Standard Practice for
Near Infrared Qualitative Analysis[1]

This standard is issued under the fixed designation E 1790; 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 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 Spectroscopy[2]
E 1252 Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Infrared Analysis[2]
E 1655 Practices for Infrared, Multivariate, Quantitative Analysis[2]

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 surface.

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

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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 E13.11 on Chemometrics.

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

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.

5.2.1 Problems with this type of analysis include the following: insufficient separation of the groups in the multidimensional space to allow for classification (indicating insufficient differences among the spectra of the materials involved), inadequate representation of measurement variability within

groups during training (indicating an insufficient number or variety of training samples), or poor detection limits for minor contaminants.

5.2.2 To optimize the methods against these potential problem areas, generation of a method occurs in three stages. In the first, or training stage, known samples are presented to the instrument. The data collected are then presented to one of the various algorithms and are thus used to "train" the algorithm to recognize the various different materials.

5.2.3 In the second, or validation stage, the ability of the algorithm to correctly recognize materials not in the training set of samples is tested.

5.2.4 In the third, or use stage, unknown samples are presented to the instrument, which then compares the data so obtained to the data from the known samples and decides whether the data from the unknown agrees with the data from any of the known materials. The unknown material is classified as whichever material gives the closest agreement to the data.

5.2.5 Optionally, the algorithm may provide for the case in which the data from the unknown does not agree with that from any of the knowns sufficiently well to permit identification, and refuse to identify the unknown sample.

5.3 Samples to be identified during the use stage must be in the same phase and physical condition as the known samples were during the training stage.

5.3.1 Liquids may be run neat or in solution. In either case, the optical pathlength of the sample cell should be fixed, be the same for all liquids to be compared with a given unknown, and be specified as part of the method. While an algorithm may be trained on data incorporating variations in these characteristics, greater accuracy will be achieved when extraneous variations are reduced. The unknown, of course, should also be run in a cell under the same conditions as the training samples. If a solution is used, the amount of dilution should also be specified.

5.3.2 Some solids may be run as-is if they have one or more suitably flat surfaces; others may need to be ground. If solid samples are ground, the same procedure should be used for all materials in a given library, and that procedure should be specified as part of the method.

5.3.3 The unknowns must also be treated in the same manner as the training samples. It is particularly important that if the samples must be ground, the unknown samples should be ground to the same particle size as the known samples included in the library.

6. Algorithms Used

6.1 This section describes some of the computerized algorithms that have been found effective for qualitative analysis in the NIR spectral region. This section is mainly for reference. Descriptions of multivariate methods of statistical data analysis tend to be inherently abstract mathematically and resistant to reduction to words. A number of books exist in both the statistical and chemometric literature that describe methods of multivariate analysis at varying levels of mathematical abstrac-

tion (see, for example, Refs (1-5),[3] a useful starting point but far from exhaustive list); most of the algorithms used for NIR qualitative analysis are relatively straightforward applications of these methods.

6.1.1 Implementations of these algorithms are available in standard generic statistical software packages (for example, SAS, BMDP, and SPSS). In addition, the manufacturers of modern NIR spectrometers include implementations of these algorithms in their proprietary software packages that run on the auxiliary computers supplied with the spectrometers; this approach has the advantage that the software matches the format and nature of the data generated by the spectrometer. In either case, the details of the algorithms and their implementations are usually transparent to the user.

6.2 Calculation of Mahalanobis distances has been described (5-9) in the literature directly for application to NIR spectra. The Mahalanobis distance is a way of measuring whether a given sample falls within a given region of multidimensional space, since a small distance indicates that the sample is "close to" the center of the region, and thus within it. The training samples define a region of space so that a multidimensional ellipsoid includes a specified fraction of these samples; the distance from the center of the region to the ellipsoid surface (that is, the equivalent of a "diameter") defines the Mahalanobis distance. The Mahalanobis distance is calculated from the matrix equation:

$$D_i{}^2 = (\mathbf{x}_u - \bar{\mathbf{x}}(i))^t \, \mathbf{M} \, (\mathbf{x}_u - \bar{\mathbf{x}}(i)) \qquad (1)$$

where:
D_i = Mahalanobis distance of the unknown sample from the center of the ellipsoid for the ith member (class of samples) of the library,
$\mathbf{x}_u$ = the vector of absorption readings for the unknown sample to be identified, taken at different wavelengths,
$\bar{\mathbf{x}}(i)$ = the average of the readings for several different samples of the type of material representing the ith member of the library, and
$\mathbf{M}$ = matrix inverse of the pooled within-group variance-covariance matrix (described in Appendix X1; see Refs (3, 7) for more details on this and Refs (1-5) for more general discussions of the mathematical background).

6.2.1 The confidence interval for the Mahalanobis distance has been shown to be distributed such that $p \cdot D$ has an F distribution with k and $n\text{-}k\text{-}1$ df (9), where $p=(n\text{-}k\text{-}1)/nk$, n = number of spectra and k = number of wavelengths (or frequencies) used.

6.2.2 To train the algorithm, the user should take many spectra of each standard to introduce the inherent variability of the material into the training data. These readings then define the region of multidimensional space that is characteristic of that group of material; it is important to ensure that the training samples do in fact include all of the natural variability of the material.

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[3] The boldface numbers in parentheses refer to the list of references at the end of this practice.

6.2.3 A special case of this approach deals with the analysis of clear (non-scattering) liquids. In this case, pure materials have no inherent variability, so the size of the group, which is determined by the variability of the samples (and which becomes effectively zero for pure, non-scattering liquids), collapses to a single point in multidimensional space, that is, the "diameter" collapses to practically zero. In this case, the region of acceptance for unknowns is so small that instrument noise, or other minor and otherwise unimportant variations of the measurement conditions, can cause valid samples to appear outside the region defined for that material.

6.2.3.1 There are two ways to deal with this situation. The first way is to replace the computation of Mahalanobis distances between the unknown samples and known materials with the computation of Euclidean distances. This is accomplished readily by replacing the matrix inverse of the pooled within-group variance-covariance matrix by a unit matrix (one in which all elements are zero except for the elements on the main diagonal, which are unity).

6.2.3.2 A second approach is to introduce random variability into the data artificially. This has been accomplished successfully by creating several copies of the data and then adding a small random number to every absorption value in the expanded data set. A careful compromise must be drawn between small values of added noise (which will leave each group still approximating a point too closely) and too large values, which will cause the data to have too high an equivalent noise and mask differences between different materials.

6.3 Principal component analysis (PCA) has been recognized as one method for compressing the information from many wavelengths into a few independent components **(1-5, 10-14)**. Besides compressing the data, the principal components tend to segregate the different sources of variability in a set of spectra. By adding a group distance measurement, PCA can be used to perform qualitative NIR analysis.

6.3.1 The basic steps to performing a PCA-based distance measurement are as follows:

6.3.1.1 *Step 1*—A training set, or library of samples, is formed that represents the groups (materials) to be distinguished and so identified. Each group should be represented by several samples.

6.3.1.2 *Step 2*—The spectra of the samples or groups are resolved into principal components. The number of principal components necessary for adequate representation of the samples is determined by some measurement of the residual variation in the library spectra.

6.3.1.3 *Step 3*—For each principal component of the PCA-space group, the mean values and standard deviations are calculated from the sample scores for each member of that group. Because the principal components are orthogonal, each standard deviation (distance) is in an orthogonal direction.

6.3.1.4 *Step 4*—In order to classify future samples, the cross-products of the NIR spectrum of each sample with the principal components obtained from the training library are computed. The distance measure from any group is calculated using the following equation:

$$D_i = (\text{score}_i - \text{group}_i)/S_i \tag{2}$$

where:
D_i = distance along the i*th* principal component axis from the mean of the scores for that group,
score_i = sample score for the i*th* principal component,
group_i = mean of the group's scores for the i*th* principal component, and
S_i = standard deviation of the scores of the i $_{th}$ principal component for the corresponding group.

Note that even though the principal components are calculated from the entire dataset, the standard deviations, as well as the mean values, are calculated from each group individually. If the distance for all principal components is smaller than some cutoff value, then the sample is classified as part of the group. Whitfield, et al **(9)** treat the criteria for determining the cutoff value in detail. Inspection of Whitfield's tables reveals that a rule-of-thumb value of 3 may be used for a large enough number of samples.

6.3.2 One popular variation of this approach is called Simple Model of Class Analogies (SIMCA) **(15, 16)**. In SIMCA, each group is resolved into its own principal components. Steps 1 through 4 are performed as if each group was the library. Multiple groups are tested by using multiple libraries of principal components.

6.4 *Correlation*:

6.4.1 The correlation coefficient **(17)** has long been used as a measure of similarity between two sets of numbers. It is also possible to use the correlation coefficient between two spectra as a way of classifying samples.

6.4.2 The correlation coefficient (*r*) is generally defined as the ratio of explained variance to total variance. It is applied to qualitative NIR analysis by calculating the correlation coefficient between a known and unknown spectrum. (Eq 3) describes this procedure:

$$r = \frac{\sum\limits_{1}^{I} X_i Y_i}{\sqrt{\sum\limits_{1}^{I} X_i^2 \sum\limits_{1}^{I} Y_i^2}} \tag{3}$$

where:
I = number of wavelengths in the spectrum,
X_i = absorbance of the unknown sample at the i *th* wavelength, and
Y_i = absorbance of the known's spectrum at the i*th* wavelength.

(Eq 3) assumes that both *X* and *Y* have been previously mean centered (that is, the mean value of the data at each wavelength has been computed and subtracted from each spectrum's value at the corresponding wavelength).

6.4.3 When the unknown and known spectra are identical, or differ only by a constant multiplicative factor (normally due to phenomena such as pathlength or particle size), (Eq 3) will yield an answer of 1. When the spectra differ, *r* will decrease from 1. An unknown sample is typically classified by calculating its correlation coefficient with all of the spectra in a library. The library spectrum with the correlation coefficient closest to 1 is identified as being the most similar to the sample.

6.4.4 The advantage of the correlation technique is that only one known sample is necessary in order to characterize a

group. This makes it quite suitable for identification. However, it is more difficult to build a group of multiple samples and perform qualification by correlation. Group distances are not a linear function of the correlation coefficient r.

6.4.5 Caution should be exercised in using the correlation on untreated NIR spectra. The broad bands of many NIR spectra and baseline difference can lead to misidentification. Spectra that differ by only one or two band positions (that is, homologous compounds) are typically difficult to classify by the correlation technique. The best results are obtained when the spectra are pretreated to maximize the difference between the groups to be classified. The commonly used methods to pretreat the data are using the derivative of a spectrum and limiting the wavelength range. The derivative approach improves the contrast between spectra of similar compounds. Limiting the wavelength range can restrict the comparison to those spectral features that correspond to key functional groups.

6.4.6 The distribution of the correlation coefficient is a rather complicated function (see Ref (**1**), p. 105) of the measured value, but a graphical presentation is available (see Ref (**18**), p. 71).

6.5 The use of multidimensional direction cosines has also been used effectively as a method of determining the degree of agreement between two spectra or transformations thereof (**19,20,21**). By letting X stand for the multidimensional vector representing one (for example, the spectrum of the "unknown") and letting Y stand for the multidimensional vector representing the other spectrum (for example, the "library spectrum"), then the equation

$$\cos(\theta) = X \, Y / |X| \, |Y| \tag{4}$$

results in a value for θ that varies from zero (for a completely random relationship) to unity (for a perfect match). Since the value unity for cosine(θ) corresponds to a value of θ of zero, one way to consider this approach is as a measure of multidimensional distance in polar coordinates, with the radius vector ignored. This approach is particularly applicable to the comparison of powdered solids, since the radius vector in this case corresponds to the repack variations of the spectra, which is often (although not always) ignored usefully when making spectral comparisons.

7. Keywords

7.1 molecular spectroscopy; near-infrared; qualitative analysis

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APPENDIX

(Nonmandatory Information)

X1. CALCULATION OF MAHALANOBIS DISTANCES

X1.1 To compute **M**, the matrix inverse of the pooled within-group variance-covariance matrix, requires the matrix inversion of the matrix formed as described below to be performed. Matrix inversion routines can be found in virtually any book addressing computational statistics or mathematics and will not be described here.

X1.2 To form the matrix that is to be inverted, consider a dataset consisting of data from p different materials, samples of which were measured at f wavelengths (or frequencies). Use i to index over the different materials and j to index over the different wavelengths. Where convenient, also use r and c to index over the different wavelengths. For each material, we have spectra from n_i samples, with each spectrum, thus consisting of readings at the f wavelengths; use m to index over the n_i samples corresponding to each of the p materials. The total number of spectra in the set of data is n, which $= \sum_i n_i$.

X1.3 Use $x_{mj}(i)$ to represent the individual absorbance values for each reading of a given sample m of material i at a given wavelength i; use $\bar{x}_j(i)$ to represent the mean absorbance for this i^{th} material.

X1.4 The matrix to be inverted is of dimension f by f. Each term of the matrix is formed from the following procedure:

X1.4.1 The mean absorbance, $\bar{x}_j(i)$, of each material i at each wavelength i is computed:

$$\bar{x}_j(i) = \sum_m x_{mj}(i) \tag{X1.1}$$

X1.4.2 The mean absorbance for the data from a given material at each wavelength is subtracted from each absorbance reading for that material at that wavelength. We use x' to indicate the mean-corrected absorbance:

$$x'_{mj}(i) = x_{mj}(i) - \bar{x}_j(i) \tag{X1.2}$$

X1.4.3 The element in the rth row and c^{th} column of the matrix V (call this V_{rc}) is computed by adding together the corresponding contribution from each of the p materials (these contributions will be described in X1.4.4):

$$\mathbf{V}_{rc} = \sum_i V_{rc}(i) \tag{X1.3}$$

X1.4.4 The contributions, $V_{rc}(i)$, are computed as the sum over all the spectra corresponding to the mth material, of the product of the mean-corrected absorbances at the rth and c^{th} wavelengths:

$$V_{rc}(i) = \sum_m (x'_{mr}(i) \cdot x'_{mc}(i)/(n-p) \tag{X1.4}$$

X1.4.5 The matrix **M** is calculated by taking the inverse of the matrix **V**.

NOTE X1.1—The Mahalanobis distance defined above will be a factor of n-p larger than that defined in 16.2 of Practice E 1655. The matrix **V**

above is essentially $\mathbf{XX^t}/(n-p)$ in the notation of E 1655. $\mathbf{M}$, which is the inverse of $\mathbf{V}$, will be a factor of $n-p$ larger than $(\mathbf{XX^t})^+$. The scaling is done here to ensure that the metric used for classification is not overly sensitive to the size of the library, n.

NOTE X1.2—If $f > n$, the matrix $\mathbf{V}$ cannot be directly inverted. Mathematics similar to that described in Practice E 1655 can be used to estimate an inverse.

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