Designation: ~~D7214 – 07a (Reapproved 2012)~~ D7214 – 07a (Reapproved 2019)

Standard Test Method for
Determination of the Oxidation of Used Lubricants by FT-IR Using Peak Area Increase Calculation[1]

This standard is issued under the fixed designation D7214; 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.

INTRODUCTION

This test method was jointly developed with "Groupement Francais de Coordination" (GFC), technical committee LM5 and "Coordinating European Council" (CEC) Surveillance Group T-048 for the purpose of monitoring the oxidation stability of artificially aged automotive transmission fluids. This test method has been used in the CEC L-48-A-00 method as an end of test measurement parameter.

1. Scope

1.1 This test method covers the determination of the oxidation of used lubricants by FT-IR (Fourier Transform Infrared Spectroscopy). It measures the concentration change of constituents containing a carbonyl function that have formed during the oxidation of the lubricant.

1.2 This test method may be used to indicate relative changes that occur in an oil under oxidizing conditions. The test method is not intended to measure an absolute oxidation property that can be used to predict performance of an oil in service.

1.3 This test method was developed for transmission oils which have been degraded either in service, or in a laboratory test, for example a bulk oxidation test. It may be used for other in-service oils, but the stated precision may not apply.

1.4 The results of this test method may be affected by the presence of other components with an absorbance band in the zone of ~~1600–1800~~1600 cm^{-1} to 1800 cm^{-1}. Low PAI values may be difficult to determine in those cases. Section 6 describes these possible interferences in more detail.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *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:*[2]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

E131 Terminology Relating to Molecular Spectroscopy

E1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests

E1866 Guide for Establishing Spectrophotometer Performance Tests

2.2 *CEC Standard:*

CEC L-48-A-00 Oxidation Stability of Lubricating Oils Used in Automotive Transmissions by Artificial Aging[3]

3. Terminology

3.1 *Definitions*—For terminology relating to molecular spectroscopic methods, refer to Terminology E131.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *carbonyl region, n*—region of the FT-IR spectrum corresponding to the absorbance of compounds containing a carbonyl function. Depending on the nature of the carbonyl compounds, this region is usually located between approximately 1820 cm^{-1} and 1650 cm^{-1}.

3.2.2 *differential spectrum, n*—FT-IR absorbance spectrum resulting from the subtraction of the fresh oil from the used oil.

3.2.3 *PAI (peak area increase), n*—area of the carbonyl region of the differential FT-IR spectrum, divided by the cell pathlength in millimetres. In this standard, PAI refers to a relative measurement of the oxidation of a used lubricant by FT-IR.

4. Summary of Test Method

4.1 FT-IR spectra of the fresh oil and of the used oil are recorded in a transmission cell of known pathlength. Both spectra are converted to absorbance and then subtracted. Using this resulting differential spectrum, a baseline is set under the peak corresponding to the carbonyl region around 1650 cm^{-1} and 1820 cm^{-1} and the area created by this baseline and the carbonyl peak is calculated. The area of the carbonyl region is divided by the cell pathlength in millimetres and this result is reported as Peak Area Increase (PAI).

5. Significance and Use

5.1 The PAI is representative of the quantity of all the compounds containing a carbonyl function that have formed by the oxidation of the lubricant (aldehydes, ketones, carboxylic acids, esters, anhydrides, etc.). The PAI gives representative information on the chemical degradation of the lubricant which has been caused by oxidation.

5.2 This test method was developed for transmission oils and is used in the CEC L-48-A-00 test (Oxidation Stability of Lubricating Oils Used in Automotive Transmissions by Artificial Aging) as a parameter for the end of test evaluation.

6. Interferences

6.1 Some specific cases (very viscous oil, use of ester as base stock, high soot content) may require a dilution of the sample and a specific area calculation, which are described in 14.1 – 14.3. In those cases, the result is corrected by a dilution factor, which is applied to the sample.

7. Apparatus

7.1 *FT-IR Spectrophotometer,* suitable for recording measurements between 1650 cm^{-1} and 1820 cm^{-1} and with a resolution of 4 cm^{-1}.

7.2 *Transmission Cell,* with windows of potassium bromide, having a known pathlength of approximately ~~0.025~~0.025 mm to ~~0.1 mm.~~0.1 mm.

7.3 *Syringe, or Other Automated or Semi-Automated Device,* with adequate volume to fill the cell, for example, 2 mL.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Heptane,* used as cleaning solvent. Other solvents and solvent mixtures may be used provided they adequately clean the cell(s) between samples. A 50/50 mixture of cyclohexane and toluene has been found to be useful in cleaning cells after highly contaminated and degraded samples have been run. (**Warning**—Flammable.)

8.3 *PAO4,* used as dilution oil (PAO4: PolyAlphaOlefin with a kinematic viscosity at ~~100°C~~100 °C of approximately ~~4 mm~~4 mm^2/s)

---

[3] Available from Coordinating European Council (CEC), c/o Interlynk Administrative Services, Ltd., P.O. Box 6475, Earl Shilton, Leicester, LE9 9ZB, U.K.

9. Calibration and Standardization

9.1 *Calculation of the Cell Pathlength*—Use a cell with a known pathlength of approximately ~~0.025~~0.025 mm to ~~0.1 mm.~~ 0.1 mm. Calibrate the infrared cell pathlength using the interference fringe method:

9.1.1 Acquire the single beam background infrared spectrum. Using the empty infrared cell in the infrared spectrometer sample compartment, acquire the cell single beam infrared spectrum. Calculate the transmittance spectrum by dividing the cell single beam spectrum by the background single beam spectrum. Optionally, convert the transmittance spectrum to an absorbance spectrum by taking the negative logarithm (base 10) of the transmittance spectrum. The fringe calculation may be done on either the transmittance or absorbance. spectrum. The final spectrum is obtained by subtraction of the background spectrum from the cell spectrum.

NOTE 1—This computation is generally an integral part of the infrared spectrometer software.

9.1.2 Choose 2 minima separated by about 20 measurable interference fringes as shown in Fig. 1. Count the number of interference fringes between the lower and the higher wavenumbers, referred to as λ_1 and λ_2.

NOTE 2—The spectral range may be chosen freely in an area where the fringes are regular.

9.1.3 The cell pathlength is calculated by the formula:

$$e = \frac{5 \cdot n}{(\lambda_1 - \lambda_2)} \tag{1}$$

where:

e = the pathlength in mm, and
n = the number of fringes between λ_1 and λ_2.

9.2 *Instrument Performance Checks:*

9.2.1 Periodically, the performance of the FT-IR instrument should be monitored using the Level 0 procedure of Practice E1421. If significant change in performance is noted, then testing should be suspended until the cause of the performance change is diagnosed and corrected.

9.2.2 Alternative instrument performance tests conforming to the recommendations of Guide E1866 may be substituted for the Practice E1421 test.
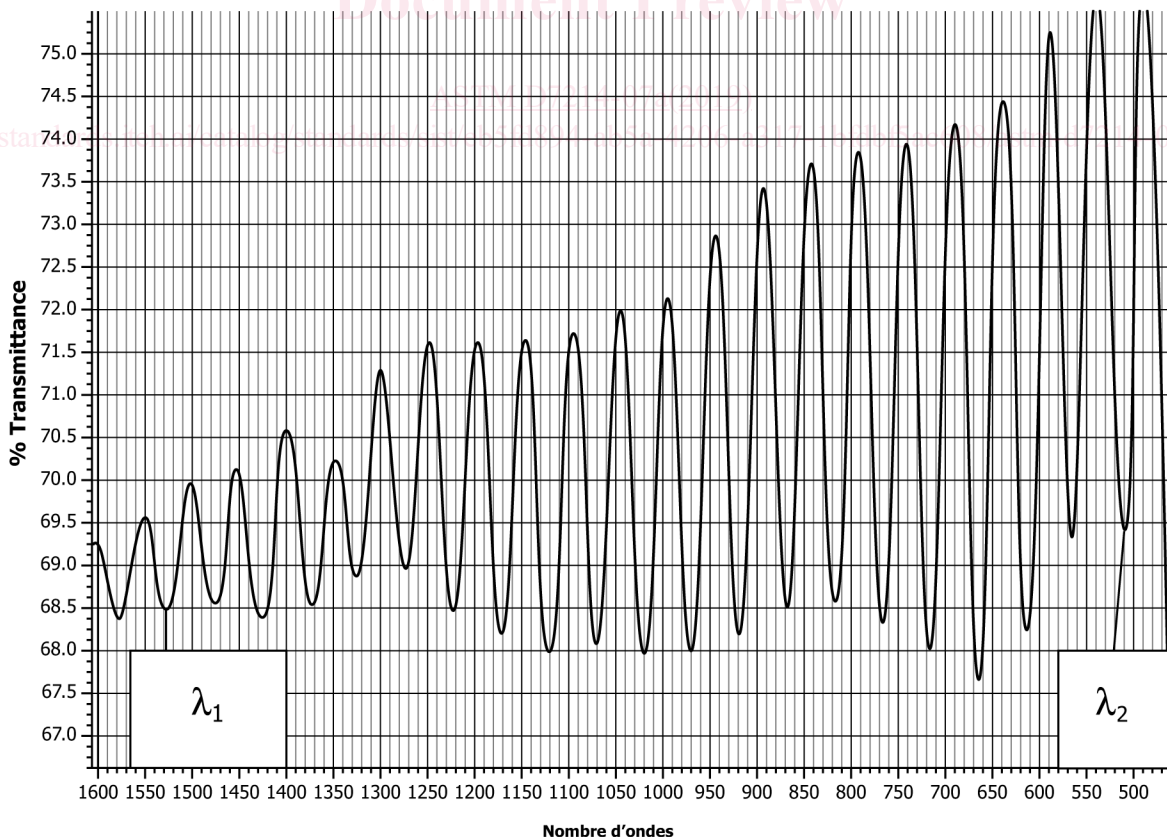

FIG. 1 Example of Interference Fringes for Cell Pathlength Calculation

10. Conditioning

10.1 Before using the infrared cell ensure that it is clean by washing through with a suitable solvent, for example, heptane. Dry the cell using dry air or nitrogen, if necessary. Calibrate this cell as described in Section 9.

11. Preparation of Sample of Used Oil

11.1 Refer to Practice D4057 (Manual Sampling) or Practice D4177 (Automatic Sampling) for proper sampling techniques.

11.2 When sampling used lubricants, the specimen shall be representative of the system sampled and shall be free of contamination from external sources. As used oil can change appreciably in storage, test samples as soon as possible after removal from the lubricating system and note the dates of sampling and testing.

11.3 If the sample of used oil contains visible sediment, heat to ~~60~~60 °C $\pm$ ~~5°C~~5 °C in the original container and agitate until all of the sediment is homogeneously suspended in the oil. If the original container is a can or if it is glass and more than three-fourths full, transfer the entire sample to a clear-glass bottle having a capacity at least one third greater than the volume of the sample. Transfer all traces of sediment from the original container to the bottle by vigorous agitation of portions of the sample in the original container.

12. Procedure

12.1 Acquire a single beam background spectrum. This background spectrum may be used in the conversion of all subsequent spectra for at least one day.

12.2 With a syringe or other injection device, fill the cell with the fresh oil, and record its single beam sample spectrum. Convert this spectrum to a transmittance spectrum by dividing it by the single beam background spectrum and to a fresh oil absorbance spectrum by taking the negative logarithm (base 10) of the transmittance spectrum. Accumulate an adequate number of scans for a satisfactory noise level of < 2 mAbs ~~@2000~~ @ 2000 cm^{-1}.

NOTE 3—Assuming there are no absorbance peaks in the range from ~~2050~~2050 cm^{-1} to ~~1950 cm~~1950 cm^{-1} for the sample, the noise level may be estimated as the standard deviation of the absorbance data over this spectral range.

12.3 Empty and clean the cell. Heptane may be used. Fill the cell with the aged oil, and record its single beam sample spectrum. Convert this spectrum to a transmittance spectrum by dividing by the single beam background spectrum, and to an aged oil absorbance spectrum by taking the negative logarithm (base 10) of the transmittance spectrum.

NOTE 4—It may happen that the aged oil is too viscous to fill the cell. Then it is possible to proceed to a dilution as described in 12.4.1.

12.4 Generate a differential spectrum by subtracting the fresh oil absorbance spectrum from the aged oil absorbance spectrum (see Fig. 2). Locate and zoom on the carbonyl region centered at 1720 cm^{-1}. Processing may continue if the maximum absorbance of this carbonyl region is lower than 1.5.

NOTE 5—Since the carbonyl region absorption minima (close to ~~1820 cm~~1820 cm^{-1} and ~~1650 cm~~1650 cm^{-1}) can vary with the type of oil sample being tested, it was decided not to use fixed baseline limits for calculating the area A.

NOTE 6—The carbonyl band may consist of more than one peak maxima.

NOTE 7—Do not calculate the differential peak area by difference of the peak area of the aged oil with the peak area of the fresh oil.
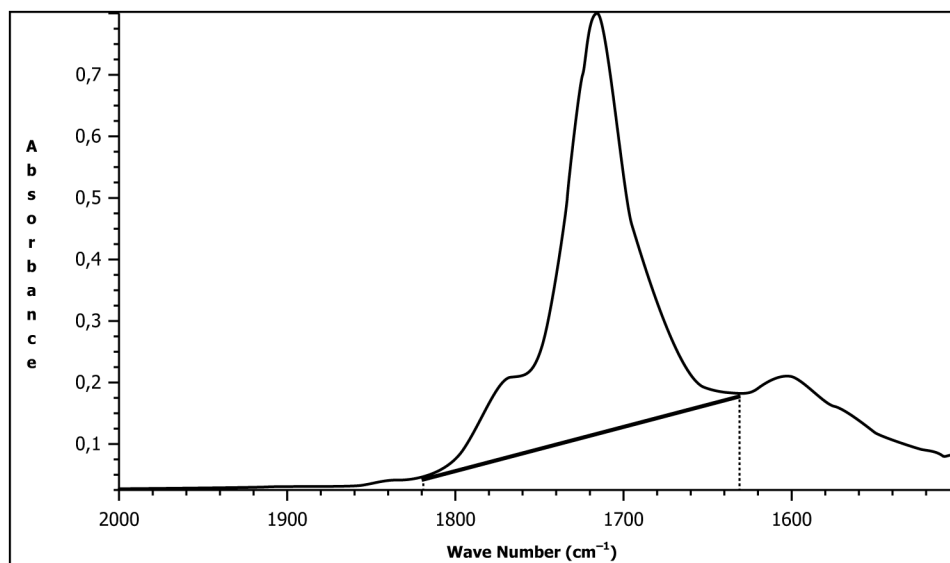

FIG. 2 Area of Spectrum Showing the Result of the Automatic Subtraction by Computer of Aged Oil Spectrum and Fresh Oil Spectrum