



Designation: D7415 – 22

Standard 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) Spectrometry¹

This standard is issued under the fixed designation D7415; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope*

1.1 This test method covers monitoring sulfate by-products in in-service petroleum and hydrocarbon based diesel crankcase engine and motor oils that have a sulfur content of greater than 500 ppm. This test method should not be employed when low-sulfur fuels are used for combustion.

1.2 This test method uses Fourier Transform Infrared (FT-IR) spectrometry for monitoring build-up of sulfate by-products in in-service petroleum and hydrocarbon based lubricants as a result of normal machinery operation. Sulfate by-products can result from the introduction of sulfur from combustion or from the oxidation of sulfur-containing base oil additives. This test method is designed as a fast, simple spectroscopic check for monitoring of sulfate by-products 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 sulfate by-products in the oil.

1.3 Acquisition of FT-IR spectral data for measuring sulfate by-products in in-service oil and lubricant samples is described in Practice D7418. In this test method, measurement and data interpretation parameters for sulfate by-products 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 sulfate by-products 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 sulfate by-product 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 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*

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

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)
- 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
- 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
- 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.

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.

4. Summary of Test Method

4.1 This test method uses FT-IR spectrometry to monitor sulfate by-product 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 sulfate by-products are measured using the peak height or area measurements described herein.

5. Significance and Use

5.1 An increase in sulfate material can be an indicator of oil degradation caused by oxidation of sulfur in the oil and sulfur in fuel. It can also indicate the breakdown or oxidation of some key additives in the oil such as antiwear and extreme pressure additives as well as blow-by concerns. As oxidized sulfur from blow-by enters the lubricant, it will consume the overbase additive to generate sulfate by-products. Monitoring of sulfate by-products is therefore an important parameter in determining overall machinery health and in determining additive depletion 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**), base number tests (Test Methods **D974** and **D4739**), and other FT-IR oil analysis methods for nitration (Test Method **D7624**), oxidation (Test Method **D7414**), and additive depletion (Test Method **D7412**), 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 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 Oxidation by-products can be a major source of interference in the measurement of sulfate by-products. When oxidation by-products are present, the low levels of sulfate by-products associated with the use of low-sulfur fuels for combustion cannot be adequately measured.

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 Sulfate By-Products Value:*

11.1.1 *Procedure A (Direct Trend Analysis)*—Sulfate by-products 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 sulfate by-products in the spectrum of diesel crankcase oil.

11.1.2 *Procedure B (Differential Trend Analysis)*—Sulfate by-products value 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 sulfate by-products 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:

$$\begin{aligned} &\text{Sulfate By-Products in Abs/cm} \\ &= \text{Sulfate By-Products in Abs/0.100 mm} * 100 \end{aligned}$$

12.3 *Trending*—Data shall be recorded and reported at selected time intervals during the lubricant’s life. Ideally, sulfate by-products values would be compared to that of the

newly formulated oil and plotted over time to visualize the relative changes in sulfate by-products 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 sulfate by-products 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 sulfate by-products 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 Bias⁴

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 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:

$$r = 0.0663x + 0.3361 \quad (1)$$

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:

$$R = 0.0476x + 1.753 \quad (2)$$

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 **13.1.2** would have an approximate 95 % probability of being correct.

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

TABLE 1 Parameters for Measuring Sulfate By-Products in In-Service Petroleum and Hydrocarbon Based Lubricants

Method	Measurement, cm ⁻¹	Baseline Point(s), cm ⁻¹
Procedure A (Direct Trend Analysis)	Area from 1180 to 1120	Minima 2200 to 1900 and 650 to 550
Procedure B (Differential Trend Analysis)	Height at 1150	Single point at 1950

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1669. Contact ASTM Customer Service at service@astm.org.

⁵ 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.