Designation: D7415 – 09

# 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) Spectrometry[1]

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 reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 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 and health practices and determine the applicability of regulatory limitations prior to use.*

## 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

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.96 on In-Service Lubricant Testing and Condition Monitoring Services.

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

[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.

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D2896 Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration
D4739 Test Method for Base Number Determination by Potentiometric Hydrochloric Acid Titration
D5185 Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in 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
E131 Terminology Relating to Molecular Spectroscopy
E2412 Practice for Condition Monitoring of Used 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.

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 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), base number tests (Test Methods D974 and D4739) and other FT-IR oil analysis methods for nitration (Practice E2412), oxidation (Test Method D7414), 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 Practice D7418.

10.2 *Differential Trend Analysis Only*—Collect the absorption spectrum of a reference oil sample according to the procedure specified in Practice D7418.

10.3 Collect the absorption spectrum of an in-service oil sample according to the procedure specified in Practice D7418.

10.4 *Data Processing*—All data are normalized to a pathlength of 0.100 mm according to the procedure specified in 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
= Sulfate By-Products in Abs/0.100 mm * 100

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.

**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 |

12.4 *Statistical Analysis and Alarm Limits*—For statistical analysis and setting alarm limits, refer to Practice E2412, Annex A3 on "Distribution Profiles and Statistical Analysis."

12.5 *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 Bias (Interim) [4]

13.1 *Precision*—The precision of the test method has not yet been determined by a formal interlaboratory study. Preliminary examinations of repeatability have shown that the difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20:

repeatability = 0.30 absorbance units/0.100 mm for Procedure A (direct trend analysis)
repeatability = 0.31 absorbance units/cm for Procedure B (differential trend analysis)

The reproducibility of this test method is being determined and will be available on or before May 1, 2013.

13.2 *Bias*—The procedures in this test method have no bias because the sulfate by-products values can be defined only in the terms of the test method and no accepted reference method or value is available.

## 14. Keywords

14.1 condition monitoring; differential trend analysis; direct trend analysis; Fourier transform infrared; FT-IR; hydrocarbon based lubricants; in-service petroleum lubricants; infrared; IR; lubricants; oils; sulfate by-products

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1669.

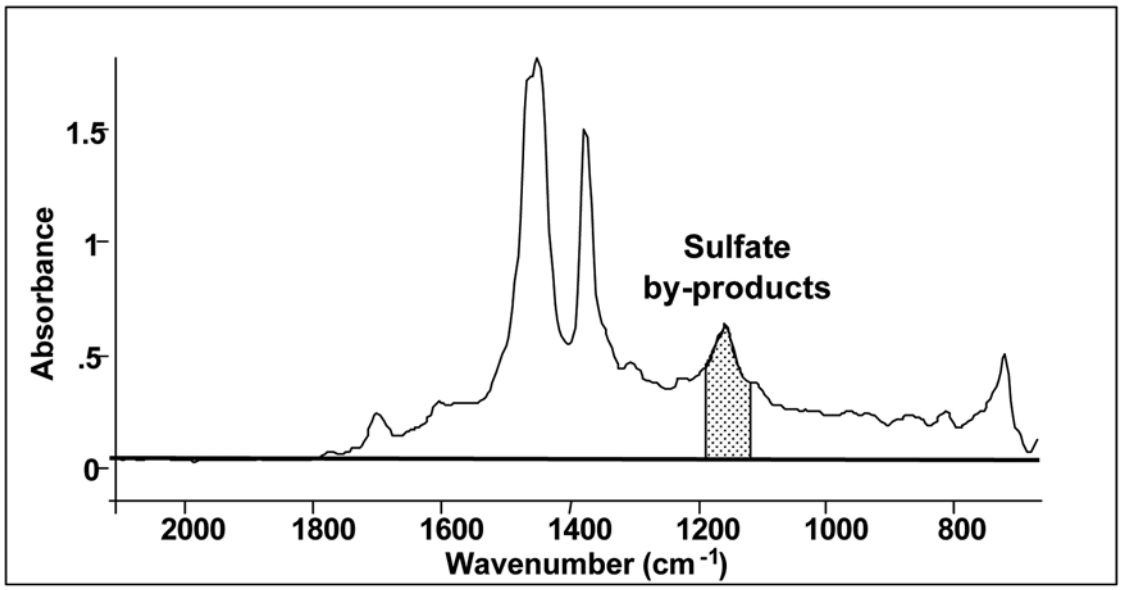


**FIG. 1 Sulfate By-Products Measurement in the Spectrum of a Diesel Crankcase Oil for Direct Trend Analysis (Procedure A)**

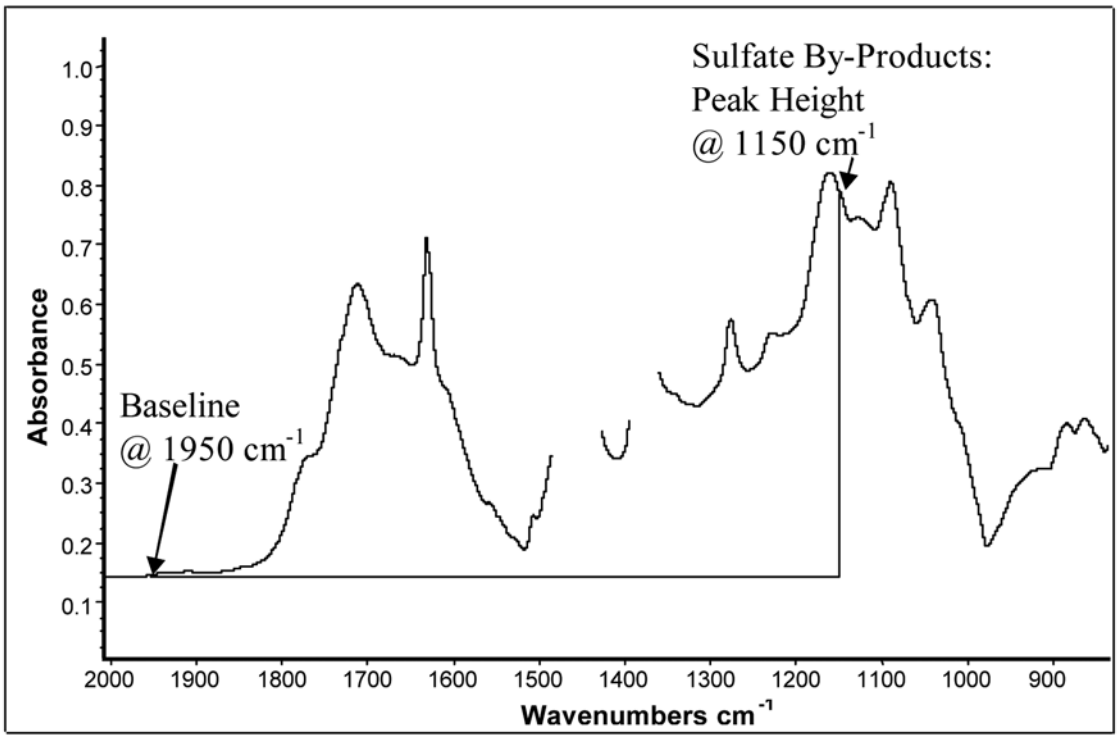


**FIG. 2 Sulfate By-Products Measurement in the Differential Spectrum of a Petroleum Crankcase Lubricant for Differential Trend Analysis (Procedure B)**

## REFERENCES

(1) Toms, L. A., and Toms, A. M., *Machinery Oil Analysis: Methods, Automation & Benefits*, 3rd edition, STLE, 2008.

(**2**) Coates, J., and Setti, L.,"Infrared Spectroscopy as a Tool for Monitoring Oil Degradation," *Aspects of Lubricant Oxidation*, ASTM Special Technical Publication 916, ASTM International, 1986, pp. 57-78.

(**3**) Garry, M., "Applied Interpretation of FT-IR Oil Analysis Results for Improving Predictive Maintenance Programs," Proceedings of the 1992 Joint Oil Analysis Program International Condition Monitoring Conference, *JOAP-TSC*, 1992, pp. 233-254.

(**4**) Powell, J., and Compton, D., "Automated FTIR Spectrometry for Monitoring Hydrocarbon-Based Engine Oils," *Lubrication Engineering*, 49, 3, March 1993, pp. 233-239.

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(**6**) Lukas, M., and Anderson, D., "Laboratory Used Oil Analysis Methods," *CRC/STLE Tribology Data Handbook*, Booser, E., ed., CRC Press, 1997.

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