 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 the phosphate antiwear 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[4]

13.1 *Precision*—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 No. RR:D02-1883.[5]

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:

$$r = 0.0819x - 0.1122 \tag{2}$$

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:

$$R = 0.0621x + 2.024 \tag{3}$$

where:

x = the average of two test results.