



Designation: **D7415–18** **D7415 – 21**

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 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

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 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 \(ICP-AES\)](#)
- ~~[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](#)
- [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](#)
- ~~[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

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.

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 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](#); ~~[D2896](#)~~, and ~~[D6304](#)~~[D2896](#)), base number tests (Test Methods [D974](#) and [D4739](#)), and other FT-IR oil analysis methods for nitration (~~Practice~~ (Test Method [E2412](#)[D7624](#)), oxidation (Test Method [D7414](#)), 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 detergents, dispersants, demulsifiers and overbase additives, will interfere with the sulfate by-products measurement.

6.2 Contaminants such as esters, polyols, glycols, and alcohols will also interfere with the measurement of sulfate by-products.

6.3 Oxidation by-products can be a major source of interference in the measurement of sulfate by-products. Because of this interference, 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.

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) sulfate by-product level (L1, for example, a fresh oil) and a used oil sample having a high sulfate by-product level (H1) followed by a second run of the oil sample having a low sulfate by-product 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 sulfate by-products (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:

Sulfate By-Products in Abs/cm

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