



Designation: E 1421 – 99 (Reapproved 2004)

# Standard Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests<sup>1</sup>

This standard is issued under the fixed designation E 1421; 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 ( $\epsilon$ ) 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 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 E 1866 for a discussion of how these tests may be modified.

1.2.3 Spectrometer performance tests for FT-NIR spectrometers are described in Practice E 1944.

1.2.4 Performance tests for dispersive MIR instruments are described in Practice E 932.

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:*<sup>2</sup>

E 131 Terminology Relating to Molecular Spectroscopy

E 932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrophotometers

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and is the direct responsibility of Subcommittee E13.03 on Infrared Spectroscopy.

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<sup>2</sup> 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.

E 1866 Guide for Establishing Spectrophotometer Performance Tests

E 1944 Practice for Describing and Measuring Performance of 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 E 131. All identifications of spectral regions and absorption band positions are given in wavenumbers ( $\text{cm}^{-1}$ ), 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  $3082 \text{ cm}^{-1}$ ).

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 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 affect 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  $0.1\text{ cm}^{-1}$ . Make sure that the film holder does not vignette 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  $38\text{-}\mu\text{m}$  (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 as SRM 1921.<sup>3</sup>

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

<sup>3</sup> SRM 1921 is available from the Standard Reference Materials Program, Building 202, Room 204, National Institute of Standards and Technology, Gaithersburg, MD 20899-0001.

## 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 *Philosophy*—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 E 1866 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  $38\text{-}\mu\text{m}$  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

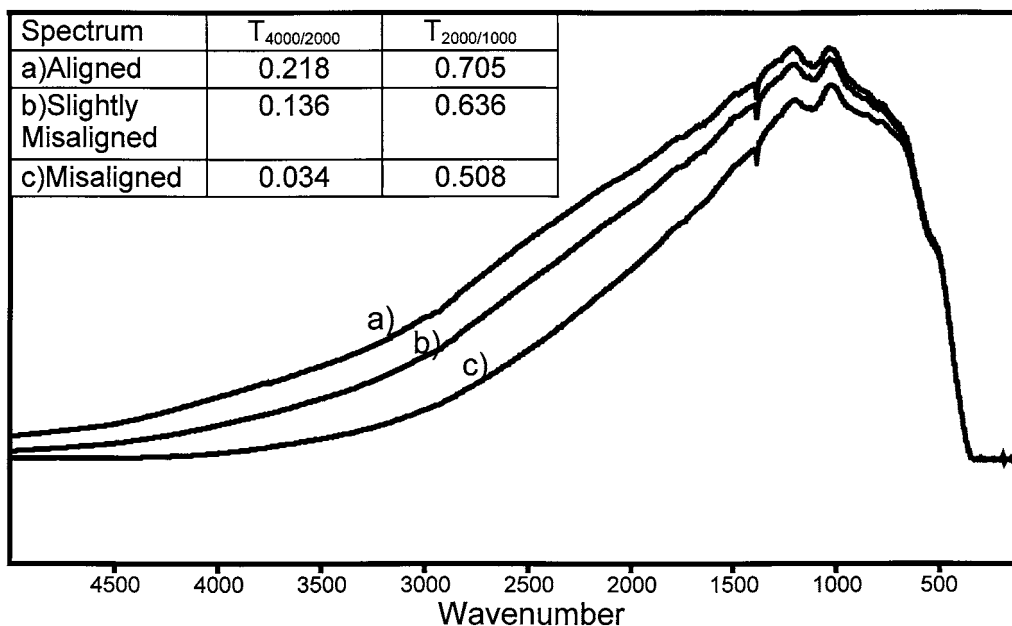


FIG. 1 Effect of Misalignment on Single-Beam Energy Spectra

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:

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

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.

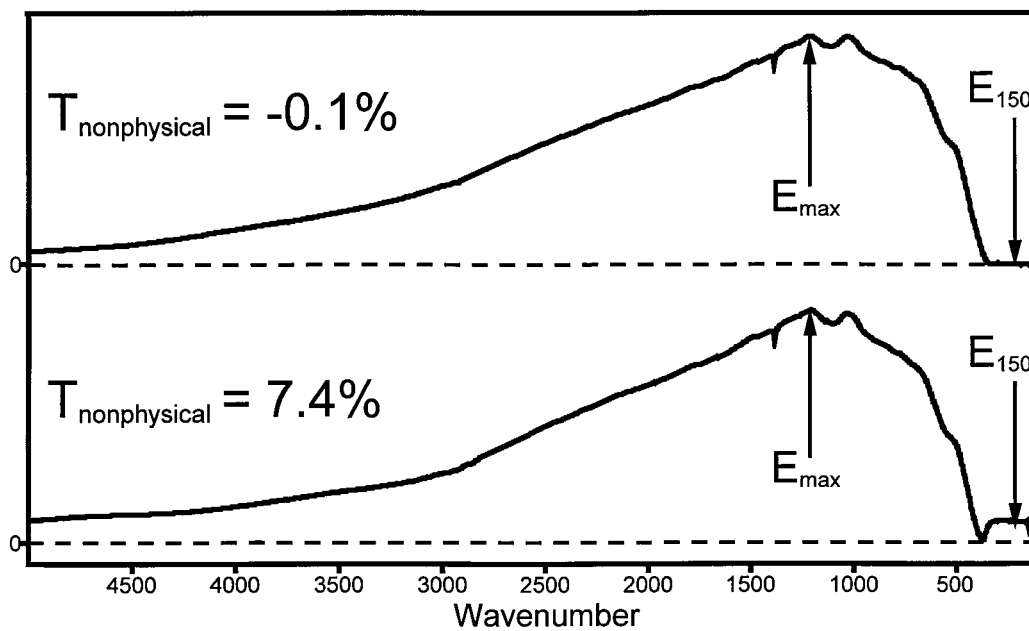


FIG. 2 Example of Nonphysical Energy

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  $3440\text{ cm}^{-1}$  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  $100\text{ cm}^{-1}$  range centered at 4000, 2000, 1000, and  $500\text{ cm}^{-1}$ . 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.<sup>4</sup>

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.

<sup>4</sup> 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.

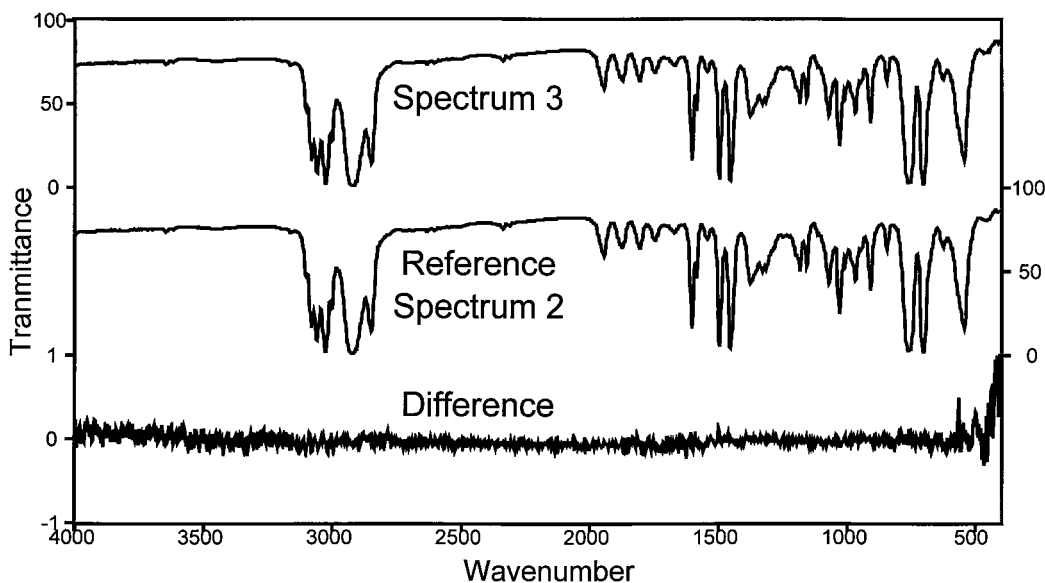


FIG. 3 Example of Transmittance Spectra Subtraction

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  $3600\text{ cm}^{-1}$  and near  $1600\text{ cm}^{-1}$ ) 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  $2360\text{ cm}^{-1}$  and sharp spike near  $667\text{ cm}^{-1}$ ).

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  $3200\text{ cm}^{-1}$ , a carbonyl absorption at  $1720\text{ cm}^{-1}$  and C-O absorptions in the range of  $1050$  to  $1000\text{ cm}^{-1}$  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 instru-

ment 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 E 1866. 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 E 1866 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 E 1866 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

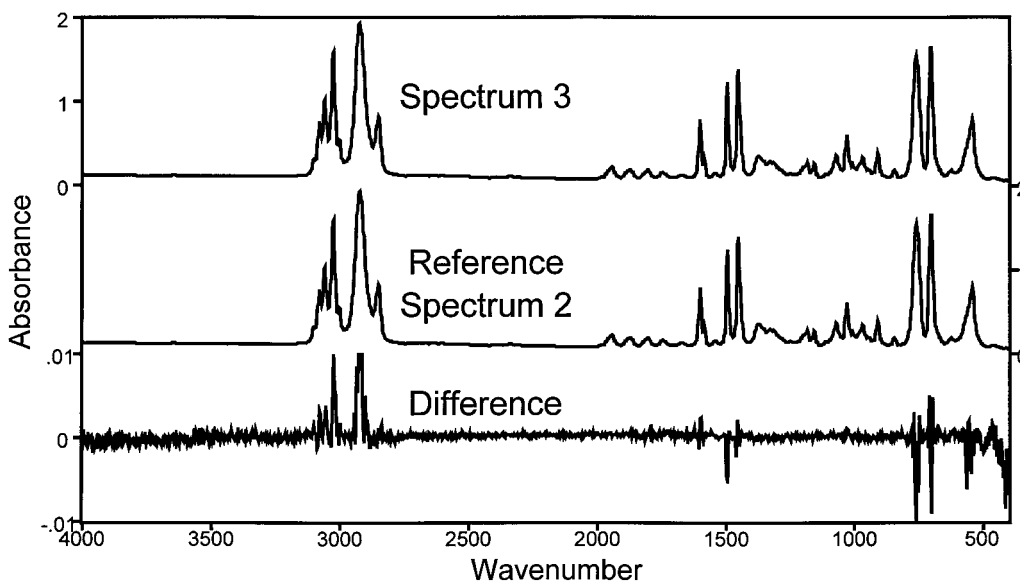


FIG. 4 Example of Absorbance Spectra Subtraction

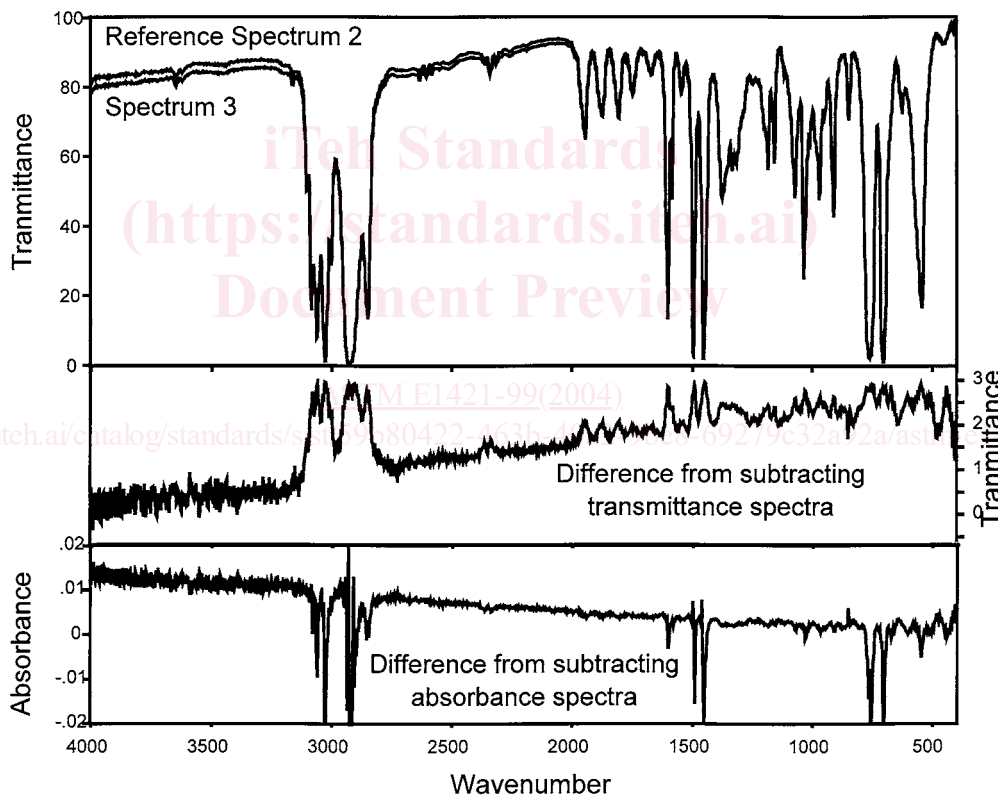


FIG. 5 Effect of Baseline Variations on Subtraction Results

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 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