



Designation: D7624 – 22

# Standard 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<sup>1</sup>

This standard is issued under the fixed designation D7624; 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 nitration in gasoline and natural gas engine oils as well as in other types of lubricants where nitration by-products may form due to the combustion process or other routes of formation of nitration compounds.

1.2 This test method uses FT-IR spectroscopy for monitoring build-up of nitration by-products in in-service petroleum and hydrocarbon-based lubricants as a result of normal machinery operation. Nitration levels in gasoline and natural gas engine oils rise as combustion by-products react with the oil as a result of exhaust gas recirculation or a blow-by. This test method is designed as a fast, simple spectroscopic check for monitoring of nitration 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 nitration in the oil.

1.3 Acquisition of FT-IR spectral data for measuring nitration in in-service oil and lubricant samples is described in Practice D7418. In this test method, measurement and data interpretation parameters for nitration 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 nitration in in-service petroleum and hydrocarbon-based lubricants. For direct trend analysis, values are recorded directly from absorption spectra and reported in units of 100\*absorbance per 0.1 mm pathlength (or equivalently absorbance units per centimetre). For differential trend analysis, values are recorded from the differential spectra (spectrum obtained by subtraction of the 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).

Warnings or alarm limits can be set on the basis of a fixed maximum value for a single measurement or, alternatively, can be based on a rate of change of the response measured (1).<sup>2</sup> In either case, such 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 nitration 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>  
D445 Test Method for Kinematic Viscosity of Transparent

<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.

<sup>3</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.

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

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)

**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

**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

**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:

3.1.1 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**.

3.1.2 *machinery health, n*—a qualitative expression of the operational status of a machine sub-component, 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 nitration 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 nitration are measured using the peak height measurements described herein.

### 5. Significance and Use

5.1 There is a wide variety of nitration compounds that may be produced and accumulate when oils react with gaseous nitrates formed during the engine combustion process. These nitration products may increase the viscosity, acidity and

insolubles in the oil, which may lead to ring sticking and filter plugging. Monitoring of nitration 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**), 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 additive depletion (Test Method **D7412**), which also assess elements of the oil's condition (**1-6**).

### 6. Interferences

6.1 Refer to Practice **D7418** for a list of common interferences 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.

6.3 Some aromatic compounds absorb in the 1600  $\text{cm}^{-1}$  and 1500  $\text{cm}^{-1}$  regions and may interfere with the nitration signal.

### 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 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 spectrum of a reference oil sample, according to the procedure specified in Section 9 of Practice **D7418**.

10.3 Collect the 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 of Nitration Values**

11.1 *Procedure A (Direct Trend Analysis)*—Nitration by the direct trending method is calculated from the oil sample spectrum using the measurement peak and baseline points listed in Table 1.

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

11.3 *Reporting:*

11.3.1 *Procedure A (Direct Trend Analysis)*—Values are reported in units of absorbance per centimetre (Abs/cm), calculated as follows:

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

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

$$\text{Nitration in Abs/cm} = \text{Nitration in Abs}/0.100 \text{ mm} \times 100 \quad (2)$$

**12. Report**

12.1 *Trending*—Data shall be recorded and reported at selected time intervals during the lubricant’s life. Ideally, nitration values would be compared to that of the newly formulated oil and plotted over time to visualize the relative changes in nitration 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 nitration are based on the type of machinery and its previous history associated with this parameter.

12.2 *Effects of Oil Formulation*—The compositions of various oil formulations can have an effect on the results reported for nitration 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**

13.1 *Precision*—The precision of this test method is based on an interlaboratory study of conducted in 2018. 8 laboratories tested 15 different materials. Every “test result” represents

an individual determination. Each laboratory was asked to submit 2 replicate test results, from a single operator, for each material. Practice E 691 was followed for the design and analysis of the data; the details are given in ASTM Research Report RR:D02-1895.<sup>4</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:

$$y = 0.1783x + 0.0758 \quad (3)$$

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:

$$y = 0.987x + 0.2796 \quad (4)$$

where:

$x$  = the average of two test results.

NOTE 2—Practice E691 does not provide a standardized methodology to arrive at equations describing the relationship between precision versus level. These equations are an empirical fit of the data.

13.1.3 *Precision Data*—See Table 2.

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

13.1.5 Any judgment in accordance with statements in 13.1.1 and 13.1.2 would have an approximate 95 % probability of being correct.

13.2 *Bias*—The procedure in this test method for measuring nitration has no bias because the value for nitration 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; infrared; in-service petroleum lubricants; IR; lubricants; nitration; oils

<sup>4</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1895. Contact ASTM Customer Service at service@astm.org.

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

Method	Measurement, cm <sup>-1</sup>	Baseline Point(s), cm <sup>-1</sup>
Procedure A (Direct Trend Analysis)	Height at 1630	Minima 1655 to 1640 and 1620 to 1595
Procedure B (Differential Trend Analysis)	Height at 1630	Minima 1655 to 1640 and 1620 to 1595