INTERNATIONAL STANDARD

ISO
15063

First edition
2004-08-15

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

Plastiques — Polyols pour utilisation dans la production de polyuréthannes — Détermination de l'indice d'hydroxyle par spectroscopie NIR

Reference number
ISO 15063:2004(E)

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Foreword

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ISO 15063 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

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Introduction

International Standards have been published which deal with the determination of hydroxyl values of polyols and surface-active agents using conventional chemistry based on esterification reactions (ISO 14900, ISO 4326, ISO 4327, ISO 4629, ISO 2554 and ISO 6796). This International Standard provides a guide for the determination of hydroxyl numbers of polyols using NIR spectroscopy. It is based on ASTM D 6342-98, *Standard Practice for Polyurethane Raw Materials: Determining Hydroxyl Number of Polyols by Near Infrared (NIR) Spectroscopy*, and on work conducted by laboratories associated with the Japan Urethane Raw Materials Association.

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

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions prior to use.

1 Scope

This International Standard establishes guidelines for the determination of hydroxyl numbers of polyols using NIR (near infrared) spectroscopy. Definitions and calibration techniques are given. Procedures for selecting calibration materials and for collecting and treating data to develop NIR calibrations are outlined. Criteria for building, evaluating and validating the NIR calibration model are also described. Procedures for sample handling, data gathering and evaluation are included.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 14900, *Plastics — Polyols for use in the production of polyurethane — Determination of hydroxyl number*

ASTM E 168, *Standard Practices for General Techniques of Infrared Quantitative Analysis*

ASTM E 1655-00, *Standard Practices for Infrared Multivariate Quantitative Analysis*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
hydroxyl number
OH#
hydroxyl value
HV
number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of sample

3.2
polyurethane
polymer prepared by the reaction of an organic di- or polyisocyanate with compounds containing two or more hydroxyl groups

4   Principle

4.1   Application

It is necessary to know the hydroxyl number of polyols in order to properly formulate polyurethane systems. This International Standard is suitable for use in research, quality control, specification testing and process control.

4.2   Procedures employed

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

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

4.2.3   Statistical tests are used to detect outliers during the development of the calibration model. Outliers may include high-leverage samples and materials whose hydroxyl numbers are inconsistent with the model.

4.2.4   Validation of the calibration model is performed by using the model to analyse a set of validation materials. 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 model.

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

4.3   Limitations

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

4.3.2   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 Clause 15. These procedures generally require a completely new validation and statistical analysis of errors on the new instrument.

4.3.3   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 the 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 ASTM E 1655, is a tool that can be used to detect the possibility of problems such as those mentioned above.

5   Instrumentation

5.1   General

A complete description of all applicable types of NIR instrumentation is beyond the scope of this International Standard. Only a general outline of key factors is given here. Consult the instrument manufacturer's literature

for details of a specific instrument. The implementation of this International Standard requires that the NIR spectrometer has been installed in compliance with the manufacturer's specifications.

5.2   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.

5.3   Light dispersion

5.3.1   General

Spectrometers can be classified based on the procedure by which the instrument accomplishes wavelength selection.

5.3.2   Monochromator instrument

Grating monochromator instruments, often called "dispersive" instruments, are commonly used in the laboratory and for process applications. In a holographic grating system, the grating is rotated so that only a narrow band of wavelengths is transmitted to a single detector at given time.

5.3.3   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.

5.3.4   Acoustic optic tuneable 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 non-colinear 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.

5.3.5   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.

5.3.6   Fourier transform (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 FT techniques. 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 instrument.

5.4   Sampling system

5.4.1   General

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

5.4.2 Cuvette

Quartz or glass cuvettes with fixed or adjustable pathlengths can be used in the laboratory.

5.4.3 Flow-through cell

This type of cell can be used for continuous or intermittent monitoring of liquid samples.

5.4.4 Probes

5.4.4.1 Transmission probe

Transmission probes combined with optical fibres are ideal for analysing clear liquids, slurries, suspensions and other high-viscosity samples. Low absorptivity in the NIR region permits sampling pathlengths of up to 10 cm.

5.4.4.2 Immersion probe

The immersion system uses a bi-directional optical-fibre bundle and variable-pathlength probe for sample measurements. Radiation from the source is transmitted to the test sample by the inner ring of fibres, and diffuse transmitted radiation is collected by the outer ring of fibres for detection.

5.4.4.3 Attenuated total reflection (ATR) probe

Attenuated total reflection occurs when an absorbing medium (the test 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 plate and rod for specific applications. Single or multiple reflection units are available. ATR sampling accessories are available for the laboratory and, in the form of fibre-optic probes, can be used for on-line analysis. This is an advantage when handling viscous liquids and highly absorbing materials.

5.5 Software

5.5.1 The ideal software should have the following capabilities:

a) the capability to record all sample identification and spectral data accurately and to access the reference data;

b) the capability to record the date and time of day that all spectra and files were recorded or created;

c) the capability to move or copy spectra, or both, from file to file;

d) the capability to add or subtract spectral data, and to average spectra;

e) the ability to perform transformations of $\log(1/R)$ optical data into derivatives or other forms of mathematical treatment, and to reverse the transformation;

f) the ability to compute multiple linear regression (MLR), principal-components regression (PCR) or partial least-squares (PLS) regression;

g) the capability to store PCR or PCS loading, weights, scores or other desirable data, and to display these data for subsequent examination and interpretation;

h) 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;

i) the capability to perform cross-validation automatically;

j)   the capability to identify outliers;

k)   the capability to develop and save regression equations and analyse a sample to calculate a hydroxyl number.

5.6   Software packages

Most NIR instruments provide necessary software for collecting and modelling data. Several non-instrumental companies also supply chemometric software packages that can be used to analyse NIR data.

6   Near-IR spectral measurements

6.1   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:

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

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

6.2   For most types of instrument, the radiant power incident on the test sample cannot be measured directly. Instead, a reference (background) measurement of the radiant power is made without the test sample being present in the light beam. A measurement is then conducted with the test sample present, and the ratio T is calculated. The background measurement may be conducted in a variety of ways, depending on the application and instrumentation. The test sample and its holder may be physically removed from the light beam and a background measurement made on the "empty beam". The sample holder (cell) may be emptied, and a background measurement may be taken for the empty cell. The cell may 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 and one half passed through the test sample and the other half through an empty cell or through a background material in the cell. The particular background referencing scheme that is used may vary among instruments, and among applications. The same sample background referencing scheme must be employed for the measurement of all spectra of calibration materials, validation materials and unknown test samples. Any differences between instrument conditions used for referencing and measurement should be minimized.

6.3   Traditionally, a test sample is brought to the instrument manually 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 be used to pass liquid continuously through an optical cell in the instrument for continuous analysis. With optical fibres, the test sample can be analysed remotely from the instrument. Light is sent to the test sample through an optical fibre or fibres and returned to the instrument by means of another fibre or group of fibres. Instruments have been developed that use a single fibre to transmit and receive the light, in addition to those which use bundles of fibres for this purpose. Detectors and light sources external to the instrument can also be used, in which case only one fibre or bundle is needed. The appropriate grade of optical fibre for use in the NIR range needs to be specified. Generally, these are fibres with low water content (low OH). Total fibre length should not exceed the manufacturer's recommendations.

6.4   For most NIR instruments, 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 programme 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 materials, validation materials and test samples.

6.5   For definitions and further description of general infrared techniques, refer to ASTM E 168.

7   Feasibility calibration

7.1   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.

7.2   A set of calibration materials having all of the characteristics of the samples of interest should be identified. The calibration materials chosen should include the expected hydroxyl number ranges and all the possible interferences in the sample matrix. In addition, interrelations between components in the samples should be avoided unless these interactions are expected in the routine samples being analysed. The number of calibration materials should be large (preferably 30 to 50 materials, especially if PLS regression is used to evaluate the calibration model) and they should be evenly distributed throughout the hydroxyl number range. The range of the calibration material set should cover at least three times, but preferably at least five times the standard deviation of the reference method. An independent set of materials, known as the validation material set, should be identified and set aside to evaluate the calibration model for feasibility. The size of the validation set will depend on the number of materials used to evaluate the calibration model, generally one material for every four materials used in the calibration. If materials with a wide range of hydroxyl number are not available, it may be necessary to perform spiking experiments to expand the range and to optimize the regression line. Blending materials to achieve varying hydroxyl numbers is preferred over spiking. If spiking is utilized, care must be taken to avoid changes that may affect the matrix and ultimately compatibility with the spectra of the calibration set.

7.3   Calibration materials should 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. Calibration material spectra should 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 cannot be controlled, the range of variation should be included in the calibration material set.

7.4   The calibration material set should be analysed at least in duplicate by the primary or reference method. If the range of materials is less than five times the standard deviation of the reference method, then r replicate analyses should 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.

7.5   A calibration model is developed using one of several available methods, for example MLR, PCR or PLS. The quality of the calibration curve can be tested by several statistical tools described in Clause 11. The calibration model is tested using cross-validation methods (see 11.8.5). Other statistics can also be used to judge the overall quality of the calibration.

7.6   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 materials 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 Clause 11.

7.7   If the calibration set consists of a range of different types of polyols, and reliable calibration cannot be obtained, it may be necessary to group materials by chemical type 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.

8   Selection of calibration materials

8.1   Materials selected for the calibration set will ideally comply with the following guidelines as well as those established in 7.2.

a)   The materials chosen should include all components which are expected to be present in the samples of interest.