



Standard Practice for Polyurethane Raw Materials: Determining Hydroxyl Number of Polyols by Near Infrared (NIR) Spectroscopy¹

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1. Scope*

1.1 This standard covers a practice for the determination of hydroxyl numbers of polyols using NIR spectroscopy.

1.2 Definitions, terms, and calibration techniques are described. Procedures for selecting samples, and collecting and treating data for developing NIR calibrations are outlined. Criteria for building, evaluating, and validating the NIR calibration model are also described. Finally, the procedure for sample handling, data gathering and evaluation are described.

1.3 The implementation of this standard requires that the NIR spectrometer has been installed in compliance with the manufacturer's specifications.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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.*

NOTE 1—This standard is equivalent ISO 15063.

2. Referenced Documents

2.1 ASTM Standards:²

D883 Terminology Relating to Plastics

D4274 Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols

D4855 Practice for Comparing Test Methods (Withdrawn 2008)³

¹ This practice is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.22 on Cellular Materials - Plastics and Elastomers.

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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.

³ The last approved version of this historical standard is referenced on www.astm.org.

E131 Terminology Relating to Molecular Spectroscopy

E168 Practices for General Techniques of Infrared Quantitative Analysis

E222 Test Methods for Hydroxyl Groups Using Acetic Anhydride Acetylation

E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

E456 Terminology Relating to Quality and Statistics

E1655 Practices for Infrared Multivariate Quantitative Analysis

E1899 Test Method for Hydroxyl Groups Using Reaction with *p*-Toluenesulfonyl Isocyanate (TSI) and Potentiometric Titration with Tetrabutylammonium Hydroxide

2.2 ISO Standard:

ISO 15063 Plastics—Polyols for use in the production of polyurethanes—Determination of hydroxyl number by NIR spectroscopy

3. Terminology

3.1 *Definitions*—Terminology used in this practice follows that defined in Terminology D883. For terminology related to molecular spectroscopy methods, refer to Terminology E131. For terms relating to multivariate analysis, refer to Practice E1655.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *hydroxyl number*—the milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of sample.

4. Summary of Practice

4.1 Multivariate mathematics is applied to correlate the NIR absorbance values for a set of calibration samples to the respective reference hydroxyl number for each sample. The resultant multivariate calibration model is then applied to the analysis of unknown samples to provide an estimate of their hydroxyl numbers.

4.2 Multilinear regression (MLR), principal components regression (PCR), and partial least squares regression (PLS) are the mathematical techniques used for the development of the calibration model.

4.3 Statistical tests are used to detect outliers during the development of the calibration model. Outliers can include

*A Summary of Changes section appears at the end of this standard

high leverage samples and samples whose hydroxyl numbers are inconsistent with the model.

4.4 Validation of the calibration model is performed by using the model to analyze a set of validation samples. The hydroxyl number estimates for the validation set are statistically compared to the reference hydroxyl number for this set to test for agreement of the model with the reference method.

4.5 Statistical expressions are given for calculating the precision and bias of the NIR method relative to the reference method.

5. Significance and Use

5.1 General Utility:

5.1.1 It is necessary to know the hydroxyl number of polyols in order to formulate polyurethane systems.

5.1.2 This practice is suitable for research, quality control, specification testing, and process control.

5.2 Limitations:

5.2.1 Factors affecting the NIR spectra of the analyte polyols need to be determined before a calibration procedure is started. Chemical structure, interferences, any nonlinearities, the effect of temperature, and the interaction of the analyte with other sample components such as catalyst, water and other polyols needs to be understood in order to properly select samples that will model those effects which cannot be adequately controlled.

5.2.2 Calibrations are generally considered valid only for the specific NIR instrument used to generate the calibration. Using different instruments (even when made by the same manufacturer) for calibration and analysis can seriously affect the accuracy and precision of the measured hydroxyl number. Procedures used for transferring calibrations between instruments are problematic and are to be utilized with caution following the guidelines in Section 16. These procedures generally require a completely new validation and statistical analysis of errors on the new instrument.

5.2.3 The analytical results are statistically valid only for the range of hydroxyl numbers used in the calibration. Extrapolation to lower or higher hydroxyl values can increase the errors and degrade precision. Likewise, the analytical results are only valid for the same chemical composition as used for the calibration set. A significant change in composition or contaminants can also affect the results. Outlier detection, as discussed in Practices E1655, is a tool that can be used to detect the possibility of problems such as those mentioned above.

6. Instrumentation

6.1 *Introduction*—A complete description of all applicable types of NIR instrumentation is beyond the scope of this standard. Only a general outline is given here. A diagram of a typical NIR spectrometer is shown in Fig. 1.

6.2 *Light Source and Detector*—Tungsten-halogen lamps with quartz envelopes usually serve as the energy sources for NIR instruments. Most of the detectors used for NIR are solid-state semiconductors. PbS, PbSe, and InGaAs detectors are most commonly used.

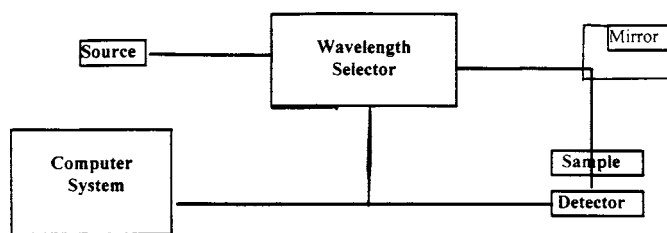


FIG. 1 Schematic of a Near-IR System

6.3 *Light Dispersion*—Spectrophotometers can be classified based on the procedure by which the instrument accomplishes wavelength selection.

6.3.1 *Monochromator Instrument*—Grating monochromator instruments, often called “dispersive” instruments, are commonly used in the laboratory and for process applications. In a halographic grating system, the grating is rotated so that only a narrow band of wavelengths is transmitted to a single detector at a given time.

6.3.2 *Filter-Wheel Instrument*—In this type of NIR instrument, one or several narrow band filters are mounted on a turret wheel so that the individual wavelengths are presented to a single detector sequentially.

6.3.3 *Acoustic Optic Tunable Filter (AOTF) Instrument*—The AOTF is a continuous variant of the fixed-filter photometer with no moving optical parts for wavelength selection. A birefringent TeO₂ crystal is used in a noncollinear configuration in which acoustic and optical waves move through the crystal at different angles. Variations in the acoustic frequency cause the crystal lattice spacing to change. That in turn causes the crystal to act as a variable transmission diffraction grating for one wavelength. The main advantage of using AOTF instruments is the speed. A wavelength or an assembly of wavelengths can be changed hundreds of times per second under computer control.

6.3.4 *Light-Emitting Diode (LED) Instrument*—Each wavelength band is produced by a different diode. The major advantages of the system are its small size and compactness, stability of construction with no moving parts, and low power consumption.

6.3.5 *Fourier Transfer (FT) Instrument*—In FT-NIR instruments, the light is divided into two beams whose relative paths are varied by use of a moving optical element. The beams are recombined to produce an interference pattern that contains all of the wavelengths of interest. The interference pattern is mathematically converted into spectral data using Fourier transform. FT interferometer optics provide complete spectra with very high wavelength resolution. FT signal averaging also provides higher signal-to-noise ratios in general than can be achieved with other types of instruments.

6.4 *Sampling System*—Depending upon the applications, several different sampling systems can be used in the laboratory or for on-line instruments, or both.

6.4.1 *Cuvette*—Quartz or glass cuvettes with fixed or adjustable pathlengths can be used in the laboratory.

6.4.2 *Flow-Through Cell*—This type of cell can be used for continuous or intermittent monitoring of liquid sample.

6.4.3 *Probes*:

6.4.3.1 Transmission Probe—Transmission probes combined with optic fibers are ideal for analyzing clear liquids, slurries, suspensions, and other high viscosity samples. Low absorptivity in the NIR region permits sampling pathlengths of up to 10 cm.

6.4.3.2 Immersion Probe—The immersion system uses a bi-directional optic fiber bundle and variable pathlength probe for sample measurements. Radiation from the source is transmitted to the sample by the inner ring of fibers, and diffuse transmitted radiation is collected by the outer ring of fibers for detection.

6.4.3.3 Attenuated Total Reflection (ATR) Probe—Attenuated total reflection occurs when an absorbing medium (the sample) is in close contact with the surface of a crystal material of higher refractive index. At an optimized angle, the NIR beam reflects internally along the crystal faces, penetrating a few microns into the sample surface, where selective absorption occurs. The resulting spectrum is very close to the conventional transmission spectrum for the sample. There are many designs of ATR plates and rods for specific applications. Single or multiple reflection units are available. ATR sampling accessories are available for the laboratory and, in the form of fiber optic probes, can be used for on-line analysis. This is an advantage when handling viscous liquids and highly absorbing materials.

6.5 Software—The ideal software has the following capabilities:

6.5.1 The capability to record all sample identification and spectral data accurately and to access the reference data,

6.5.2 The capability to record the date and time of day that all spectra and files were recorded or created,

6.5.3 The capability to move or copy spectra, or both, from file to file,

6.5.4 The capability to add or subtract spectral data, and to average spectra,

6.5.5 The capability to perform transformations of log I/R optical data into derivatives, or other forms of mathematical treatment, and to reverse the transformation,

6.5.6 The capability to compute multiple linear regression (MLR), principal component regression (PCR), and partial least squares regression (PLS),

6.5.7 The capability to store PCR or PLS loading, weights, scores or other desirable data, and to display these data for subsequent examination and interpretation,

6.5.8 The capability to enable the operator to evaluate the calibration model by computing the standard error of validation (SEV), coefficient of regression, and the root mean square deviation (RMSD), and to display various plots,

6.5.9 The capability to perform cross-validation automatically,

6.5.10 The capability to identify an outlier(s), and

6.5.11 The capability to develop and save regression equations and analyze a sample to calculate a hydroxyl number.

6.6 Software Packages—Most NIR instruments provide necessary software for collecting and modeling data. Several non-instrumental companies also supply chemometric software packages that can be used to analyze NIR data.

7. Near-IR Spectral Measurements

7.1 NIR spectral measurements are based on Beer's law, namely, the absorbance of a homogeneous sample containing an absorbing substance is linearly proportional to the concentration of the absorbing species. The absorbance of a sample is defined as the logarithm to the base ten of the reciprocal of the Transmittance (T):

$$A = \log_{10}(1/T) \quad (1)$$

where:

T = the ratio of radiant power transmitted by the sample to the radiant power incident on the sample.

7.1.1 For most types of instrumentation, the radiant power incident on the sample cannot be measured directly. Instead, a reference (background) measurement of the radiant power is made without the sample being present in the light beam.

7.1.2 A measurement is then conducted with the sample present, and the ratio, T , is calculated. The background measurement can be conducted in a variety of ways depending on the application and instrumentation. The sample and its holder can be physically removed from the light beam and a background measurement made on the "empty beam". The sample holder (cell) can be emptied, and a background measurement taken for the empty cell. The cell can be filled with a material that has minimal absorption in the spectral range of interest, and the background measurement taken. Alternatively, the light beam may be split or alternately passed through the sample and through an empty beam, and empty cell, or a background material in the cell.

7.1.3 The particular background referencing scheme that is used can vary among instruments, and among applications. The same sample background referencing scheme must be employed for the measurement of all spectra of calibration samples, validation samples, and unknown samples to be analyzed. Any differences between instrument conditions used for referencing and measurement are to be minimized.

7.2 Traditionally, a sample is manually brought to the instrument and placed in a suitable optical container (a cell, vial, or cuvette with windows that transmit in the region of interest). Alternatively, transfer pipes can continuously flow liquid through an optical cell in the instrument for continuous analysis. With optical fibers, the sample can be analyzed remotely from the instrument. Light is sent to the sample through an optical fiber or fibers and returned to the instrument by means of another fiber or group of fibers. Instruments have been developed that use a single fiber to transmit and receive the light, as well as use bundles of fibers for this purpose. Detectors and light sources external to the instrument can also be used, in which case only one fiber or bundle is needed. The appropriate grade of optical fibers for use in the NIR range needs to be specified. Generally, these are fibers with low water content (Low-OH). Total fiber length is not to exceed manufacturer's recommendations.

7.3 For most NIR instrumentation, a variety of adjustable parameters is available to control the collection and computation of the spectral data. These parameters control the optical and digital resolution and the rate of data acquisition (scan

speed). Other important program parameters include the number of wavelengths, number of scans, and number of data points. Additional instrumental considerations for multivariate calibrations include temperature control and compensation, cell pathlength uniformity, and wavelength stability. It is essential that all adjustable parameters and other factors not included in the model that control the collection and computation of spectral data be maintained constant while collecting spectra of calibration samples, validation samples, and samples for analysis.

7.4 For definitions and further description of general infrared techniques, refer to Practice E168.

8. Procedure to Develop a Feasibility Calibration

8.1 For each type of polyol or new process to produce the polyol, it is necessary to perform a feasibility calibration. The relationship between NIR spectra and the hydroxyl number is generally evaluated during a feasibility study which will identify the possible interferences and determine whether an adequate model can be constructed for the desired precision. Following a successful feasibility study, the calibration can be expanded and validated.

8.2 A sample set having all of the characteristics of the samples of interest is to be identified. The samples chosen are to include the expected hydroxyl number ranges and all the possible interferences in the sample matrix. In addition, interrelations between components in the samples are to be avoided unless these interactions are expected in the routine samples being analyzed. The number of samples is to be large (preferably 30 to 50 samples, especially if PLS regression is used to evaluate the calibration model) and is to be evenly distributed throughout the hydroxyl number range. The range of the sample set is to cover at least three times, but preferably at least five times the standard deviation of the reference method. An independent set of samples, known as the validation sample set, is to be identified and set aside to evaluate the calibration model for feasibility. The size of the validation set will depend on the number of samples used to evaluate the calibration model, generally one sample for every four samples used in the calibration.

8.2.1 If samples with a wide range of hydroxyl number are not available, it can be necessary to perform spiking experiments to expand the range and to optimize the regression line. Blending samples to achieve varying hydroxyl numbers is preferred over spiking. If spiking is utilized, care must be taken to avoid changes that can affect the matrix and ultimately compatibility with the spectra of the calibration set.

8.3 Samples are to be collected in a manner which reflects the actual process conditions and sample handling techniques which are expected to be used during routine collection for analysis. Sample spectra are to be collected in a manner which reflects the actual conditions, techniques, and sample handling procedures which are expected to be employed. If these and other such variations can not be controlled, the range of variation is to be included in the sample set of calibration.

8.4 The calibration sample set is to be analyzed at least in duplicate by the primary or reference method. If the range of

samples is less than five times the standard deviation of the reference method, then r replicate analyses are to be performed such that $(r)^{1/2}$ times the range of the calibration set is greater than three times (preferably five times) the standard deviation of the reference method.

8.5 A calibration model is developed using one of several available methods, for example, MLR, PCR, and PLS. The quality of the calibration curve can be tested by several statistical tools described in Section 12. The calibration model is tested using cross-validation methods (see 12.8.4). Other statistics can also be used to judge the overall quality of the calibration.

8.6 If the statistical analysis of the calibration and validation sets suggests the method is capable of providing adequate precision, the model can be tuned by adding additional samples to assure a boxcar distribution (an even distribution of values along a defined interval of the hydroxyl number range). A final model can be developed and validated as described in Section 12.

8.7 If the calibration set consists of a range of different types of polyols, and reliable calibration cannot be obtained, it is necessary to group samples by chemistry, and to develop a separate calibration model for each chemical grouping. Examples of possible groups are polyether, polyester, segregation based on the manufacturing technique (that is, the EO/PO ratio), or the functionality.

9. Selection of Calibration Samples

9.1 Samples selected for the calibration set will ideally comply with the following guidelines as well as those established in 8.2:

9.1.1 The samples chosen are to include all components which are expected to be present in the samples of interest,

9.1.2 The samples chosen are to include and ideally exceed the expected hydroxyl number range,

9.1.3 The sample hydroxyl numbers are to be evenly distributed throughout the calibration range as to provide a “boxcar” distribution of samples (evenly distributed throughout the range of interest),

9.1.4 The number of samples chosen are to be large enough to statistically define the relationship between the spectral variables and the hydroxyl numbers to be modeled, and

9.1.5 The spectra of all samples are to be similar to avoid erroneous modeling. For example, the same path length is to be used for all samples, and the baseline, peak maxima, and peak minima are to be similar. See 8.7.

9.2 The model is to exclude all potential sources of variation that can be excluded in the actual applications. If these sources cannot be eliminated they must be included in the sample set, if possible. Sources of variation can include the following:

9.2.1 Chemical composition:

9.2.2 Physical characteristics, and

9.2.3 Sample handling, temperature, and humidity.

9.3 The number of samples required to calibrate the NIR model is dependent on the complexity of the samples being analyzed. Simple models which contain only a few components that vary in concentration will have only a small number

of spectral variables and typically do not require a large sample set to define relationships. On the other hand, complex systems containing several components which vary in concentration will require a large number of samples to define the relationships and to assure the model development is adequate.

9.3.1 If a multivariate model is developed with 5 or fewer variables (wavelengths in MLR or factors in PCR or PLS), the calibration must contain a minimum of 30 samples after elimination of outliers.

9.3.2 If a multivariate model is developed with k (>5) variables (wavelengths in MLR or factors in PCR or PLS), the calibration set must include a minimum of 6 k samples after elimination of outliers.

10. Collecting NIR Spectra

10.1 Before developing a calibration model, it is necessary to determine the optimal pathlength at which to perform the analysis. The optimal pathlength is dependent upon the analytical wavelength(s) chosen for the analysis. For determining the optimal pathlength, the highest hydroxyl number spectrum (that is, sample that will have the highest maximum absorbance value) in the sample set is compared for the cuvettes with different pathlength such that the maximum absorbance is less than 1 absorbance unit.

10.2 Samples can be scanned in duplicate or triplicate in order to assess and reduce sources of spectral variation. If there is poor agreement between reference and NIR results, or if there are significant differences between duplicate NIR scans, the source of the error must be identified. Multiple NIR scans and multiple replicates by the reference method will help to identify the cause of a poor fit.

10.3 Analyzing duplicate samples (as opposed to replicate measurement of the same sample) reveals sampling problems due to heterogeneity. To avoid the possibility of systematic errors, samples are to be scanned in random order.

10.4 NIR spectra of polyols are affected by temperature. The physical constraints present at the instrument location are to be taken into account when deciding how to deal with these effects when developing the calibration.

10.4.1 If the analysis is to be performed in a temperature-controlled laboratory, samples are to be scanned at the standard room temperature after allowing for temperature equilibration of the sample. If room temperature is not stable, a temperature-controlled cell is to be considered.

10.4.2 If the hydroxyl number will be analyzed at a temperature other than room temperature, it is important to ensure that the sample temperature has stabilized prior to performing an analysis. The time needed to reach temperature equilibration can vary from sample to sample and is dependent on the temperature and pathlength at which the analysis is to be performed.

10.4.3 If the analysis is to be done in a less controlled environment, for example, a warehouse, temperature variations can be built into the calibration data by scanning samples over the range of expected temperatures and including these data in the calibration set.

10.4.4 Depending on how tight the production specifications are and how accurate the lab method is, the time required to reach an acceptable temperature can be crucial. It is necessary to determine the optimal equilibration time for the various products in order to reduce total analysis time or to tighten production specifications.

11. Reference Method and Reference Values

11.1 The hydroxyl numbers in the calibration set must be determined by a standard analytical method (Test Methods **D4274** or other suitable standard method). The precision of the primary analytical method must be well characterized in order to define realistic accuracy limits for NIR calibration.

11.2 Reference analyses are to be performed in replicate as described in **8.4**. Blind replicates are to also be undertaken to further ascertain the true accuracy of the method. The average of the replicates is to be used as the calibration value for each sample.

11.3 It is important to perform both the reference analysis and the NIR spectral analysis within as short a time period as possible.

12. Developing Calibration Model

12.1 *Determining the Wavelength Regions*—For hydroxyl number determination, two primary wavelength regions can be used: the R-OH combination band (2000 to 2300 nm) and R-OH first overtone band (1380 to 1500 nm). Additional spectral regions can also be added to the model to correct for an interfering absorbance.

12.2 Data Pretreatment:

12.2.1 Various types of data preprocessing algorithms can be applied to the spectral data prior to the development of a calibration model. A complete description of all possible preprocessing methods is beyond the scope of this standard.

12.2.2 Generally, the calibration performance of NIR spectra is improved by a derivative mathematical treatment. Baseline shifts are reduced and peak shape and resolution of peak position are improved. There is no single best treatment, but second derivative has proven to be most useful for hydroxyl number determination. When validating a method, several different mathematical treatments are to be used to determine which one produces the best calibration.

12.3 Multivariate Mathematical Techniques:

12.3.1 Multivariate mathematical techniques are used to relate the spectra measured for a set of calibration samples to the hydroxyl numbers obtained for this set of samples from a reference test. The object is to establish a multivariate calibration model that can be applied to the spectra of future unknown samples to estimate hydroxyl numbers.

12.3.2 Three types of regression are commonly used for developing the calibration model: multilinear regression; principal components regression; and partial least squares. Generally, if the sample matrices are simple and only one or two analytical wavelengths is needed, MLR is used. If the matrix is complex or if more than two wavelengths are required for desired accuracy, PCR or PLS is used. All mathematical

treatments of multivariate calibration can be found in Section 12 of Practices E1655.

12.4 *Multilinear Regression:*

12.4.1 The simplest algorithm used in NIR spectroscopy is multilinear regression. It provides a solution to the Beer's Law equation which correlates changes in absorbance with changes in hydroxyl number in the polyol.

12.4.2 The choice of the number of wavelengths to use in MLR is a critical factor in the model development. If too few wavelengths are used, a less precise model will be developed. If too many wavelengths are used, colinearity among the absorption values at these wavelengths can lead to an unstable model.

12.4.3 The choice of specific wavelengths to include in a multilinear regression model is also a critical factor in the model development.

12.4.4 Refer to Practices E1655 for detailed mathematics of MLR.

12.5 *Principal Components Regression:*

12.5.1 It is possible to create a set of a few eigenvectors (principal components) that represent the changes in the absorbances that are common to all samples.

12.5.2 As with wavelength selection in multilinear regression, the choice of the number of principal components to use in the regression is a critical factor in the model development. If too few principal components are used, a less precise model will be developed. If too many principal components are used, noise of the calibration samples will be incorporated into the model leading to unstable estimations.

12.5.3 The optimum number of principal components for a model is related to the number of spectrally distinguishable components in the calibration spectra.

12.5.4 Refer to Practices E1655 for detailed mathematics of PCR.

12.6 *Partial Least Squares Regression:*

12.6.1 PLS is the most commonly used alternative regression method to MLR and PCR. PLS is another spectral decomposition technique that is closely related to PCR. Instead of first decomposing the spectral matrix into a set of eigenvectors and scores, and regressing the scores of the calibration set against their concentrations as a separate step, PLS actually uses the concentration information during the decomposition process.

12.6.2 The PLS regression method is to only be used when there are at least 30 individual samples. When fewer samples are analyzed and modeled by the PLS algorithm, over-fitting typically occurs. This limits the robustness of the calibration model.

12.6.3 During the calculation, the PLS algorithm develops factors rather than the slopes and intercepts seen in the MLR algorithm. Each factor will describe a combination of variations, rather than the single variations of interest.

12.6.4 Generally, the total number of factors that are calculated correspond approximately to the number of constituents which vary in the sample population. If the polyol samples differ in hydroxyl number, moisture, and temperature, 3 to 4

factors generally provide sufficient correlation for hydroxyl number determination.

12.6.5 Refer to Practices E1655 for detailed mathematics of PLS.

12.7 *Evaluating Calibration Models:*

12.7.1 Various statistics are used to evaluate and optimize the performance of calibration models.

12.7.2 Standard error of calibration (SEC) is defined as:

$$SEC = (\sum (Y_{nir} - Y_{ref})^2 / df)^{1/2} \quad (2)$$

where:

Y_{nir} = the value estimated by the model for the calibration sample.

Y_{ref} = the corresponding reference value, and df is the number of degrees of freedom in the calibration model.

df is typically equal to $n-k$, where n is the number of calibration samples, and k is the number of variables (wavelengths in MLR or factors in PCR or PLS) used in the model. If the spectral data and reference values are mean centered prior to the development of the calibration model, then $df=n-k-1$.

12.7.3 The SEC is used in estimating the expected agreement between values calculated using the calibration models and values measured by the reference method. The errors include contributions from errors in the reference values for the calibration set, spectral errors in the calibration set, and model errors (using wrong number of variables, nonlinear relationships, etc.).

12.7.4 The SEC is the standard deviation for the difference between reference and NIR calculated values for samples within the calibration set. It is an indication of the total residual error due to the particular regression equation to which it applies. The SEC will generally decrease when the number of independent variables used in the model increases, indicating that increasing the number of terms will allow more variation in the data to be explained. However, over-fitting by using too many variables (factors) for the model will result in an overly optimistic estimate of the model performance (the SEC will be too low). The SEC statistic is a useful estimate of the theoretical best accuracy obtainable for a specified set of variables used to develop a calibration model.

12.7.5 Additional statistical tests for evaluating the multivariate model can be found in 15.5 of Practices E1655.

12.8 *Optimizing the Number of Variables in a Model:*

12.8.1 Determining how many variables (wavelengths in MLR or factors in PCR and PLS) to use in a model is a critical step in the model development. In general, if too few variables are used, a less accurate model will result. If too many variables are used, the estimates from the model can be unstable. In this case, small changes in the spectrum on the order of the spectral noise can produce statistically significant changes in the estimates.

12.8.2 The maximum number of variables, k , that are to be used in developing a calibration model is related to the number of detectable, spectrally distinguishable features that are present in the calibration set. This can include non-component related matters such as offsets and scatter effects.

12.8.3 Models can be built using fewer than k variables provided that such models exhibit adequate precision and pass validation.

12.8.4 Knowledge of the precision of the reference method is also useful in determining how many variables to include in a model. Comparison of the standard error of calibration against the standard deviation calculated from the reference method repeatability provides an indication of the maximum number of variables to include in a model. Standard errors of calibration that are lower than the standard deviation for the reference method indicate over-fitting of the data.

12.8.5 Cross-validation procedures are also used to estimate the optimum number of variables that are to be included in a model. A detailed description of the cross-validation procedure can be found in 15.3.6 of Practices **E1655**. A PRESS (predicted residual error sum of squares) value can be calculated as:

$$PRESS = \sum (Y_{nir} - Y_{ref})^2 \quad (3)$$

12.8.6 A standard error of cross validation (SECV) is calculated as:

$$SECV = (\sum (Y_{nir} - Y_{ref})^2 / n)^{1/2} \quad (4)$$

12.8.7 PRESS or SECV values can be calculated as a function of the number of variables used in the model. A plot of PRESS (or SECV) values versus the number of variables is often used to determine the minimum PRESS corresponding with the optimum number of variables in the calibration model. If no minimum occurs, the first point at which the PRESS or SECV reaches a more or less constant level can provide an indication of the maximum number of variables to include. Usually, the first minimum is taken.

12.8.8 These methods for estimating the number of variables to use in a model are intended only as guidelines. None of the methods can be relied upon always to produce a stable model. The ultimate test for the number of variables is whether or not the model can be validated as described below. The number of variables used in a model must ultimately be chosen to produce a model with desired precision.

12.9 Confidence Limits for an Estimated Value:

12.9.1 The confidence limits (CL) for a hydroxyl number estimated by a MLR or PLS model are given by:

$$CL = t \text{ SEC } (1 + D^2)^{1/2} \quad (5)$$

where t = the student's t value for the number of degrees of freedom in the model, and D^2 is the Mahalanobis distance statistic defined in 16.2 of Practices **E1655**. The confidence limits for an estimated hydroxyl number are often referred to as the confidence bands or confidence intervals for the estimate.

12.9.2 The confidence limits calculated by the above equation are only an approximation since any uncertainty in the spectral data is ignored.

12.10 Determining Outliers:

12.10.1 During the calibration process, outliers are to be identified and the merit of retaining them in the calibration set is to be carefully considered. For a detailed description of the outlier statistics, refer to Section 16 of Practices **E1655**.

12.10.2 Two types of outliers can be identified during the calibration procedures. The first type of outlier is a sample that

represents an extreme chemical composition relative to the remainder of the calibration set. The second type of outlier is one for which the estimated value differs from the reference value by a statistically significant amount. Other types of outliers can be identified by inspection of data to determine differences in spectra. Outlier statistics are used to identify samples that have unusually high leverage on the multivariate regression.

12.10.3 Remove all outliers which negatively affect the model prior to finalization to avoid erroneous results.

13. Validation of a Multivariate Model

13.1 Validation of the model is accomplished by predicting analyte concentrations for an independent set of samples with known analyte levels and statistically analyzing the model's response.

13.2 A validation set is chosen using the same criteria given (see Section 9) for calibration samples. In addition, the following criteria are to be followed:

13.2.1 The samples chosen are to span the range of hydroxyl number in the calibration set: any samples which do not fall within the range of the model are to be excluded,

13.2.2 The samples are to be evenly distributed throughout the range of hydroxyl number to assure a "boxcar" distribution, and

13.2.3 The samples chosen are to have spectra similar to those in the calibration set and are to span the range of all spectral variables. For example, the variability normally encountered during the manufacturing operation, sampling, and analyses is to be incorporated.

13.3 Validation spectra are to be collected using the same procedures as were used for the calibration set. The developed model is then used to predict the analyte concentrations and perform the statistics as described in 18.4 through 18.10 of Practices **E1655**.

13.4 The standard error of validation (SEV) can be calculated as indicated in 18.6 of Practices **E1655**. SEV is the standard deviation in the difference between the reference method value and the NIR method value for the samples in the validation set.

14. Precision of Near-IR Estimated Values

14.1 Section 19 of Practices **E1655** describes the procedure for measurement of precision of the estimated hydroxyl numbers in polyols.

15. Major Source of Calibration and Analysis Error

15.1 Section 20 of Practices **E1655** lists the most prominent sources of error in applying this type of practice, including general sources of spectral measurement error, sampling related error, calibration error, and analysis error.

15.2 Where the error inherent in the primary method used in the correlation is known, this information can be used to correct the standard error of the calibration (SEC). The corrected SEC then gives an estimate of the error in the calibration model separate from the error in the primary method.

$$SEC_{corrected} = SEC_{apparent} - \left[\sigma^2 \cdot df / x^2_{df \alpha} \right] \quad (6)$$

where:

- $SEC_{apparent}$ = the calculated SEC for the model,
- σ^2 = the variance in the reference method,
- df = the degrees of freedom in the reference value data used to calculate σ^2 ,
- α = the desired degree of uncertainty in the result, and
- x^2 = the value given in the appropriate standard statistical tables.

16. Calibration Transfer

16.1 Calibration transfer refers to a process by which a calibration model developed using data from one spectrometer is applied for the analysis of spectra collected on a second spectrometer.

16.2 When a calibration transfer procedure is developed, it is necessary to demonstrate that the performance of the model is not degraded during the transfer. Each calibration transfer procedure must be tested at least once by performing a full validation of the transferred model.

16.3 Calibration transfer is simpler if limited to the same type of NIR instrument having the same optical system or a system with less resolution.

16.4 Calibration transfer is limited to the same sampling system.

17. Calibration Quality Control

17.1 When NIR multivariate analysis is used to estimate hydroxyl number in polyols, it is desirable to periodically test the analysis (instrument and model) with control samples to ensure that the performance of the analysis is unchanged.

17.2 *Monitoring Performance of Instrument:*

17.2.1 The instrument used for determining hydroxyl number is to be periodically checked using self-diagnostic functions in the instrument.

17.2.2 The noise level and the wavelength drift over time is to be monitored periodically.

17.3 *Monitoring Performance of Calibration Model:*

17.3.1 When a NIR multivariate analysis is used to estimate hydroxyl number, it is necessary to continuously test the model (and instrument) and continuously update the model with fresh

samples. This procedure will allow the model to incorporate the current variations (which can be unknown to the operator) that are occurring in new samples as well as variations to the instrument and associated equipment such as sample cells and other parts of the optical bench.

17.3.2 The samples used for testing and updating of the model are to be within the hydroxyl number range of the original model since extrapolation of the model is not permitted. These tests require that the NIR values and the reference results agree within the confidence intervals determined when optimizing the number of variables via the standard error of calibration (SEC).

17.3.3 If the test samples fall outside the confidence interval used in 12.9, consideration is to be given to updating the model with the new sample(s). The instrument is to be first checked to make sure its operational performance is within the design test criteria for variables such as wavelength accuracy, light source intensity, signal stability, etc. If all these criteria are within the normal range of operation, the new sample(s) is (are) to be used to replace the oldest calibration samples of approximately the same hydroxyl number and the calibration model recalculated.

17.3.4 Calibration samples are to be replaced with current samples on a regular basis even if test samples fall within the confidence intervals of the test criteria discussed in 12.9. The continual refreshment of a model will incorporate subtle changes in raw materials or process conditions that can creep in and change the accuracy of the model. There are no firm rules for timing and extent of model upgrading. This depends on the number and variety of samples in the model, the frequency of model use and resources available to do the work. As an average guideline, for a 50-sample model that is used daily to measure 10 or more samples, it is suggested that about one sample per week be exchanged with a new sample such that a new model would be generated yearly. The new reference samples are to replace the oldest calibration sample available, which is close to the same hydroxyl number. The new spectral data are to be acquired in exactly the same manner and same time period as the calibration and validation sets.

18. Keywords

18.1 chemometrics; hydroxyl number; MLR; multivariate analysis; near-infrared analysis; NIR; PCR. PLS; polyol; polyurethane; raw material

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SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D6342 - 08) that may impact the use of this standard. (August 1, 2012)

- (1) Added that this standard is equivalent to ISO 15063 (Note 1).
- (2) Various editorial corrections were made throughout.

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