**Designation: D 6342 – 98 (Reapproved 2003)**

# Standard Practice for Polyurethane Raw Materials: Determining Hydroxyl Number of Polyols by Near Infrared (NIR) Spectroscopy[1]

This standard is issued under the fixed designation D 6342; 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 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 *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—There is no equivalent or similar ISO standard.

## 2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 883 Terminology Relating to Plastics
D 4274 Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols
D 4855 Practice for Comparing Test Methods
E 131 Terminology Relating to Molecular Spectroscopy
E 168 Practice for General Techniques of Infrared Quantitative Analysis
E 222 Hydroxyl Groups Using Acetic Anhydride Acetylation
E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers
E 456 Terminology Relating to Quality and Statistics
E 1655 Practices for Infrared, Multivariate, Quantitative Analysis
E 1899 Hydroxyl Groups by Toluenesulfonyl Isocyanate

## 3. Terminology

3.1 *Definitions*—Terminology used in this practice follows that defined in Terminology D 883. For terminology related to molecular spectroscopy methods, refer to Terminology E 131. For terms relating to multivariate analysis, refer to Practice E 1655.

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 may include 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.

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[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.

## 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 can not 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 should 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 E 1655, 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.

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

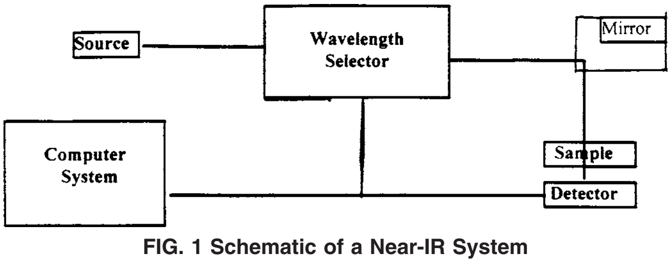

FIG. 1 Schematic of a Near-IR System

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 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 $TeO_2$ 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 causes 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 path lengths can be used in the laboratory.

6.4.2 *Flow-Through Cell*—This type 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