Designation: ~~D7214 – 22~~ D7214 – 23

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 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, health, and 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.*

[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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***A Summary of Changes section appears at the end of this standard**

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
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
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

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. For definitions of terms related to in-service oil condition monitoring, refer to Practice D7418 and Terminology D4175.

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 the 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 millimeters 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 Refer to Practice D7418 for a list of common interferents 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.

[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.

7. Apparatus

7.1 Fourier transform infrared spectrometer equipped with sample cell, filter (optional) and pumping system (optional) as specified in Practice D7418.

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

7.1.1.1 Other cell window types such as Zinc Selenide, with a known pathlength of approximately 0.025 mm to 0.1 mm, may also be used. ZnSe is known to have a greater durability in the presence of moisture.

7.1.2 *Syringe, Automated, or Semi-Automated Device (Pumping System),* with adequate volume to fill the cell.

7.2 *FT-IR Spectral Acquisition Parameters*—Set FT-IR spectral acquisition parameters according to instructions in Practice D7418.

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. 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 Determine the cell pathlength daily as specified in Practice D7418.

9.2.1 Cell path shall be determined whenever maintenance is performed on the cell.

9.3 *Instrument Performance Checks* shall be performed in accordance with Practice D7418.

10. Preparation of Sample of Used Oil

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

10.2 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.

10.3 If the sample of used oil contains visible sediment, heat to 60 °C ± 5 °C in the original container and agitate until all of the sediment is homogeneously suspended in the oil.

10.4 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.

10.5 Transfer all traces of sediment from the original container to the bottle by vigorous agitation of portions of the sample in the original container.

11. Procedure

11.1 Collect a single beam background spectrum according to the procedure specified in Practice D7418.

11.2 Collect a spectra of both the new oil and the aged oil according to the procedure specified in Practice D7418.

NOTE 1—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 11.3.1.

11.2.1 Between collection of spectra, the cell must be emptied and cleaned. Heptane or other suitable solvent may be used.

11.3 Generate a differential spectrum by subtracting the fresh oil absorbance spectrum from the aged oil absorbance spectrum (see Fig. 1). 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 2—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 3—The carbonyl band may consist of more than one peak maxima.

NOTE 4—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.

11.3.1 If the maximum absorbance of the carbonyl region of the differential spectrum is *higher* than 1.5, both the fresh and aged oils should be diluted using the same dilution factor (D) (within 1 % accuracy) until the absorbance is less than 1.5 – as per Practice D7418, Appendix X3.

11.3.1.1 PAO4 is recommended as dilution oil.

11.3.1.2 Example: A 50 % (1:1) wt/wt dilution yields $D = 2$.

NOTE 5—Commonly chosen dilution factors are between 2 and 10.

11.3.2 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. 1. These minima are usually close to 1820 cm^{-1} and 1650 cm^{-1} within ± 20 cm^{-1}.

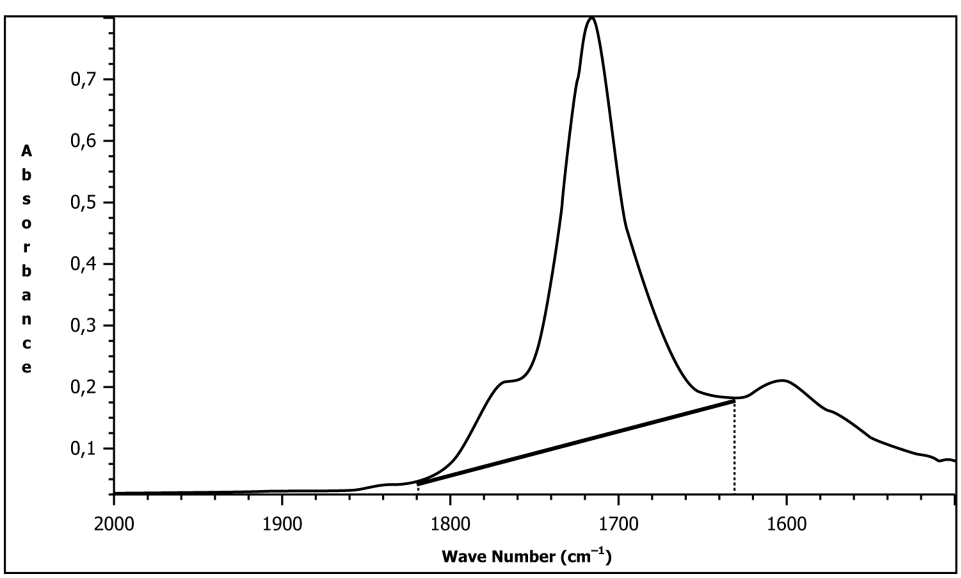

FIG. 1 Area of Spectrum Showing the Result of the Subtraction of Aged Oil Spectrum and Fresh Oil Spectrum

11.3.3 Calculate and record the differential peak area as area A. (This may be done automatically with the spectrometer software.)

12. Calculation of Results

12.1 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:

$$PAI = \frac{\text{area A}}{e\ (\text{mm})} \times D \quad (1)$$

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

13. Procedures for Interferences

13.1 The results of this test method may be affected by the presence of other components with an absorbance band in the zone of 1600 cm^{-1} to 1800 cm^{-1}. Low PAI values may be difficult to determine in those cases. The following procedures may be used if interferences are present.

13.2 *Soot-Containing Oils*—The presence of soot degrades the spectra by decreasing the transmittance level. This case may require a dilution as described in 11.3 in order to obtain an absorbance lower than 1.5.

13.3 *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.

13.3.1 Check the shape of the spectrum before interpreting it.

13.3.2 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.

13.3.3 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.

13.3.4 *Example 1* (see Fig. 2)—This differential spectrum is representative of a lubricant containing no ester base oil or containing

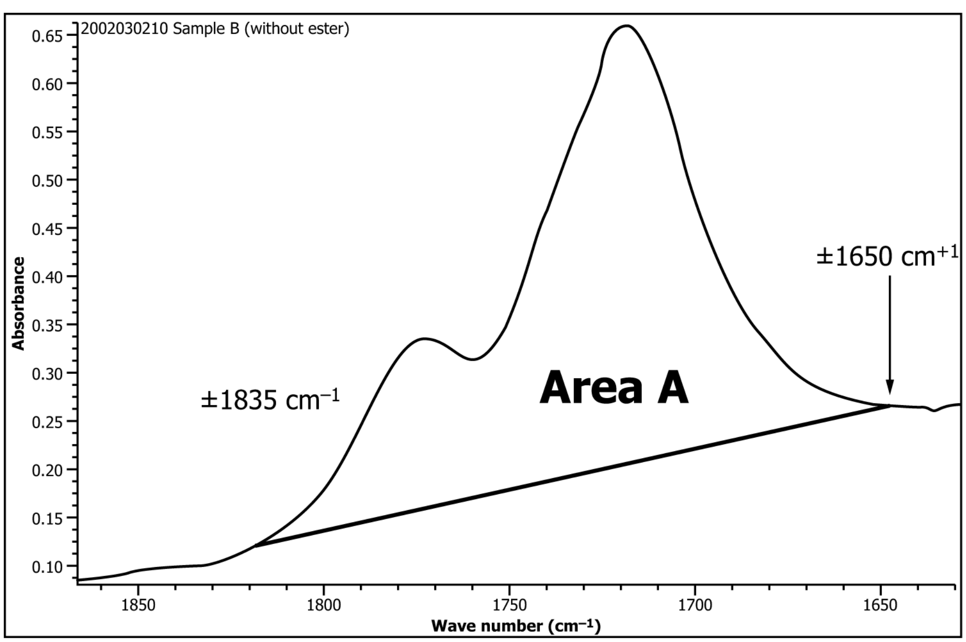

FIG. 2 Example 1

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. 1. These minima are usually close to 1620 cm^{-1} and 1850 cm^{-1} within 20 cm^{-1}.

13.3.5 *Example 2* (see Fig. 3)—There is a small residual negative peak at 1740 cm^{-1}. This negative peak does not cross the baseline between 1650 cm^{-1} and 1820 cm^{-1}.

13.3.5.1 Draw a first baseline close to 1650 cm^{-1} and 1820 cm^{-1} as described in 11.3. This baseline creates the area A_1.

13.3.5.2 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}.

13.3.5.3 The PAI is calculated from the area A defined here by:

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

13.3.6 *Example 3* (see Fig. 4)—There is a tall residual negative peak at 1740 cm^{-1} crossing the baseline between 1650 cm^{-1} and 1820 cm^{-1}.

13.3.6.1 Draw a first baseline close to 1650 cm^{-1} and ~~1820 cm~~1820 cm^{-1} as described in 11.3. This baseline creates the areas $A_1 + A_2 - A_3$.

13.3.6.2 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}.

13.3.6.3 The PAI is calculated from the area A defined here by:

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

13.3.7 *Example 4* (see Fig. 5)—There is a residual positive peak at 1740 cm^{-1}.

13.3.7.1 Draw a first baseline close to 1650 cm^{-1} and 1820 cm^{-1} as described in 11.3. This baseline creates the areas $A_1 + A_2$.

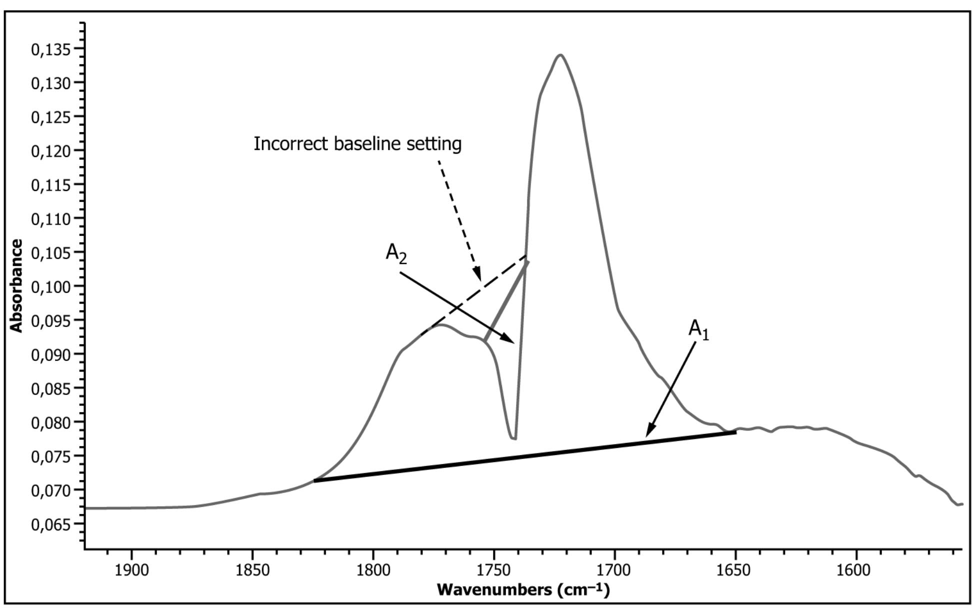

FIG. 3 Example 2

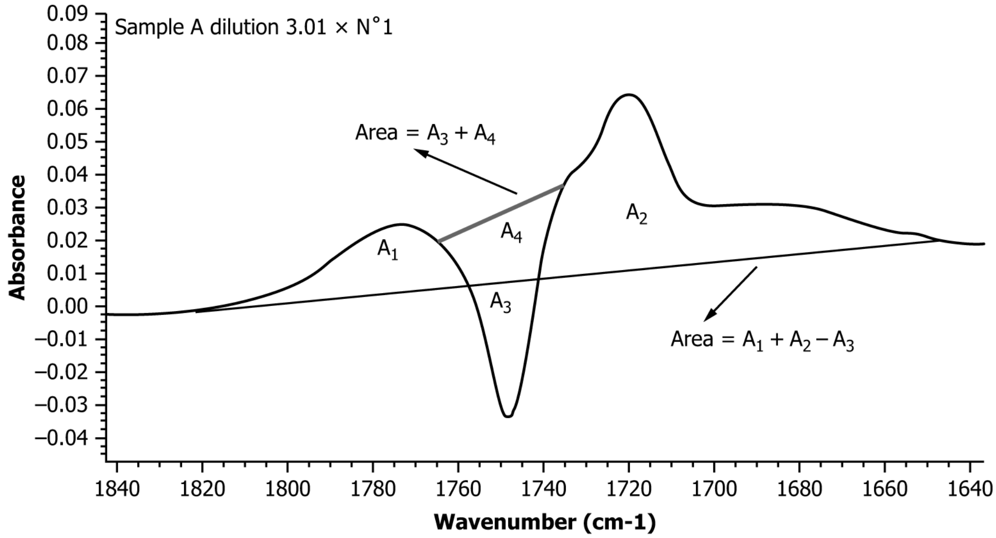

FIG. 4 Example 3

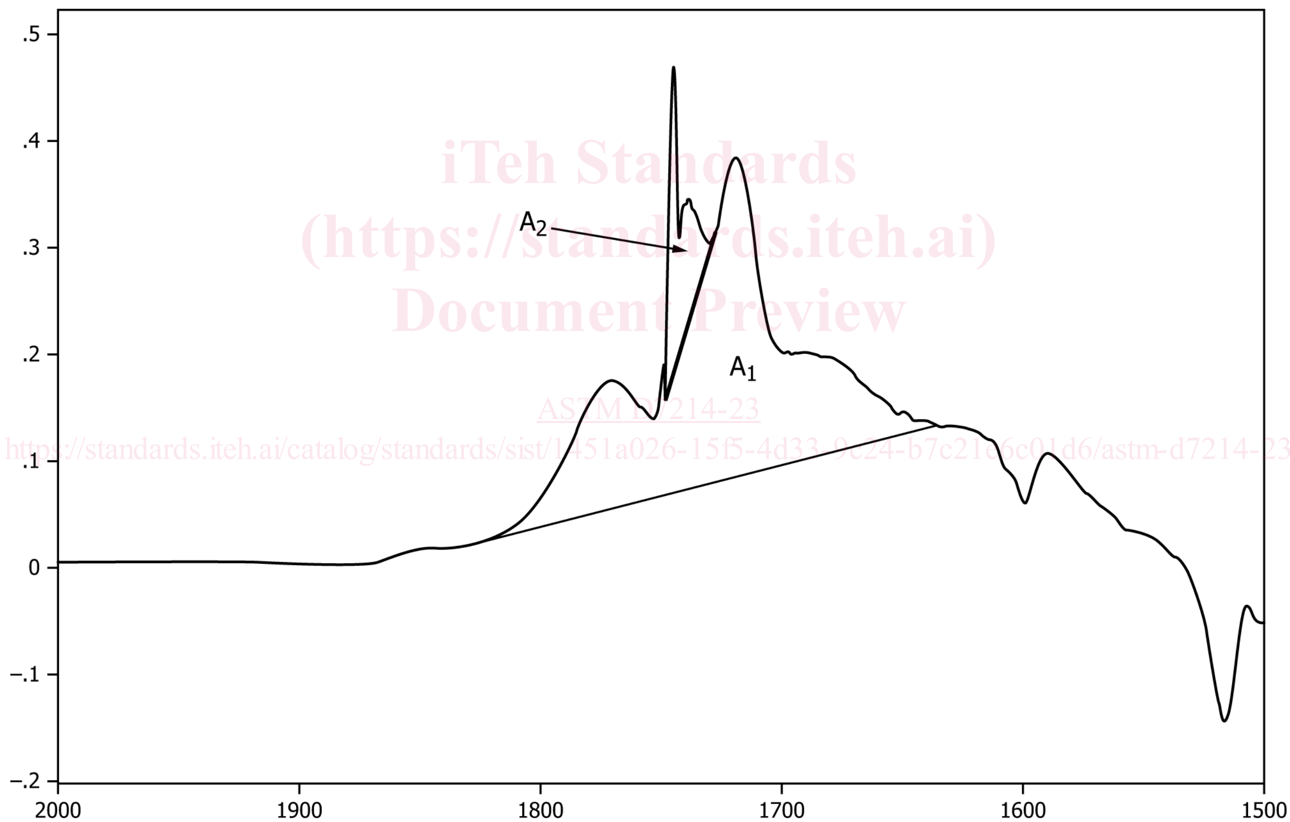

FIG. 5 Example 4

13.3.7.2 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 at approximately 1780 cm^{-1}.

13.3.7.3 The PAI is calculated from the area A defined here by:

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