Designation: D 7214 – 07

An American National Standard

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 D 7214; 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 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance

E 131 Terminology Relating to Molecular Spectroscopy

E 1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests

E 1866 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 E 131.

3.2 *Definitions of Terms Specific to This Standard:*

[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.

Current edition approved July 15, 2007. Published August 2007. Originally approved in 2006. Last previous edition approved in 2006 as D 7214–06.

[2] 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.

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

***A Summary of Changes section appears at the end of 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 to 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 of approximately 4 mm^2/s)

9. Calibration and Standardization

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

9.1.1 Acquire the background infrared spectrum. Insert the empty infrared cell into the infrared spectrometer sample compartment and acquire the cell infrared 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:

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

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 E 1421. 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 E 1866 may be substituted for the Practice E 1421 test.

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 D 4057 (Manual Sampling) or Practice D 4177 (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

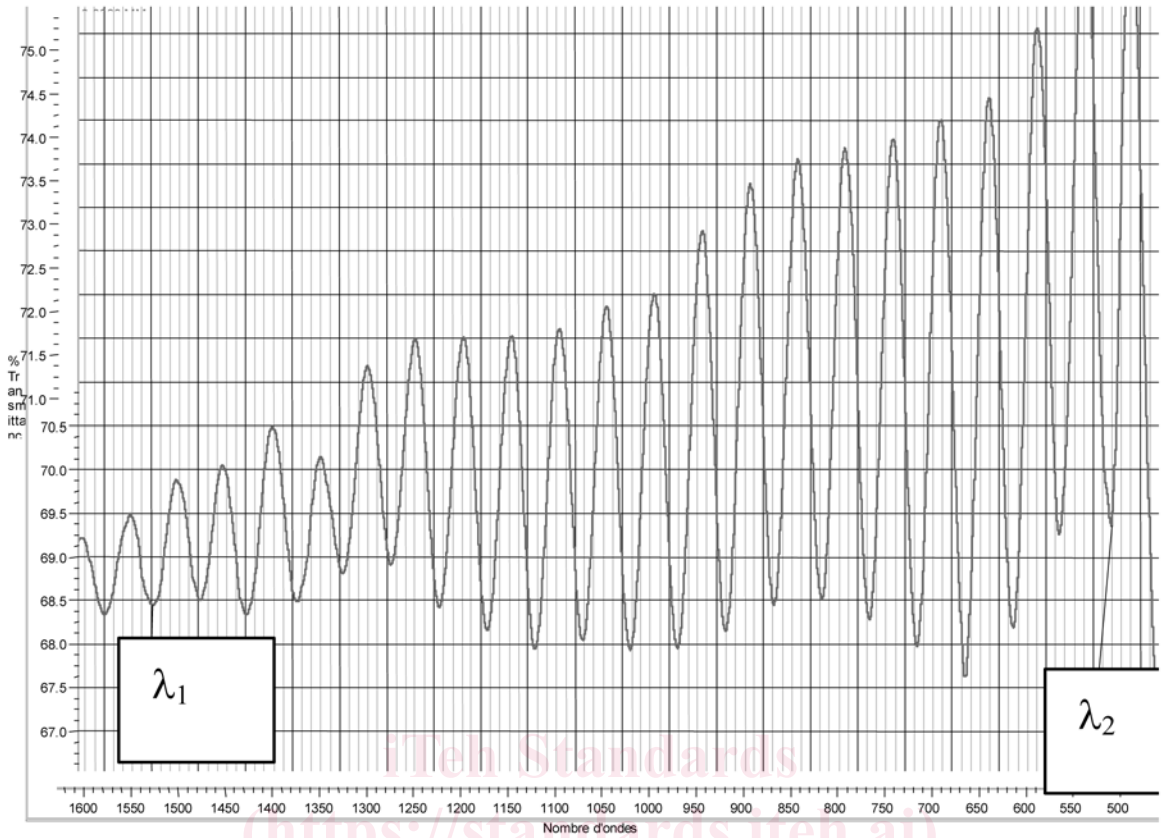

FIG. 1 Example of Interference Fringes for Cell Pathlength Calculation

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 ± 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 Record the background spectrum, and subtract it from all subsequent spectra at least once per day.

12.2 With a syringe or other injection device, fill the cell with the fresh oil, and record its spectrum. Accumulate an adequate number of scans for a satisfactory signal to noise ratio of < 2 mAbs @2000 cm^{-1}.

12.3 Empty and clean the cell with heptane, fill it with the aged oil and record its spectrum.

NOTE 3—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 Convert fresh and aged oil spectra to absorbance and subtract them; a differential spectrum is obtained (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 4—Since the carbonyl region absorption minima (close to 1820 cm^{-1} and 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 5—The carbonyl band may consist of more than one peak maxima.

NOTE 6—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.

12.4.1 If the maximum absorbance of the carbonyl region of the differential spectrum is *higher* than 1.5: dilute with 1 % accuracy by weight both fresh and aged oils with the same dilution factor, D (PAO 4 is recommended as dilution oil). For example, D = 2 for a 50 % (1:1) wt/wt dilution. Record the two spectra, convert them to absorbance and subtract them. If the maximum absorbance of the carbonyl region is still higher than 1.5, then use a higher dilution factor. This occurrence could happen in the case of ester or soot-containing oils.

NOTE 7—The cell pathlength may be changed to 0.05 mm or 0.025 mm if absorbance in the assessment area is greater than 1.5.

NOTE 8—Dilution factors are commonly chosen between 2 and 10.

12.4.2 If the maximum absorbance of the carbonyl region of the differential spectrum is *lower* than 1.5: draw a base line connecting the absorption minima located at each side of this region as shown on the spectrum in Fig. 2. These minima are usually close to 1820 cm^{-1} and 1650 cm^{-1} within ± 20 cm^{-1}. Calculate and record the differential peak area as area A. (This may be done automatically with the spectrometer software.)

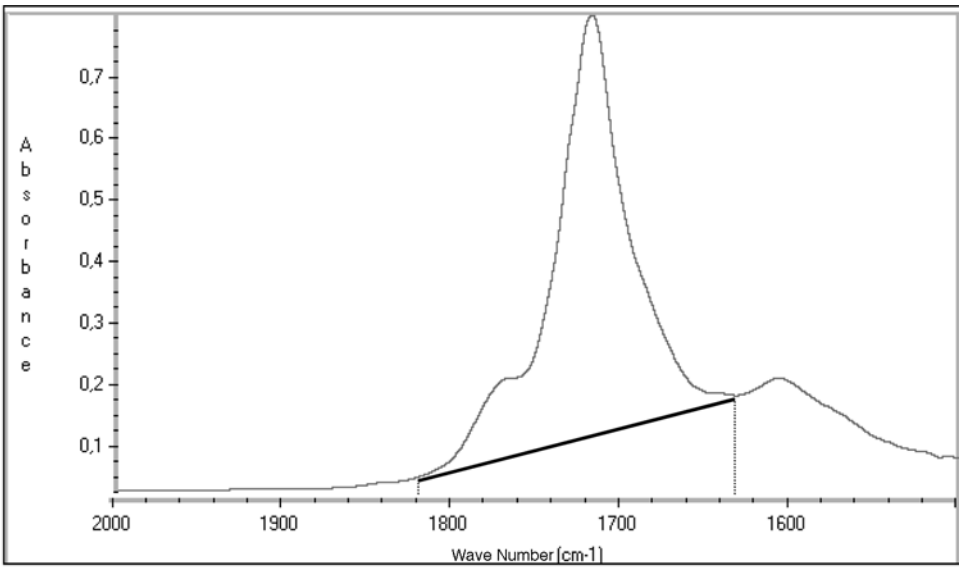

FIG. 2 Area of Spectrum Showing the Result of the Automatic Subtraction by Computer of Aged Oil Spectrum and Fresh Oil Spectrum

13. Calculation of Results

13.1 The results are reported as PAI (peak area increase): carbonyl region area, A multiplied by the dilution factor, *D* and divided by the cell pathlength, *e* in mm:

$$\text{PAI} = \frac{\text{area A}}{e\ (\text{mm})} \times D \qquad (2)$$

13.1.1 If no dilution was needed, the dilution factor, *D* is 1.

14. Procedures for Interferences

14.1 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 cm^{-1}. Low PAI values may be difficult to determine in those cases. The following procedures may be used if interferences are present.

14.2 *Soot-Containing Oils*—The presence of soot degrades the spectra by decreasing the transmittance level. This case may require a dilution as described in 12.4 in order to obtain an absorbance lower than 1.5.

14.3 *Ester-Containing Oils*—The ester functions contained in some lubricants, especially those formulated with ester base oil, interfere with the oxidation peak. Dilution may be needed with these types of lubricants and it is recommended to use a cell with a small pathlength (0.05 mm maximum). Check the shape of the spectrum before interpreting it. The residual positive or negative peaks at 1740 cm^{-1} showing the presence of ester function may make it difficult to correctly perform the subtraction operation between the aged oil spectrum and the fresh oil spectrum. The different examples below show the different cases that could be encountered and describe the baselines settings needed to eliminate these ester residual interfering peaks.

14.3.1 *Example 1* (see Fig. 3)—This differential spectrum is representative of a lubricant containing no ester base oil or containing ester but showing no interference. In this case, draw the baseline between the absorption minima located on either side of this region as shown on the spectrum in Fig. 2. These minima are usually close to 1620 cm^{-1} and 1850 cm^{-1} within 20 cm^{-1}.

14.3.2 *Example 2* (see Fig. 4)—There is a small residual negative peak at 1740 cm^{-1}. This negative peak does not cross the baseline between 1650 and 1820 cm^{-1}. Draw a first baseline close to 1650 and 1820 cm^{-1} as described in 12.4. This baseline creates the area A_1. Draw a second baseline above the residual peak creating the area A_2, representative of the ester interference. This second baseline has to be set in order to obtain a peak shape similar to a peak showing no interference as shown in Example 1, that is, a peak at approximately 1730 cm^{-1} and a smaller peak at approximately 1780 cm^{-1}. The PAI is calculated from the area A defined here by:

$$\text{Area A} = A_1 + A_2$$

14.3.3 *Example 3* (see Fig. 5)—There is a tall residual negative peak at 1740 cm^{-1} crossing the baseline between 1650 and 1820 cm^{-1}. Draw a first baseline close to 1650 and 1820 cm^{-1} as described in 12.4. This baseline creates the areas $A_1 + A_2 - A_3$. Draw a second baseline above the residual peak creating the areas $A_3 + A_4$, representative of the ester interference. This second baseline has to be set in order to obtain a peak shape similar to a peak showing no interference as shown in Example 1, that is, a peak at approximately 1730 cm^{-1} and a smaller peak at approximately 1780 cm^{-1}. The PAI is calculated from the area A defined here by:

$$\text{Area A} = (A_1 + A_2 - A_3) + (A_3 + A_4) = A_1 + A_2 + A_4$$

14.3.4 *Example 4* (see Fig. 6)—There is a residual positive peak at 1740 cm^{-1}. Draw a first baseline close to 1650 and 1820 cm^{-1} as described in 12.4. This baseline creates the areas $A_1 + A_2$. Draw a second baseline under the residual peak creating the area A_2, representative of the ester interference. This second baseline has to be set in order to obtain a peak shape similar to a peak showing no interference as shown in Example 1, that is, a peak at approximately 1730 cm^{-1} and a smaller peak