



Designation: E 1790 – 00

Standard Practice for Near Infrared Qualitative Analysis¹

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1. Scope

1.1 This practice covers the use of near-infrared (NIR) spectroscopy for the qualitative analysis of liquids and solids. The practice is written under the assumption that most NIR qualitative analyses will be performed with instruments designed specifically for this region and equipped with computerized data handling algorithms. In principle, however, the practice also applies to work with liquid samples using instruments designed for operation over the ultraviolet (UV), visible, and mid-infrared (IR) regions if suitable data handling capabilities are available. Many Fourier Transform Infrared (FTIR) (normally considered mid-IR instruments) have NIR capability, or at least extended-range beamsplitters that allow operation to 1.2 μm; this practice also applies to data from these instruments.

1.2 *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 Spectroscopy²
- E 1252 Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Infrared Analysis²
- E 1655 Practices for Infrared, Multivariate, Quantitative Analysis²

3. Terminology

3.1 **Definitions**—For definitions of general terms and symbols pertaining to NIR spectroscopy and statistical computations, refer to Terminology E 131.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *interactance, n*—the phenomenon whereby radiant energy entering the surface of a material is scattered by the material back to the surface, but at a different portion of the surface.

¹ This practice is under the jurisdiction of ASTM Committee E-13 on Molecular Spectroscopy and is the direct responsibility of Subcommittee E13.11 on Chemometrics.

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

3.2.1.1 *Discussion*—This differs from diffuse reflectance, where the returning radiation exits the same portion of the surface of the material as the illuminating radiation entered.

3.2.2 *training sample (otherwise called a “reference sample” or “standard”), n*—a quantity of material of known composition or properties, or both, presented to an instrument for measurement in order to find relationships between the measurements and the composition or properties, or both, of the sample.

3.2.2.1 *Discussion*—This term is typically used in conjunction with computerized methods for ascertaining the relationships.

Training samples for quantitative analysis (also called “calibration samples,” as in Practices E 1655) have different requirements than training samples used for qualitative analysis.

4. Significance and Use

4.1 NIR spectroscopy is a widely used technique for quantitative analysis, and it is also becoming more widely used for the identification of organic materials, that is, qualitative analysis. In general, however, the concept of qualitative analysis as used in the NIR spectral region differs from that used in the mid-IR spectral region in that NIR qualitative analysis refers to the process of automated comparison of the spectra of unknown materials to the spectra of known materials in order to identify the unknown. This approach constitutes a library search method in which each user generates his own library.

4.2 Historically, NIR spectroscopy as practiced with classical UV-VIS-NIR instruments using methods similar to those described in Practice E 1252 was not considered to be a strong technique for qualitative analysis. Although the positions and intensities of absorption bands in specific wavelength ranges were used to confirm the presence of certain functional groups, the spectra were not considered to be specific enough to allow unequivocal identification of unknown materials. A few important libraries of NIR spectra were developed for qualitative purposes, but the lack of suitable data handling facilities limited the scope of qualitative analysis severely. Furthermore, earlier work was limited almost entirely to liquid samples.

4.3 Currently, the mid-IR procedure of deducing the structure of an unknown material via analysis of the locations, strengths, and positional shifts of individual absorption bands is generally not used in the NIR.

4.4 With the development of specialized NIR instruments and mathematical algorithms for treating the data, it became possible to obtain a wealth of information from NIR spectra that had hitherto gone unused. While the mathematical algorithms described in this practice can be applied to spectral data in any region, this practice describes their application to the NIR.

4.5 The application of NIR spectroscopy to qualitative analysis in the manner described is relatively new, and procedures for this application are still evolving. The application of chemometric methods to spectroscopy has limitations, and the limitations are not all defined yet since the techniques are relatively new. One area of concern to some scientists is the effect of low-level contaminants. Any analytical methodology has its detection limits, and NIR is no different in this regard, but neither would we expect it to be any worse. Since the relatively broad character of NIR bands makes it unlikely that a contaminant would not overlap any of the measured wavelengths, the question would only be one of degree: whether a given amount of contaminant could be detected. The user must be aware of the probable contaminants he is liable to run into and account for the possibility of this occurring, perhaps by including deliberately contaminated samples in the training set.

5. General

5.1 NIR qualitative analysis is conducted by comparison of NIR absorption spectra of unknown materials with those of known reference materials. Since the absorption bands of many substances of interest are less distinctive in the NIR than in the mid-IR spectral region, the analytical capability of the technique relies heavily on the accuracy of the absorption measurements and the relationship of the relative absorbances at different wavelengths. Materials to be identified are measured by a NIR spectrometer, and the spectral data thus generated are saved in an auxiliary computer attached to the spectrometer proper. One of the several algorithms described in Section 6 is then applied to the data in order to generate classification criteria, which can then be applied to data from unknown samples in order to classify (or identify) them as being the same as one of the previously seen materials. Good chemical laboratory practice should be followed to help ensure reproducible results for each material. The preparation and presentation of samples to the instrument should be consistent within a library, and unknowns should be treated the same way that the training samples were.

5.1.1 The technique is applicable to liquids, solids, and gases. For analysis of gases, multipath vapor cells capable of achieving up to 100-metre path lengths may be required. Spectra of vapors and gases may be sensitive to the total sample pressure, and this has to be determined for each type of sample.

5.1.2 Unknown samples to be identified may be prescreened based on criteria other than their NIR spectra (for example, visual inspection). The training samples (that is, the “knowns” used to teach the algorithm what different materials look like) may also be similarly prescreened and grouped into libraries of similar materials (for example, liquids and solids). The unknown is then compared with only those materials in the appropriate library. The prescreening will help reduce the

chance of false identification, although care must be taken that an unknown material not in the library is not identified as a similar material that is in the library.

5.1.3 Measurements may be made via transmission, reflection, or any other optical setup suitable for collecting NIR spectra. In practice, only transmission and diffuse reflection have been in common use.

5.1.4 Determination of the relationships between absorbances at different wavelengths for a set of materials and consolidation of these relationships into a set of criteria for identifying those materials requires the use of computerized learning algorithms. These algorithms can also take into account extraneous variations such as are found, for example, when measurements are made on powdered solids.

5.1.5 Instrumentation is commercially available for making suitable measurements in the NIR spectral region. Manufacturer's instructions should be followed to ensure correct operation, optimum accuracy, and safety before collecting data.

5.1.6 NIR spectroscopy has, as one of its paradigms, that little or no sample preparation be required. In conformance with that paradigm, sample preparation steps in other spectroscopic technologies are replaced with sample presentation methodologies in NIR analysis. The most common sample presentation methods are the following:

5.1.6.1 *Diffuse Reflectance*—Solid materials are ground into powder (or used as-is, if already in suitably fine powder form) and packed into a cup, which allows the surface of the sample to be illuminated and the reflected radiant power measured.

5.1.6.2 *“Transflectance”*—Clear or scattering liquids are placed in a cup containing a transparent window with a diffusely reflecting material behind the sample. Any radiant energy passing through the sample is reflected diffusely by the backing material, so the net measurement is just like the diffuse reflectance measurement of powdered solids.

5.1.6.3 *Transmission*—Liquids or solids are placed in cells with two transparent windows and measured by transmission.

5.1.6.4 *Fiber Probes*—Illuminating and collecting fibers are brought in parallel to the sample. A variety of optical configurations are used to couple the radiant energy from the fibers to the sample and back again, in an optical “head” of some sort. Transmittance, reflectance, and interactance have all been used at the sample end of the fiber to couple the radiation to the sample. Interactance measurements are sometimes made by the simple expedient of pressing the end of a fiber bundle containing mixed illuminating and receiving fibers against the sample surface.

5.2 To connect the mathematics with the spectroscopy used, the procedure can be generally described as follows:

(1) The spectral measurements define some multidimensional space. The axes in that space are the absorbances at the various wavelengths, or some mathematical transformation thereof.

(2) Groups of spectra for the same material define some region in the multidimensional space.

(3) The analysis involves determining which region the unknown falls in.