Designation: E1421 – 99 (Reapproved 2009)

Standard Practice for
Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests[1]

This standard is issued under the fixed designation E1421; 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 practice describes two levels of tests to measure the performance of laboratory Fourier transform mid-infrared (FT-MIR) spectrometers equipped with a standard sample holder used for transmission measurements.

1.2 This practice is not directly applicable to Fourier transform infrared (FT-IR) spectrometers equipped with various specialized sampling accessories such as flow cells or reflectance optics, nor to Fourier transform near-infrared (FT-NIR) spectrometers, nor to FT-IR spectrometers run in step scan mode.

1.2.1 If the specialized sampling accessory can be removed and replaced with a standard transmission sample holder, then this practice can be used. However, the user should recognize that the performance measured may not reflect that which is achieved when the specialized accessory is in use.

1.2.2 If the specialized sampling accessory cannot be removed, then it may be possible to employ a modified version of this practice to measure spectrometer performance. The user is referred to Guide E1866 for a discussion of how these tests may be modified.

1.2.3 Spectrometer performance tests for FT-NIR spectrometers are described in Practice E1944.

1.2.4 Performance tests for dispersive MIR instruments are described in Practice E932.

1.2.5 For FT-IR spectrometers run in a step scan mode, variations on this practice and information provided by the instrument vendor should be used.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E131 Terminology Relating to Molecular Spectroscopy
E932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers
E1866 Guide for Establishing Spectrophotometer Performance Tests
E1944 Practice for Describing and Measuring Performance of Laboratory Fourier Transform Near-Infrared (FT-NIR) Spectrometers: Level Zero and Level One Tests

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology E131. All identifications of spectral regions and absorption band positions are given in wavenumbers (cm^{-1}), and spectral energy, transmittance, and absorbance are signified in equations by the letters E, T, and A respectively. The ratio of two transmittance or absorbance values, and the ratio of energy levels at two different wavenumbers are signified by the letter R. A subscripted number signifies a spectral position in wavenumbers (for example, A_{3082}, the absorbance at 3082 cm^{-1}).

3.1.1 *level one (1) test, n*—a simple series of measurements designed to provide quantitative data on various aspects of instrument performance and information on which to base the diagnosis of problems.

3.1.2 *level zero (0) test, n*—a routine check of instrument performance, that can be done in a few minutes, designed to visually detect significant changes in instrument performance and provide a database to determine instrument function over time.

4. Significance and Use

4.1 This practice permits an analyst to compare the general performance of an instrument on any given day with the prior performance of an instrument. This practice is not necessarily meant for comparison of different instruments with each other even if the instruments are of the same type and model. This practice is not meant for comparison of the performance of one instrument operated under differing conditions.

5. Test Conditions

5.1 *Operating Conditions*—A record should be kept to document the operating conditions selected so that they can be

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[1] This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and is the direct responsibility of Subcommittee E13.03 on Infrared and Near Infrared Spectroscopy.

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[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.

duplicated. In obtaining spectrophotometric data, the analyst must select proper instrumental operating conditions such as warm-up time, purge rate, and beam splitter alignment in order to realize satisfactory instrument performance. Operating conditions for individual instruments are best obtained from the manufacturer's literature because of variations with instrument design. It should be noted that many FT-IR instruments are designed to work best when left on or in the standby mode. Also note that spectrometers are to be tested only within their respective wavenumber ranges.

NOTE 1—This practice is designed to be used in situations where the detector is not saturated. In some instruments, with some combinations of optics and detectors, the detector electronics are saturated with an empty beam. These instruments are designed to have the infrared beam attenuated in the spectrometer or sample compartment to eliminate detector saturation. Consult your instrument manual or discuss appropriate attenuation techniques with the instrument vendor.

5.2 The environment in which a spectrometer is operated can affects its performance. Spectrometers should only be operated in environments consistent with manufacturer's recommendations. Changes in the instrument environment including variations in temperature, vibration or sound levels, electrical power or magnetic fields should be recorded.

5.3 Instrumental characteristics can influence these measurements in several ways.

5.3.1 Vignetting of the beam reduces the transmittance value measured in nonabsorbing regions, and on most instruments can change the apparent wavenumber scale by a small amount, usually less than 0.1 cm^{-1}. Make sure that the film holder does not vignet the beam.

5.3.2 Focus changes can also change transmittance values, so the sample should be positioned in approximately the same location in the sample compartment each time.

5.3.3 The angle of acceptance (established by the *f* number) of the optics between the sample and detector significantly affects apparent transmittance. Changes to the optical path including the introduction of samples can alter the acceptance angle.

5.3.4 Heating of the sample by the beam or by the higher temperatures which exist inside most spectrometers changes absorbances somewhat, and even changes band ratios and locations slightly. Allow the sample to come to thermal equilibrium before measurement.

5.4 The recommended sample of matte-finish polystyrene used for these tests is approximately 38-μm (1.5-mil) thick film mounted on a card. The sample is mounted in a 2.5-cm (1-in.) circular aperture centered within the 5-cm (2.5-in.) width of the card, and centered 3.8 cm (1.5 in.) from the bottom of the card. The card should be approximately 0.25-cm (0.1-in.) thick and individually and unambiguously identified. A polystyrene film meeting these requirements is available from the National Institute of Standards and Technology (NIST) as SRM 1921.[3]

NOTE 2—Very small beam diameters can defeat the interference fringe suppression provided by the matte finish on the sample.

6. Level Zero Tests

6.1 *Nature of Tests*—Routine checks of instrument performance, these tests can be performed in a few minutes. They are designed to uncover malfunctions or other changes in instrument operation but not to specifically diagnose or quantitatively assess any malfunction. It is recommended that the level zero tests be conducted at the highest (smallest numerical value) resolution at which the instrument is typically used in normal operation. A nominal measurement time of 30 s should be used. The exact measurement time, along with the date, time, sample identification, number of scans, exact data collection and computation parameters, and operator's name, should always be recorded.

6.2 *Philosphy*—The philosophy of the tests is to use previously stored test results as bases for comparison and the visual display screen or plotter to overlay the current test results with the known, good results. If the old and new results agree, they are simply reported as no change. Level zero consists of three tests. The tests are run under the same conditions that are normally used to run a sample (that is, purge time, warm-up time, detector, etc.).

6.3 *Variations in Operating Procedure for Different Instruments*—Most of the existing FT-IR instruments should be able to use the tests in this practice without modification. However, a few instruments may not be able to perform the tests exactly as they are written. In these cases, it should be possible to obtain the same final data using a slightly different procedure. Practice E1866 and the FT-IR manufacturer should be consulted for appropriate alternative procedures.

6.4 *Sample*—The recommended sample is described in 5.3. It is a matte-finish polystyrene film (approximately 38-μm thick, in a 2.5-cm aperture). The same sample should be used for all comparisons (note serial number).

6.5 *Reference Spectra*—Two spectra acquired and stored following the last **major** instrument maintenance are used as references. Major maintenance could include changes in source, laser, detector, or optical alignment. These spectra will be identified as Reference 1 and Reference 2.

6.5.1 Reference Spectrum 1 is a single-beam energy spectrum of an empty beam. (In this and all later usage, **empty beam** means that **nothing** is in the sample path except air or the purge gas normally present within the spectrometer sample compartment). If possible, the interferogram corresponding to Reference Spectrum 1 should also be saved.

6.5.2 Reference Spectrum 2 is a transmittance spectrum of the polystyrene sample. Optionally, an absorbance spectrum may also be stored.

NOTE 3—If the instrument software will not allow for subtraction of transmittance spectra, Reference Spectrum 2 should be saved as an absorbance spectrum.

6.6 *Reproducibility of Procedures*—Care should be taken that each of the spectral measurements is made in a consistent and reproducible manner, including sample orientation (although different spectral measurements do not necessarily use the identical procedure). In particular, for those instruments having more than one sample beam or path in the main sample

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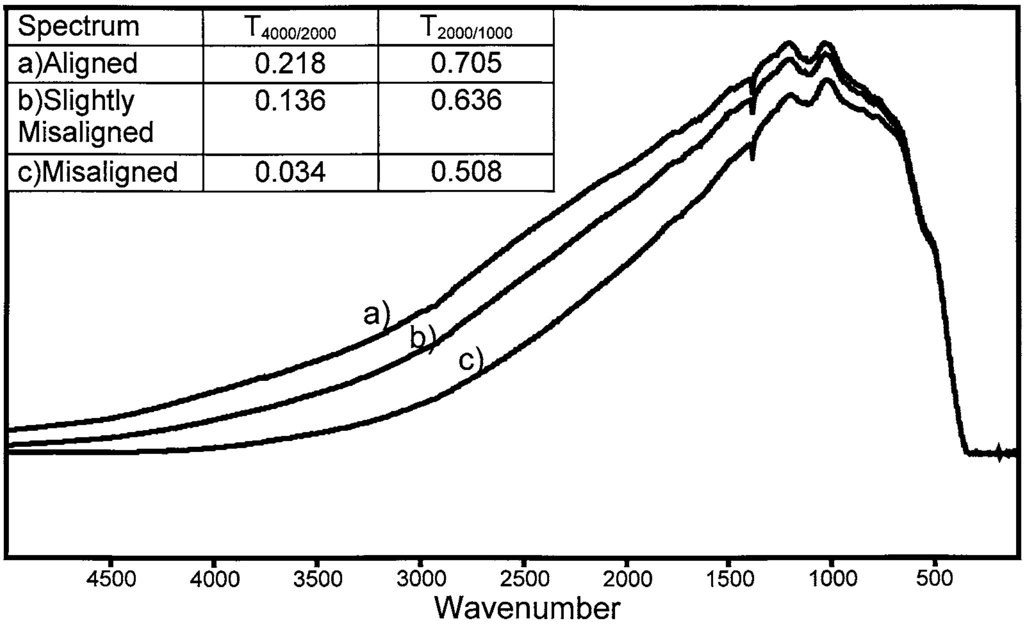
[3] SRM 1921 is available from the Standard Reference Materials Program, National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, http://www.nist.gov.



Spectrum	$T_{4000/2000}$	$T_{2000/1000}$
a)Aligned	0.218	0.705
b)Slightly Misaligned	0.136	0.636
c)Misaligned	0.034	0.508

FIG. 1 Effect of Misalignment on Single-Beam Energy Spectra

compartment, all of the test spectra always should be measured using the same path. It may be desirable to repeat the tests on each path.

6.7 *Measurements*—Acquire and store three test spectra. The test spectra will be identified hereafter as Spectrum 1, Spectrum 2, and Spectrum 3.

6.7.1 *Spectrum 1*—Acquire and store a single-beam energy spectrum of any empty beam. When possible, the interferogram of Spectrum 1 should also be stored. If Spectrum 1 is stored only as an interferogram, it must be transformed before use in the ensuing tests.

6.7.2 *Spectrum 2*—Acquire and store an empty-beam spectrum taken immediately after Spectrum 1. This spectrum should be stored as a transmittance spectrum ratioed against Spectrum 1.

6.7.3 *Spectrum 3*—Acquire and store a spectrum of the polystyrene sample reasonably soon after Spectrum 2. This spectrum should be stored as a transmittance spectrum calculated using either Spectrum 1 or Spectrum 2 as a background. Optionally, Spectrum 3 may also be stored as an absorbance spectrum. To reproducibly insert the sample, the serial number (or other identifying information) should be right side up facing the instrument detector.

NOTE 4—If the instrument software will not allow for subtraction of transmittance spectra, Spectrum 2 should be saved as an absorbance spectrum.

7. Level Zero Test Procedures

7.1 *Energy Spectrum Test*—Overlay Spectrum 1 and Reference 1. Note any change in energy level across the spectrum. Ratio Spectrum 1 to Reference Spectrum 1 to produce a transmittance spectrum, and look for significant changes from 100 %, especially at high wavenumber. Video display resolution may limit the accuracy to which this test can be interpreted if the comparison is made on-screen. In addition, if the interferogram for Spectrum 1 was saved, it may be displayed or plotted and the center burst height recorded and compared to the allowable range for the instrument. Use caution in interpreting this because minor changes in interferogram height only affect performance at high wavenumbers, and do not necessarily affect photometric performance.

NOTE 5—If the centerburst height exceeds the dynamic range of the analog-to-digital converter, the energy profile is distorted and significant nonphysical energy will be observed. If the centerburst is small relative to the dynamic range, then the signal-to-noise of the measurement may be less than optimal.

7.1.1 *Reportage*—Report by (*1*) making an overlay plot of Spectrum 1 and Reference 1, (*2*) plotting the transmittance spectrum of Spectrum 1 ratioed against Reference 1 over the range of 95 to 105 % *T*, and by reporting the following energy ratios:

$$R_{4000/2000} = E_{4000}/E_{2000} \quad (1)$$

$$R_{2000/1000} = E_{2000}/E_{1000}$$

If possible, from Spectrum 1, report the ratio between the apparent energy in the wavenumber region below the instrument cutoff and the energy in the maximum-energy region of the spectrum, for example:

$$R_{\text{nonphysical}} = E_{150}/E_{\max} \quad (2)$$

Report the date and time of both spectra used, and the actual numbers of scans and measurement times.

7.1.2 *Interpretation*—An overall drop in the energy level in which the largest percentage of change occurs at higher wavenumbers usually indicates interferometer misalignment or a reduction in source temperature. An example of the affect of misalignment is shown in Fig. 1.

7.1.2.1 If the instrument has been exposed to high humidity, this drop in energy level may reflect beamsplitter or window fogging.

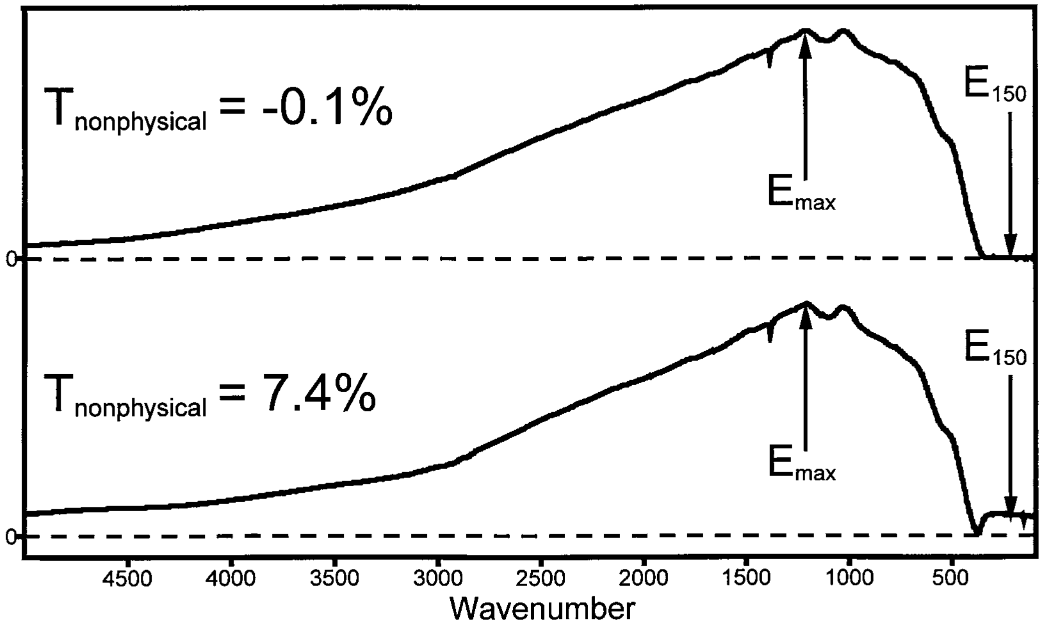


FIG. 2 Example of Nonphysical Energy

7.1.2.2 An overall drop in the energy level without wavenumber dependence suggests beam obstruction or misalignment of noninterferometer optical components.

7.1.2.3 The appearance of bands or other features indicates purge gas contributions, beam obstruction by a partially transmitting object, oil, or smoke deposition on mirrors or windows, or a forgotten sample in the beam.

7.1.2.4 With cooled detectors, the appearance of a band around 3440 cm^{-1} indicates ice deposition on the detector surface.

7.1.2.5 Non-zero energy levels below the detector cut-off (more than 0.2 % of the maximum energy level in the single beam spectrum) indicate system nonlinearities or detector saturation. Examples of systems with minimal and high levels of nonphysical energy are shown in Fig. 2.

7.1.2.6 On many instruments anomalous increases in the actual measurement time for a set number of scans indicate instrument problems (mis-triggering, white light misalignment, excessive purge rate, or interferometer drive problems).

7.2 *One Hundred Percent Line Test*—Using transmittance Spectrum 2, note the noise level and any variations from 100 % transmittance across the spectrum.

7.2.1 *Reportage*—Plot Spectrum 2, the 100 % transmittance line. The ordinate range should be 99 to 101 % *T*. If the noise or baseline drift exceeds these bounds, make plot from 90 to 110 % *T* and consider performing level one tests. Report the root mean square (RMS) (preferred) or peak-to-peak noise levels at over a 100 cm^{-1} range centered at 4000, 2000, 1000, and 500 cm^{-1}. If the instrument wavenumber ranges does not include some of these, substitute the nearest measurable wavenumber.

7.2.2 *Interpretation*—Excessive noise may result from misalignment or source malfunction (refer to the energy spectrum test) or from a malfunction in the detector or the electronics. Repetitive noise patterns (for example, spikes or sinusoids) sometimes indicate digital problems. Isolated noise spikes may be digital malfunctions or they can indicate electromagnetic interference. Positive or negative bands often indicate a rapid change in purge quality. Simultaneously positive and negative sharp bands in the water region may indicate instrumental problems or excessive water vapor in the spectrometer. Deviations from the 100 % level (usually at the higher wavenumbers) indicate interferometer, detector, or source instability.[4]

7.3 *Polystyrene Subtraction Test*—Overlay Spectrum 3 and Reference 2 and note any differences. If the instrument software will permit, subtract the stored polystyrene transmittance spectrum (Reference Spectrum 2) from this new polystyrene transmittance spectrum (Spectrum 3). Optionally, or if the instrument software does not permit the subtraction of transmission spectra, subtract the stored polystyrene absorbance spectrum (Reference Spectrum 2) from the new polystyrene absorbance spectrum (Spectrum 3). Note any changes. Subtracting transmittance spectra from each other is not appropriate for most chemical applications, but here it is relevant to the instrument's performance, and avoids possible overrange problems associated with zero or negative transmittances.

7.3.1 *Reportage*—Overlay the polystyrene spectra. Plot the subtraction result over a range of −1 to +1 % *T* if subtraction was performed on transmittance spectra or over a range of −0.01 to 0.01 *A* if the subtraction was performed on absorbance spectra.

7.3.2 *Interpretation:*

7.3.2.1 Subtraction of transmittance spectra is preferred for this test since the strongly absorbing (>1 *A*) peaks are more likely to cancel as shown in Fig. 3.

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[4] Hirschfeld, T., *Fourier Transform Infrared Spectroscopy: Applications to Chemical Systems* , Vol 2, Ferraro, J. R. and Bacile, L. J., eds., Academic Press, New York, pp. 193–239.

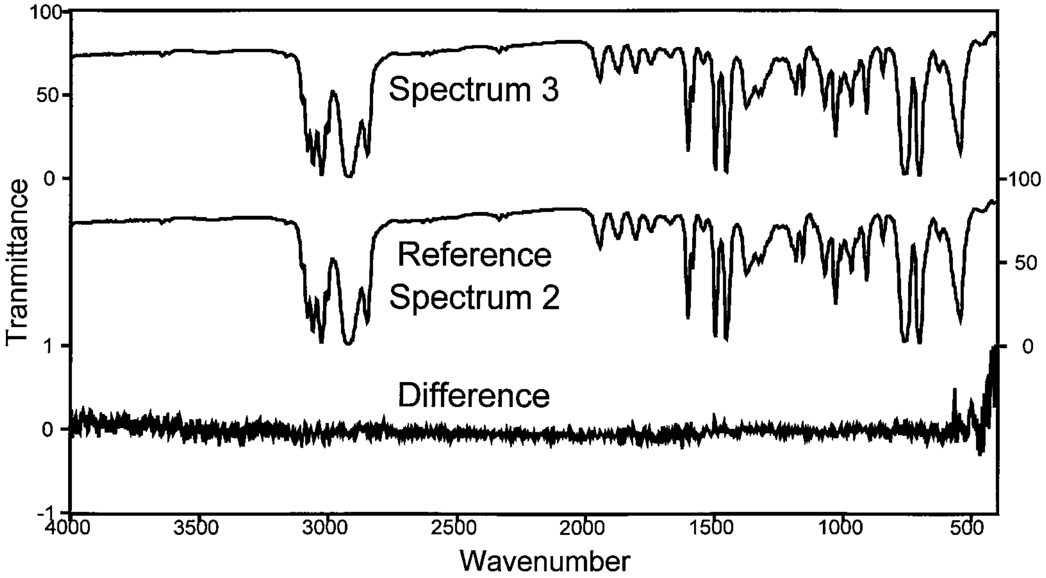

FIG. 3 Example of Transmittance Spectra Subtraction

7.3.2.2 If the subtraction is done using absorbance spectra, bands with absorbances greater than 1 will typically not completely cancel as shown in Fig. 4.

7.3.2.3 If subtractions are conducted on transmittance spectra, variations in the spectral baseline may lead to non-cancellation of spectral features as illustrated in Fig. 5. The baseline variation is much more readily identified when absorbance spectra are subtracted.

7.3.2.4 Sharp features in the water vapor absorption regions (two irregular groups of lines near 3600 cm^{-1} and near 1600 cm^{-1}) indicate excessive water vapor levels in the spectrometer or instrumental problems unless all such features point in the same direction. All band features pointing in the same direction indicate a change in purge level. A similar interpretation can be obtained from artifacts in carbon dioxide absorption regions (doublet near 2360 cm^{-1} and sharp spike near 667 cm^{-1}).

7.3.2.5 Instrumental problems may include JacQuinot vignetting, source optics or laser misalignment, or interferometer scan problems. In the subtraction spectrum, first-derivative-like bandshapes that correspond to absorption band positions indicate these instrumental problems. Artifacts appearing only at the positions of the strongest (completely absorbing) bands may indicate phasing or other problems associated with detector non-linearity. Artifacts at both medium and strong band positions indicate analog electronic, ADC, or computer problems, or sampling jitter (Zachor-Aaronsen distortion).

NOTE 6—Some polystyrene films may gradually oxidize over time, producing a broad hydroxyl absorption between 3600 and 3200 cm^{-1}, a carbonyl absorption at 1720 cm^{-1} and C-O absorptions in the range of 1050 to 1000 cm^{-1} as shown in Fig. 6. Such changes are an indication of degradation of the film and do not reflect on instrument performance. If these absorptions exceed 0.01 absorbance, it is recommended that the film be replaced.

7.4 *Polystyrene Peak, Resolution and Photometry Tests*—The interpretation of the difference spectrum generated in 7.3 can, in some cases, be somewhat subjective. For some applications, it is preferable to have numeric indications of instrument performance. In these cases, some or all of the level one polystyrene peak position, resolution and photometry tests discussed in 9.5 and 9.6 can be conducted in addition to, or in place of, the polystyrene subtraction test. The results of these tests should be plotted on performance test charts. For a more complete discussion on performance test charts see Practice E1866. If these optional tests are conducted, it is recommended that the calculation be automated.

7.5 *Polystyrene Residuals Test*—Optionally, an additional quantitative comparison of the current polystyrene spectrum (Spectrum 3) and the reference polystyrene spectrum (Reference Spectrum 2) can be conducted. Practice E1866 describes a Level A test that can be used for this purpose. This test involves fitting Spectrum 3 as a linear combination of Reference Spectrum 2, and various vectors that simulate baseline variations. The root mean square residual from the fit is calculated and charted as a measure of instrument performance. Alternatively, the fit can be conducted using PCR or PLS. See Practice E1866 for details on conducting this test.

7.5.1 It is recommended that peaks with absorbances exceeding 1.0 be excluded from the residuals calculation.

7.5.2 The residuals test is extremely sensitive to oxidation of the polystyrene film. If a change in the magnitude of the residuals is observed, the polystyrene subtraction test should be performed to determine if the change is due to the instrument or the film.

8. Level One Tests

8.1 *Nature of Test*—A series of tests, which uses only the standard matte-finish polystyrene, designed to more completely test the instrument performance. The main purpose of level one tests is to compare performance with previous results obtained on the same instrument. The tests can also be used to compare two instruments of the same model type and, with considerable caution, to roughly compare different models.

8.2 *Philosophy*—Level one tests are similar to, but more extensive than level zero tests. The reportage for level one tests

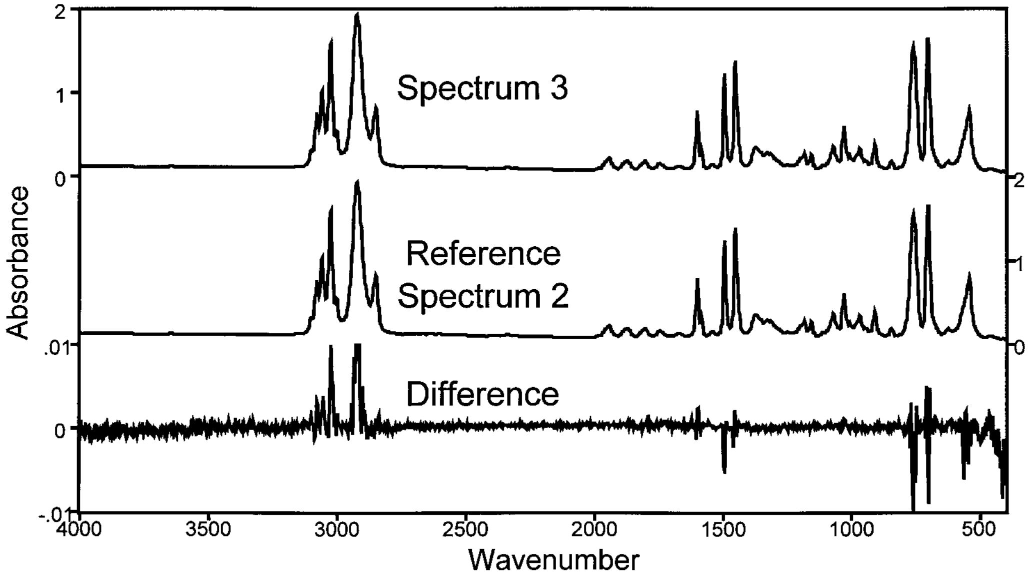

FIG. 4 Example of Absorbance Spectra Subtraction

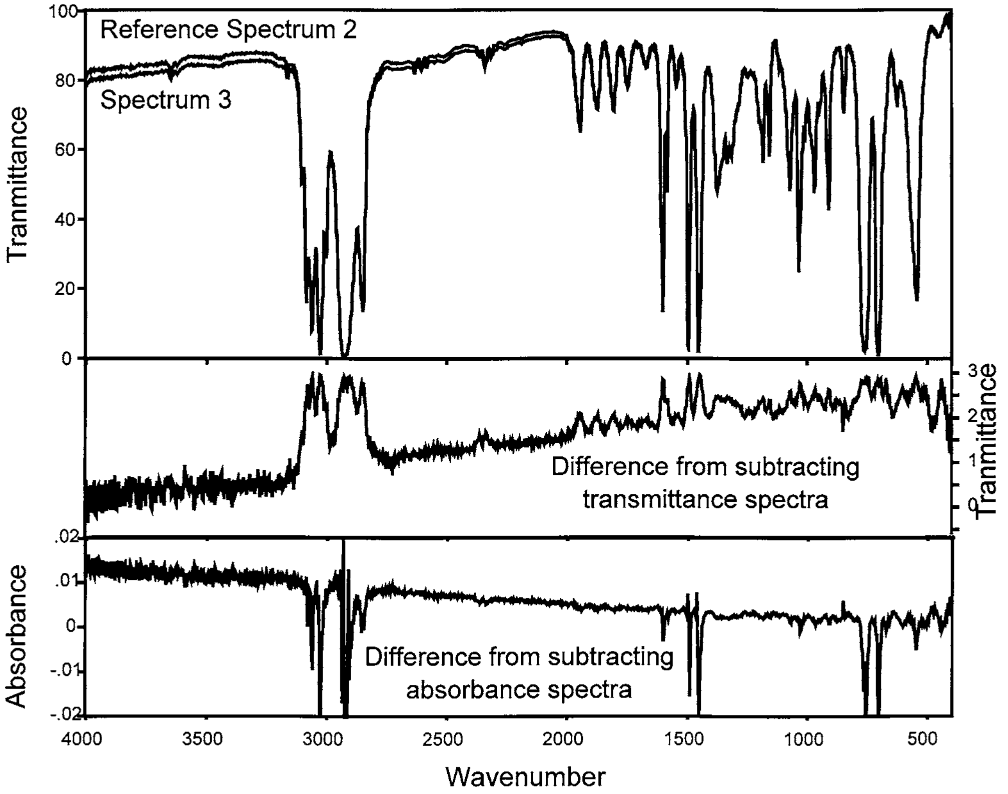

FIG. 5 Effect of Baseline Variations on Subtraction Results

is designed to facilitate diagnosis instead of just indicating malfunctions. The diagnostic content of the results is such that interpretation is beyond the scope of this practice.

8.3 *Sample*—The same matte-finish polystyrene sample described in 6.3 is used for measurements. In well-purged or evacuated spectrometers, the introduction of a water vapor or carbon dioxide sample (diluted with nitrogen or air to atmospheric pressure) may be necessary for some tests.

8.4 *Measurements*—In level one, each test requires its own measurements. For comparisons involving a single instrument or model of instrument, choose any convenient measurement parameters, preferably those which reflect the operating parameters used for measurements of analytical samples. The parameters must always be the same for comparisons. On most instruments, use the stored parameter file for the original measurements as a way to get parameter consistency. If

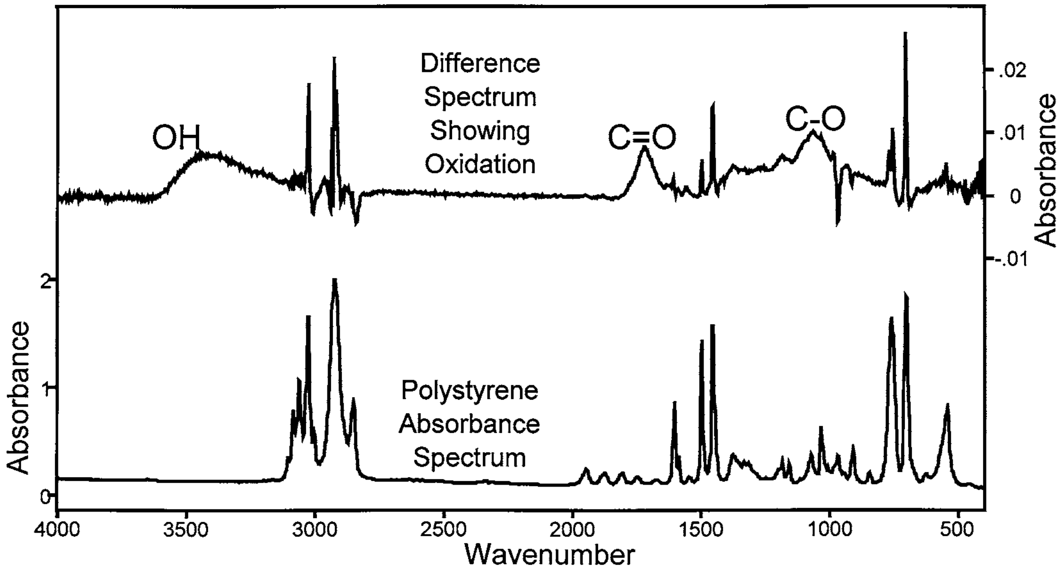

FIG. 6 Example of Effect of Polystyrene Film Oxidation

inter-instrument comparisons are attempted, several factors must be strictly adhered to before any valid comparison can be made. These factors concern the instrument lineshape function (ILS), which is the detailed way of expressing resolution. Peak positions and photometer data must be reported at the highest possible resolution. They are useful for inter-instrument comparison only to the extent that one of the instruments being compared is producing essentially undistorted (that is, Coblentz Class I) spectra.

9. Level One Test Procedures

9.1 *Energy Spectrum Test*—For an energy spectrum, obtain a single beam spectrum. The beam path in the sample compartment must be empty. Several specific indicators may be reported.

9.1.1 *Energy Ratio*—Calculate the ratio of the energy at 4000 cm^{-1} to energy at 2000 cm^{-1}. In each case, a 100-cm^{-1} wide region centered around the wavenumber position specified is used for obtaining an averaged energy value:

$$R_{4000/2000} = E_{4000}/E_{2000} \quad (3)$$

9.1.2 *Spectral Range*—Report wavenumber points where spectral energy decreases to one-tenth of the energy level found at the energy maximum for the range.

9.1.3 *Water Vapor Level*—Report water vapor band absorbances identified below. If nominal instrument resolution is 4 cm^{-1} or poorer (for example, 8 cm^{-1}), or if digital resolution is coarser than 2 cm^{-1}, confirm that the spectrum shows clear bands at the named wavenumber positions.

$$A_{H_2O}(3744) = -\log_{10}[2(E_{p1})/(E_{b1}+E_{b2})] \quad (4)$$

$$A_{H_2O}(1616) = -\log_{10}[2(E_{p2})/(E_{b3}+E_{b4})] \quad (5)$$

where E_{p1} and E_{p2} are the single beam energy values that correspond to the peaks in the water vapor spectrum which are nominally at 3744 and 1616 cm^{-1} . E_{b1}, E_{b2}, E_{b3}, and E_{b4} are the single beam energy values of baseline points on the sides of the peaks, and should be measured at 3747, 3741, 1620 and 1612 cm^{-1} respectively. The suggested measurement points are shown in Fig. 7.

9.1.4 *Carbon Dioxide (CO_2) Level*—Report the CO_2 band absorbance identified below, and in Fig. 7. E_{p3} is the single beam energy at the peak position, nominally 2362 cm^{-1}. E_{b5} and E_{b6} are baseline points on the sides of the CO_2 envelope, and are nominally at 2422 and 2302 cm^{-1} respectively:

$$A_{CO_2} = -\log_{10}[2(E_{p3})/(E_{b5}+E_{b6})] \quad (6)$$

9.1.5 *Aliphatic Hydrocarbon Level*—Report hydrocarbon C-H stretching band intensity absorbance identified below, and in Fig. 7. E_{p4} is the single beam energy at the hydrocarbon peak position, nominally 2927 cm^{-1}. E_{b7} and E_{b8} are baseline points on the sides of the CO_2 envelope, and are nominally at 2984 and 2794 cm^{-1} respectively:

$$A_{HC} = -\log_{10}[(E_{p4})/(0.7E_{b7}+0.3E_{b8})] \quad (7)$$

9.1.6 *Non-Physical Energy*—Report the ratio of the energy level found below the detector/spectrometer cutoff to the energy found at the energy maximum for the range, for example:

$$R_{non-phycical} = E_{150}/E \quad (8)$$

9.1.7 *Peculiarities*—Report any other peculiarities of the single beam spectrum. Ratioing to an old reference single beam spectrum and looking for bands is a sensitive way to detect such peculiarities.

9.2 *One Hundred Percent Line Test*—Obtain two successive single-beam spectra and calculate their transmittance. Several specific indicators can be reported.

9.2.1 *Noise Level at 500, 1000, 2000, and 4000 cm^{-1}*—A 100-cm^{-1} wide spectral portion centered around each position should be used for calculating the noise level in percent *T* units. Report values of the peak-to-peak or average RMS noise level. RMS is preferred.

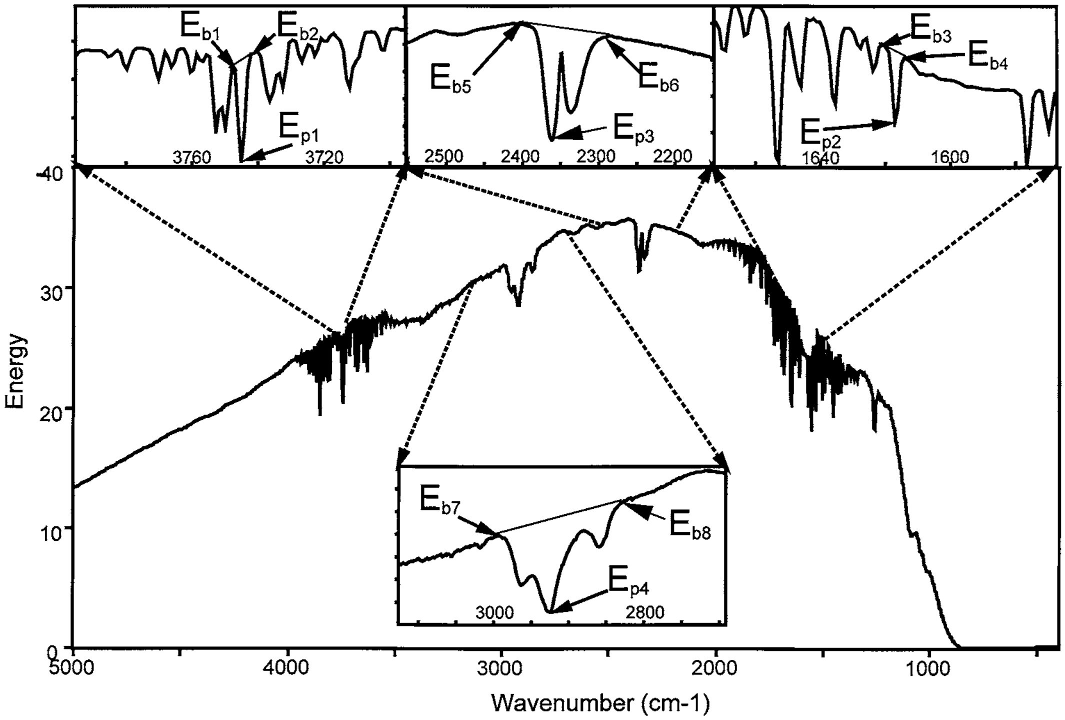

FIG. 7 Example of Water Vapor, Carbon Dioxide, and Hydrocarbon Tests

9.2.2 Calculate one hundred percent line position at each wavenumber in 9.2.1. The average transmittance value determined as part of the RMS calculation in 9.2.1 over the same 100 cm^{-1} ranges can be used.

9.2.3 *Artifacts*—Report any sinusoids or spikes in the 100 % line spectrum.

9.3 *Stability Test*—Obtain successive single beam spectra at intervals over a period of time. Use a period of time which is representative of usual stability requirements (for example, usual period of time between background spectra). Ratio all spectra to the first spectrum to obtain a set of *n*-1 transmittance spectra, and determine 100 % line position at 500, 1000, 2000, and 4000 cm^{-1} as described in 9.2.2.

9.3.1 The RMS variation in the average transmittance is an index of system stability. Large variations at the highest wavenumbers suggest source temperature flicker or variable interferometer misalignment. Variations in transmittance in all regions are less common, and suggest detector or electronic problems, or serious optical (noninterferometer) misalignments.

9.3.2 The trend and total variation in the average transmittance indicate time-dependent instabilities, usually connected to temperature variations. Simultaneous temperature measurement will reveal the connection, often with a significant time delay between temperature change, its effect on the spectrometer, and the total variation over the period.

9.3.3 Purge variations can be observed in the transmittance spectra, and quantitatively assessed by calculating the band strengths using the same bands as used in 9.1.3 and 9.1.4, as shown in the equations below:

$$\Delta T_{H_2O}(3744) = T_{p1} - [(T_{b1}+T_{b2})/2] \quad (9)$$

$$\Delta T_{H_2O}(1616) = T_{p2} - [(T_{b3}+T_{b4})/2] \quad (10)$$

$$\Delta T_{CO_2}(2362) = T_{p3} - [(T_{b5}+T_{b6})/2] \quad (11)$$

9.3.4 Other artifacts can clearly be seen in the transmittance spectra. Ice on (cooled) detector surfaces (broad band around 3440 cm^{-1}), condensed water (very broad, 2400 to 3600 cm^{-1}), and hydrocarbon contaminants (structure, between 2937 and 2850 cm^{-1}) are examples.

9.4 *Signal Averaging Test*—Obtain a pair of subspectra, each having the same number of scans. Do this for the following number scans: 1, 4, 16, 64, 256, 1024, 4096, 16 384, etc., up to the maximum measurement time of interest. Ratio each pair and calculate the noise level at 500, 1000, 2000, and 4000 cm^{-1} as described in 9.2.1. The noise level should be reduced by a factor of 2 for each successive ratioed spectrum; for example, if 1 scan gave a noise level of 1, 4 scans would give ½, 16 would given ¼, 64 would give ⅛ and so on until signal averaging fails. The percent noise level for each successive ratioed spectrum should be a factor of 2 lower; for example, 1, ½, ¼, ⅛, 1⁄16, 1⁄32, 1⁄64, 1⁄128, etc.

9.4.1 *Failure of Signal Averaging*—Report the number of scans and the measurement time for each of the pair used in the particular ratioed spectrum which has a noise level at least twice that predicted by the single scan pair. All spectrometers have a limit to their practical signal-averaging capability, often set by residual interference fringing by optical components or by the apodization-determined feet of the purge band absorptions.

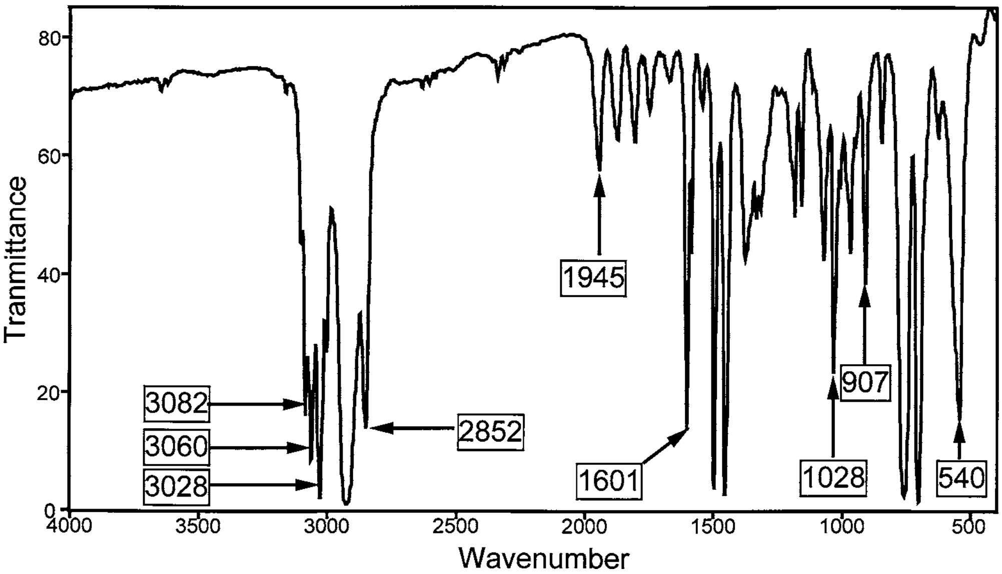

FIG. 8 Polystyrene Peaks

9.4.2 Scaling problems and digital errors are uncovered by noting any drastic (usually a factor of 2) changes in energy in the single beam spectra, or abrupt appearance of spikes or sinusoids in the ratioed spectra. These problems are rare.

9.5 *Polystyrene Test*—Obtain an empty-beam single-beam spectrum followed by a spectrum of the matte-finish standard polystyrene. Ratio the polystyrene spectrum to the empty-beam spectrum to produce a polystyrene transmittance spectrum, and convert this to the absorbance spectrum.

9.5.1 Peak positions for the following bands should be reported (see Fig. 8). These are bands recommended by International Union of Pure and Applied Chemistry (IUPAC), and the real peak positions will be somewhat different for any particular sample of polystyrene and may be affected by the interpolation method. Report the actual peak positions and the peak center finding algorithm. The preferred center of gravity algorithm for determining the peak positions is described in Annex A1. Peak positions are preferably measured on the transmittance spectrum. The digital data point interval should be specified:

$3082\ cm^{-1}$ $2852\ cm^{-1}$ $1028\ cm^{-1}$
$3060\ cm^{-1}$ $1945\ cm^{-1}$ $907\ cm^{-1}$
$3028\ cm^{-1}$ $1601\ cm^{-1}$ $540\ cm^{-1}$

9.5.1.1 *Interpretation*—A change in peak positions following maintenance may be indicative of a misalignment of optical elements. For example, a change in the relative alignment of the reference laser and the infrared (IR) beam will cause such a shift.

9.5.2 *Resolution*—An indirect method for measuring resolution is the measurement of peak ratios of narrow/broad band pairs with similar absorbances. The component absorbances are each measures as the absolute absorbance value at the specified peak's maximum (see Fig. 9 for an example of R_3):

$$R_1 = A_{3082}/A_{2849} \tag{12}$$

$$R_2 = A_{1583}/A_{1154}$$

$$R_3 = (A_{3082} - A_{3096})/(A_{2849} - A_{2870})$$

$$R_4 = (A_{1601} - A_{1564})/(A_{1583} - A_{1564})$$

$$R_5 = (A_{1028} - A_{994})/(A_{1002} - A_{994})$$

9.5.2.1 *Interpretation*—A change in resolution may be indicative of misalignment of the interferometer.

9.5.3 Midrange photometry is quite sensitive to resolution. At constant resolution, the following ratios can be calculated as described in 9.5.2:

$$R_1 = (A_{3082} - A_{2984})/(A_{3001} - A_{2984}) \tag{13}$$

$$R_2 = (A_{3060} - A_{2984})/(A_{3001} - A_{2984})$$

$$R_3 = (A_{2923} - A_{2870})/(A_{2849} - A_{2870})$$

$$R_4 = (A_{1601} - A_{1564})/(A_{1583} - A_{1564})$$

$$R_5 = (A_{1028} - A_{994})/(A_{1002} - A_{994})$$

9.5.4 The photometry of strongly absorbing bands is sometimes dominated by detector or other analog non-linearities, especially with photon detectors such as HgCdTe. This nonlinearity produces a pseudo-stray light (most commonly a negative pseudo-stray light) and can easily be seen as variations in the apparent transmittance of highly absorbing bands. It also appears as nonphysical energy below the spectrometer low-wavenumber cutoff (see 9.1.6). For this test it is desirable to use a normally (Mertz or Foreman method) phase corrected spectrum, where the phase correction array has lower resolution (for example, 100 to 200 cm^{-1}) than the bands being measured or is a stored-phase array from the empty-beam spectrum. If the instrument uses a magnitude calculation, the test can still be performed, but negative pseudostray light will be rectified to positive values. Report the transmittance at the transmittance minimum (or inverted minimum) for each of the following band positions. The highly absorbing region around each peak center can be averaged to improve the precision of

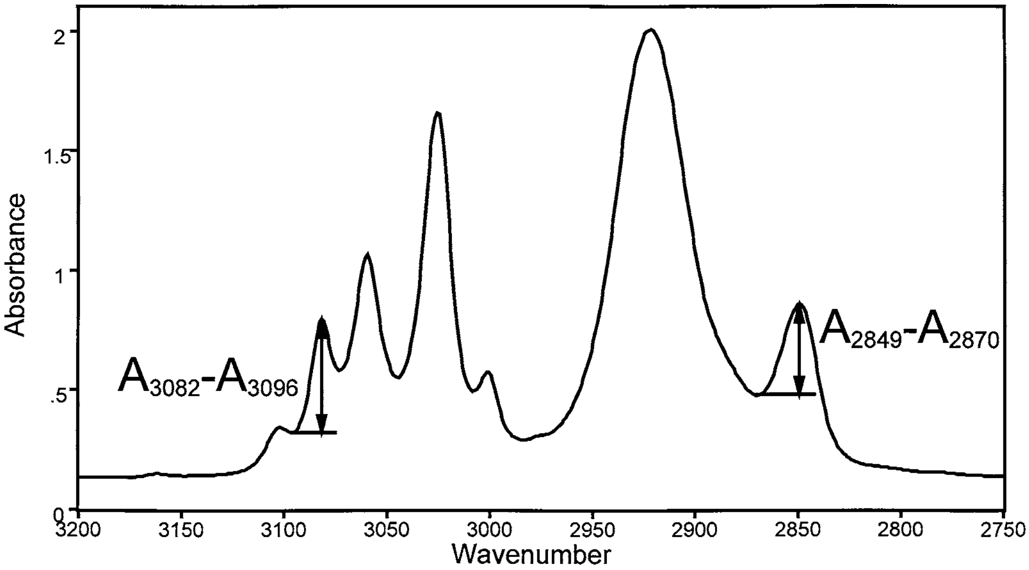

FIG. 9 Example of Resolution Test—R_3

this measurement:

3028 cm^{-1} 1493 cm^{-1} 756 cm^{-1}
2922 cm^{-1} 1453 cm^{-1} 697 cm^{-1}

9.5.4.1 *Interpretation*—For some systems, a change in the photometry of the strongly absorbing bands can be an indication of loss of lock on the zero-phase-difference (ZPD) point. If the interferogram is off center in the window used for the phase correction calculation, a distortion of the phase will occur which is most noticeable at high absorbance. Reestablishing lock may correct the problem.

9.6 *Photometric Jitter Test*—This test is quite similar to 9.5 polystyrene test, and uses the same sample and bands. Obtain an empty-beam single-beam spectrum followed by a series (for example, 30) of single-scan spectra of the matte-finish standard polystyrene. Ratio each polystyrene spectrum to the empty-beam spectrum to produce a series of polystyrene transmittance spectra.

9.6.1 *Peak Position Jitter*—Determine the RMS variation in the peak center wavenumber positions of each of the bands identified in 9.5.1, using the peak-center finding procedure. Peak position jitter is usually negligible, that is, it is usually dominated by photometric jitter and spectral noise.

9.6.2 Resolution jitter is generally found along with mid-range photometric jitter. The absorbance spectra are calculated and the RMS variation of each of the four ratios described in 9.5.2 are reported.

9.6.3 Midrange photometric jitter is often the result of sampling inaccuracy (for example, Zachor-Aaronsen distortion). Otherwise, spectral noise may be predominant. Report the RMS value of the percent *T* jitter in the following bands:

$$\begin{array}{ll} \Delta T_1 = T_{3082} - T_{2984} & \Delta T_6 = T_{1601} - T_{1564} \\ \Delta T_2 = T_{3060} - T_{2984} & \Delta T_7 = T_{1583} - T_{1564} \\ \Delta T_3 = T_{3001} - T_{2984} & \Delta T_8 = T_{1069} - T_{1104} \\ \Delta T_4 = T_{2923} - T_{2870} & \Delta T_9 = T_{1028} - T_{997} \\ \Delta T_5 = T_{2849} - T_{2870} & \Delta T_{10} = T_{1002} - T_{994} \end{array} \tag{14}$$

9.6.4 Strongly absorbing band jitter is usually the result of sampling inaccuracy or clipping in the analog circuitry. Report the RMS variation of the transmittances of each of the band centers identified in 9.5.4. If magnitude calculation is used, assume that band centers are at 0 % *T* and calculate the RMS variation from 0 % *T*, or else determine the true transmittance of each of the band centers by an independent method and use these values for calculating the RMS variations.

10. Keywords

10.1 Fourier transform infrared; FT-IR; level one test; level zero test; performance test; spectrometers

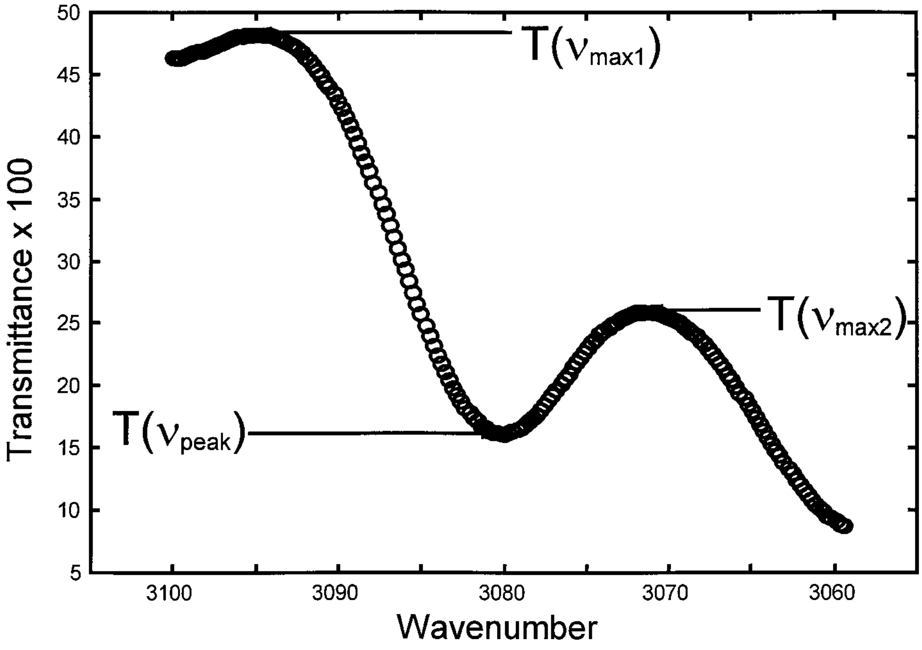

FIG. A1.1 Example of Locating Peak Minimum and Local Maxima

ANNEX

(Mandatory Information)

A1. CENTER OF GRAVITY ALGORITHM FOR PEAK LOCATION DETERMINATION

A1.1 If the polystyrene peaks calculated in 9.5.1 are to be compared to the certified peak wavenumber values published by NIST for Standard Reference Material 1921,[3] then the data collection, computation, and calculation procedures described below should be followed. This procedure is similar to one given in the literature.[5]

A1.2 Collection and Computation of Spectra

A1.2.1 The polystyrene single beam spectrum and the corresponding empty beam background spectrum should be collected at least 4 cm^{-1} resolution.

A1.2.2 In the computation of the single beam spectra, zero-filling should be employed to achieve a data point spacing smaller than 0.25 cm^{-1}. Hamming or Happ-Ganzel apodization preferably is used. If these apodizations are unavailable, triangular apodization should be used.

A1.2.3 The polystyrene single beam spectrum should be ratioed to the empty beam spectrum to produce a transmittance spectrum.

A1.3 Peak Location Computations

A1.3.1 For each peak, locate the minimum transmittance point closest to the expected peak position. The wavenumber at which the minimum occurs will be designated $\bar{\nu}_{peak}$ and the transmittance value will be designated T ($\bar{\nu}_{peak}$). See Fig. A1.1 for an example.

A1.3.2 Locate the local maxima in transmittance that occur on either side of the peak. The wavenumber and transmittance of the minimum on the high wavenumber side of the peak is designated $\bar{\nu}_{max1}$ and T ($\bar{\nu}_{max1}$) and the wavenumber and transmittance of the minimum to the low peak is designated $\bar{\nu}_{max1}$ and T ($\bar{\nu}_{max1}$) and the wavenumber side of the peak is designated $\bar{\nu}_{max2}$ and T ($\bar{\nu}_{max2}$). Number the data points between $\bar{\nu}_{max1}$ and $\bar{\nu}_{max2}$ starting with $\bar{\nu}_{max1}$ and increasing toward lower wavenumber. See Fig. A1.1 for an example.

A1.3.3 Determine which of the local maxima occurs at a lower transmittance value. If $T(\bar{\nu}_{max1}) > T(\bar{\nu}_{max2})$, then the baseline value against which the peak is defined is $T(\bar{\nu}_{max2})$. If $T(\bar{\nu}_{max2}) > T(\bar{\nu}_{max1})$, then the baseline value against which the peak is defined is $T(\bar{\nu}_{max1})$. In the example in Fig. A1.1, T ($\bar{\nu}_{max2}$) would be the baseline point. Call the wavenumber and transmittance for this point $T_{baseline}$ and $\bar{\nu}_{baseline}$.

A1.3.4 Calculate ΔT, the difference between $T_{baseline}$ and T $\bar{\nu}_{peak}$). An example of these calculations is illustrated in Fig. A1.2.

A1.3.5 Calculate $\Delta T/2$, one half the peak height relative to the baseline. On the high wavenumber side of the peak, locate the point j such that $T(\bar{\nu}_j) > T(\bar{\nu}_{peak}) + \Delta T/2 > T(\bar{\nu}_{j+1})$. On the low wavenumber side of the peak, locate the point k such that $T(\bar{\nu}_k) > T(\bar{\nu}_{peak}) + \Delta T/2 > T(\bar{\nu}_{k-1})$.

A1.3.6 Calculate the peak location using the center of gravity formula, $\bar{\nu}_{cog}$:

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[5] Cameron, D. G., Kauppinen, J. K., Moffatt, D. J., and Mantsch, H. H., *Applied Spectroscopy*, Vol 36, 1982, pp. 245–250.

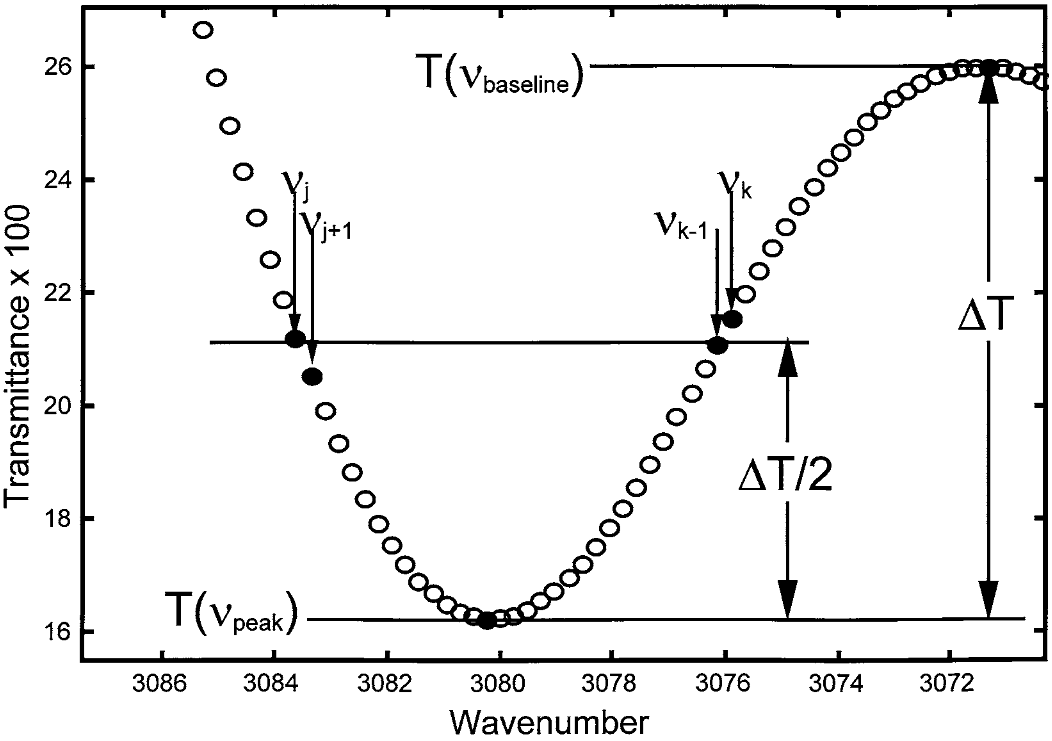

FIG. A1.2 Example of Peak Position Calculation

$$\bar{\nu}_{cog} = \delta_{\bar{\nu}} \cdot \frac{\sum_{i=j}^{k-1} \left(i - j - \frac{1}{2}\right)\left[\frac{T(\bar{\nu}_i)+T(\bar{\nu}_{i+1})}{2} - \frac{\Delta T}{2}\right]}{\sum_{i=j}^{k-1}\left[\frac{T(\bar{\nu}_i)+T(\bar{\nu}_{i+1})}{2} - \frac{\Delta T}{2}\right]} + \bar{\nu}_{j+1} \qquad (A1.1)$$

where $\delta_{\bar{\nu}}$ is the data point spacing.

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