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

This standard is issued under the fixed designation E 1944; 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 covers two levels of tests to measure the performance of laboratory Fourier transform near infrared (FT-NIR) spectrometers. This practice applies to the short-wave near infrared region, approximately 800 nm (12 500 cm^{-1}) to 1100 nm (9090.91 cm^{-1}); and the long-wavelength near infrared region, approximately 1100 nm (9090.91 cm^{-1}) to 2500 nm (4000 cm^{-1}). This practice is intended mainly for transmittance measurements of gases and liquids, although it is broadly applicable for reflectance measurements.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *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:*

E 131 Terminology Relating to Molecular Spectroscopy[2]

E 168 Practices for General Techniques of Infrared Quantitative Analysis[2]

E 932 Practices for Describing and Measuring Performance of Dispersive Infrared Spectrometers[2]

E 1252 Practice for General Techniques for Qualitative Analysis[2]

E 1421 Practice for Describing and Measuring Performance of Fourier Transform Infrared (FT-IR) Spectrometers: Level Zero and Level One Tests[2]

3. Terminology

3.1 For definitions of terms used in this practice, refer to Terminology E 131. All identifications of spectral regions and absorbance band positions are given in nanometers (nm), and wavenumbers (cm^{-1}); and spectral energy, transmittance, reflectance, and absorbance are signified by the letters E, T, R and A respectively. A subscripted number signifies a spectral position in nanometers, with wavenumbers in parenthesis (for example,
$A^{1940(5154.64)}$, denotes the absorbance at 1940 nm or 5154.64 cm^{-1}).

4. Significance and Use

4.1 This practice permits an analyst to compare the general performance of a laboratory instrument on any given day with the prior performance of that instrument. This practice is not intended for comparison of different instruments with each other, nor is it directly applicable to dedicated process FT-NIR analyzers. This practice requires the use of a check sample compatible with the instrument under test as described in 5.3.

5. Test Conditions

5.1 *Operating Conditions*—In obtaining spectrophotometric data for the check sample, the analyst must select the proper instrumental operating conditions in order to realize satisfactory instrument performance. Operating conditions for individual instruments are best obtained from the manufacturer's instructional literature due to the variations with instrument design. It should be noted that many FT-NIR instruments are designed to work best if left in standby mode when they are not in use. A record should be kept to document the operating conditions selected during a test so that they can be duplicated for future tests. Note that spectrometers are to be tested only within their respective recommended measurement wavelength (wavenumber) ranges.

5.2 Instrumental characteristics can influence these measurements in several ways. Vignetting of the beam (that is, the aperture of the sample cell is smaller than the diameter of the near infrared beam at the focus) reduces the transmittance value measured in nonabsorbing regions, and on most instruments can change the apparent wavelength (or wavenumber) scale by a small amount, usually less than 0.01 nm (0.1 cm^{-1}). Focus changes can also change transmittance values, so the sample should be positioned in the same location in the sample compartment for each measurement. The angle of acceptance (established by the *f* number) of the optics between the sample and detector significantly affects apparent transmittance. Heating of the sample by the beam or by the higher temperatures

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[1] This practice is under the jurisdiction of ASTM Committee E-13 on Molecular Spectroscopy and is the direct responsibility of Subcommittee E 13.03 on Infrared Spectroscopy.

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[2] *Annual Book of ASTM Standards*, Vol 03.06.

which exist inside most spectrometers changes absorbances somewhat, and even changes band ratios and locations slightly. Allow the sample to come to thermal equilibrium prior to measurement.

5.3 The recommended check sample should meet the following requirements: the check sample should be fully compatible with the requirements for repeatable sample presentation to the measuring spectrophotometer. The check sample should consist of a single pure compound or precisely known mixture of compounds which is spectroscopically stable over months or years. The spectra obtained from such a check sample should be known to indicate changes in the spectrophotometer, not the check sample itself. It is recommended that independent verification of the integrity of the check sample be used prior to test measurement. The check sample should be measured under precisely the sample measurement conditions of temperature, humidity, and instrument set up configuration. Suggested check samples may include, but are not limited to the following: for gases, water vapor at 5.89 Torr and 1 atmosphere in a 2 m gas cell, or methane at 18 psig pressure in a 10 cm gas cell; for liquids, pure spectroscopic grade hydrocarbon compounds (for example, toluene, decane, isooctane, etc.), or precise mixtures of these pure compounds; for reflectance measurements of solids, rare earth oxides mixed with white halon powder, or Spectralon[3]-based rare earth oxide reflectance standards. Reference reflectance standards yielding a featureless, near 100 % reflectance spectrum are pure powdered sulfur, halon, or Spectralon.

6. Level Zero Tests

6.1 *Nature of Tests*—Routine checks of instrument performance can be performed within 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. For Level Zero tests, a resolution of 4 cm^{-1} and a nominal measurement time of 30 s is recommended. Resolution and measurement times can be specified to match conditions used for routine measurement applications. The exact measurement time, along with the date, time, sample identification, number of scans, 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 reference results (known to be good). If the old and new results agree, they are simply reported as no change. Level Zero consists of three tests. Run the tests under the same conditions that you would normally use to run a sample (that is, sample temperature, purge time, warm-up time, beam splitter type, detector configuration, etc.)

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

6.4 *Sample*—The check sample used for performance tests is described in 5.3. The same sample should be used for all test comparisons (note serial number, or other identifying information, of sample) as well as orientation of the sample within the sample compartment during test measurements.

6.5 *Reference Spectra*—Two spectra acquired and stored during the last major instrument calibration are used as references. These spectra will be identified as Reference 1 and Reference 2.

6.5.1 Reference 1 is a Fourier-transformed 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 dry air or the purge gas normally present within the spectrometer sample compartment). For reflectance measurements this spectrum is a spectrum of a flat, pure reflectance standard approximating 100 % R.

6.5.2 Reference 2 is a transmittance spectrum of the check sample. For reflectance measurements this spectrum is a reflectance spectrum of the check sample.

6.6 *Repeatability of Procedures*—Care should be taken that each of the spectral measurements is made in a consistent and repeatable 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 compartment, all of the test spectra always should be measured using the same optical path.

6.7 *Measurements*—Three test spectra will be acquired and stored. The test spectra will be identified hereafter as Spectrum 1, Spectrum 2, and Spectrum 3.

6.7.1 *Spectrum 1*—An empty-beam spectrum stored as a Fourier-transformed single beam energy spectrum (or as an interferogram). If stored as an interferogram, it must be transformed before use in the ensuing tests.

6.7.2 *Spectrum 2*—An empty-beam spectrum taken immediately after Spectrum 1. This spectrum should be stored as either a Fourier-transformed single-beam energy spectrum or as a transmittance spectrum ratioed against Spectrum 1.

6.7.3 *Spectrum 3*—A spectrum of the check sample obtained reasonably soon after Spectrum 2. This spectrum should be stored as a transmittance spectrum (or reflectance spectrum, when applicable) ratioed against either Spectrum 1 or Spectrum 2, or as a single-beam energy spectrum. To reproducibly insert the sample, the serial number (or other identifying information) should be right side up facing the instrument detector (or aligned in a manner that allows repeatable measurements each time the check sample is measured).

7. Level Zero Test Procedures

7.1 *Energy Spectrum Test*—Overlay Spectrum 1 and Reference 1. Note any changes in energy level across the spectrum. Ratio Spectrum 1 to Reference 1. 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 was saved, it may be displayed or plotted and the center burst height recorded. Changes in the interferogram height are

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[3] Spectralon, available from Labsphere, Inc., P.O. Box 70, Shaker St., North Sutton, NH 03260-0070, has been found satisfactory for this purpose.

difficult to interpret since minor decreases in source temperature that only affect high frequencies can result in changes in interferogram height. These changes do not affect photometric accuracy.

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

For short−wave near infrared:

$$\mathrm{RATIO}^{800/1000(12\,500/10\,000)} = \mathrm{E}^{800/1000(12\,500/10\,000)} \qquad (1)$$

For long−wave near infrared:

$$\mathrm{RATIO}^{1500/2000(6666.67/5000)} = \mathrm{E}^{1500/2000(6666.67/5000)}$$

$$\mathrm{RATIO}^{2000/2500(5000/4000)} = \mathrm{E}^{2000/2500(5000/4000)}$$

Report the date and time of both spectra used, and the actual numbers of scans and measurement times, as well as details of the instrument set up conditions.

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 overall drop in the energy level without wavelength (wavenumber) dependence suggests beam obstruction (vignetting) or misalignment of non-interferometer optical components. 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 within the beam. With cooled detectors (for example InSb), the appearance of a broad band around 1940 nm (5154.64 cm^{-1}) indicates ice deposition on the detector surface. 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. 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*—Ratio Spectrum 2 to Spectrum 1. Note the noise level and any variations from 100 % transmittance (or reflectance) across the spectrum.

7.2.1 *Reportage*—Make an overlay plot of Spectra 1 and 2. Then ratio the two and plot the 100 % transmittance (or reflectance) line. The ordinate range should be 99 to 101 % T/R. If the noise or baseline drift exceeds these bounds, make a plot from 90 to 110 % T/R and consider performing Level One tests. Report the RMS (preferred) or peak-to-peak noise levels at over a ~8-18 nm (100 cm^{-1}) range centered at 800 nm (12 500 cm^{-1}), 1000 nm (10 000 cm^{-1}), 1500 nm (6666.67 cm^{-1}), 2000 nm (5000 cm^{-1}), 2500 nm (4000 cm^{-1}). If the instrument wavelength (wavenumber) range does not include some of these, substitute the nearest measurable wavelength (frequency).

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 within the spectrometer. Deviations from the 100 % level (usually at lower wavelengths (higher wavenumbers) indicate interferometer, detector, or source instability (see Practice E 1421).

7.3 *Check Sample Test*—Ratio Spectrum 3 to Spectrum 2 (or 1) to produce a check sample transmittance spectrum (or reflectance spectrum, when applicable). Convert all spectra to absorbance spectra. Subtract the stored absorbance check sample spectrum from this new absorbance check sample spectrum. Note any changes.

7.3.1 *Reportage*—Plot the check sample absorbance spectrum over the reported dynamic range of the instrument. Plot the subtraction result as a full scale spectrum.

7.3.2 *Interpretation*—Additional sharp features in the water vapor absorption regions indicate excessive water vapor in the sample compartment. 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).

8. Level One Tests

8.1 *Nature of Test*—The tests described for Level One use only the check sample and are designed to more thoroughly 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 is designed to facilitate diagnosis instead of only indicating malfunctions. The diagnostic content of the results is such that interpretation is beyond the scope of this practice; though guidelines are given to refer the user of this practice to more detailed discussions of instrument failure modes.[4]

8.3 *Sample*—The same check sample described in 5.3 is used for measurements.

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 that 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

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[4] Griffiths, P., de Haseth, J., Fourier Transform Infrared Spectrometry, John Wiley & Sons, New York, New York, 1986.

measurements as a way to get parameter consistency. These factors concern the instrument lineshape function (ILS), which is the detailed way of expressing resolution. The ILS is the Fourier transform of the function by which an interferogram is weighted (see Terminology E 131). Peak positions and photometer data must be reported at the highest possible resolution.

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*—For short-wave near infrared calculate the ratio of the energy at 800 nm (12 500 cm^{-1}) to energy at 1000 nm (10 000 cm^{-1}). In each case, a ~ 8 nm (100 cm^{-1}) wide region centered around the wavelength position specified is used for obtaining an averaged energy value. For long-wave near infrared calculate the ratio of the energy at 1500 nm (6666.67 cm^{-1}) to energy at 2000 nm (4000 cm^{-1}). In each case, a ~18 nm (100 cm^{-1}) wide region centered around the wavelength position specified is used for obtaining an average energy value.

$$\text{For short-wave near infrared:}$$
$$RATIO^{800/1000(12\,500/10\,000)} = E^{800/1000(12\,500/10\,000)} \quad (2)$$
$$\text{For long-wave near infrared:}$$
$$RATIO^{1500/2000(6666.67/5000)} = E^{1500/2000(6666.67/5000)}$$

9.1.2 *Spectral Range*—Report wavelength points where spectral energy reaches one-tenth of the energy level found at the energy maximum of 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. Nonlinear interpolation is strongly recommended for determining absorbances.

9.1.4 *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:

$$RATIO = E^{Below..Cutoff}/E^{Max} \quad (3)$$

9.1.5 *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 or reflectance. Several specific indicators can be reported.

9.2.1 Noise level at 800 nm (12 500 cm^{-1}), 1000 nm (10 000 cm^{-1}), 1500 nm (6666.67 cm^{-1}), 2000 nm (5000 cm^{-1}), 2500 nm (4000 cm^{-1}), A ~8-18 nm (100 cm^{-1}) wide spectral portion centered around each position should be used for calculating the noise level in percent T units (or percent R units, when applicable). Specify report as peak-to-peak or average root-mean-square (RMS) noise level. RMS is preferred.

9.2.2 One hundred percent line position at each wavelength specified in 9.2.1. The average transmittance (or reflectance) value determined as part of the RMS calculation in over the same ~8-18 nm (100 cm^{-1}) wide 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 your 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 800 nm (12 500 cm^{-1}), 1000 nm (10 000 cm^{-1}), 1500 nm (6666.67 cm^{-1}), 2000 nm (5000 cm^{-1}), 2500 nm (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 (lowest wavelengths) 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 (non-interferometer) misalignments.

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

9.3.3 Purge variations can be observed in the transmittance spectra, and quantitatively assessed by calculating the same bands as used in 9.1.3.

9.3.4 Other artifacts can clearly be seen in the transmittance spectra. Changes in the amount of ice on (cooled) detector surfaces, condensed water, and hydrocarbon contaminants are examples.

9.4 *Signal Averaging Test*—Obtain a pair of spectra, each having the same number of scans. Do this for the following number of scans: 1, 4, 16, 64, 256, 1024, 4096, 16384, etc., up to the maximum measurement time of interest. Ratio each pair and calculate the noise level at 800 nm (12 500 cm^{-1}), 1000 nm (10 000 cm^{-1}), 1500 nm (6666.67 cm^{-1}), 2000 nm (5000 cm^{-1}), 2500 nm (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 give 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 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 absorption.

9.4.2 Scaling problems and digital errors are uncovered by noting any drastic (usually 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 *Check Sample Test*—Obtain an empty-beam single beam spectrum followed by a spectrum of the check sample standard. Ratio the check sample spectrum to the clear-beam spectrum (or 100 % reflectance standard spectrum, when making reflectance measurements) to produce a check sample transmittance (or reflectance) spectrum. Convert this scan to an absorbance spectrum.

9.5.1 Peak positions for the most prominent absorbance bands should be reported. Note the band positions are often made available in the reference literature, however the actual peak positions will be somewhat different for any particular instrument when combined with a specific interpolation method. Report the actual peak positions and peak center finding algorithm. A center of gravity algorithm is preferred. The digital data point interval should be specified as a constant or repeatable resolution.

10. Keywords

10.1 calibration test; FT-NIR; Fourier transform near infrared; level one test; level zero test; performance test; spectrometers