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

Plastiques — Polyols pour la production de polyuréthannes — Détermination de l'indice d'hydroxyle par spectroscopie dans le proche infrarouge

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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

This second edition cancels and replaces the first edition (ISO 15063:2004), which has been technically revised so that the document is no longer a guidance document (as it was in the first edition) but specifies the precise requirements which have to be met when determining the hydroxyl number of a polyol. Subject matter which has remained informative in nature has been transferred to informative annexes.

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 method for the determination of hydroxyl numbers of polyols using NIR spectroscopy. It is based on ASTM D6342 and on work conducted by laboratories associated with the Japan Urethane Raw Materials Association.

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

SAFETY STATEMENT — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any regulatory requirements.

1 Scope

This International Standard specifies a method 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 processing 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.

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.

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 E1655-05, *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 General

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.

Methods of optimizing the performance of calibration models are described in Annex G.

When there is any doubt, the hydroxyl value determined by the standard method specified in ISO 14900 shall be used.

4.2 Procedure employed

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

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

4.2.3 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.

4.2.4 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 non-linearities, the 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 shall be utilized with caution when using Clause 8. These procedures generally require a completely new validation and a 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 E1655, is a tool that can be used to detect the possibility of problems such as those mentioned above.

NOTE Refer to Annex B for NIR spectral measurements.

5 Instrumentation

5.1 General

A complete description of all applicable types of NIR instrument 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, InGaAs and TGS detectors are most commonly used.

5.3 Spectrometer

Monochromator instruments, filter-wheel instruments, acousto-optic tuneable filter (AOTF) instruments, light-emitting diode (LED) instruments and Fourier transform (FT) instruments are used.

NOTE Refer to Annex C for further details of such instruments.

5.4 Sampling system

Cuvettes, flow-through cells, transmission probes, immersion probes and attenuated total reflection (ATR) probes can be used in the laboratory or for online instruments, or both.

NOTE Refer to Annex D for further details of suitable sampling systems.

5.5 Software

The software used shall have the following capabilities:

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

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

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

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

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

f) the ability to compute multilinear regressions (MLRs), principal-component regressions (PCRs) or partial least-squares (PLS) regressions;

g) the ability to store PCR or PLS regression loadings, weights, scores and other desirable data, and to display these data for subsequent examination and interpretation;

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

i) the ability to perform cross-validation automatically;

j) the ability to identify outliers;

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

NOTE 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 Developing a calibration model

6.1 Selection of calibration materials

Materials selected for the calibration set shall comply with the following requirements.

NOTE Refer to Annex E for guidance on the selection of calibration materials.

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

b) The materials chosen shall include, and ideally exceed, the expected hydroxyl number range.

c) The calibration material hydroxyl numbers shall be evenly distributed throughout the calibration range so as to provide a “boxcar” distribution (evenly distributed throughout the range of interest).

d) The number of materials chosen shall be large enough to define statistically the relationship between the spectral variables and the hydroxyl numbers to be modelled.

   Since the appropriate number of materials might vary, depending on the properties of samples, it shall be verified by means of a statistical method.

e) The spectra of all materials shall be similar to avoid erroneous modelling. For example, the same pathlength shall be used for all materials, and the baseline, peak maxima and peak minima shall be similar (see also E.1.7).

6.2 Reference method and reference values

Determine reference values as follows:

a) The hydroxyl numbers in the calibration set shall be determined by a standard analytical method (ISO 14900 or another suitable standard method). The precision of the primary analytical method shall be well characterized in order to define realistic accuracy limits for NIR calibration.

b) Reference analyses shall be performed in replicate (see E.1.4 for guidance). Also undertake blind replicates to ascertain the true accuracy of the method. Use the average of the replicates as the calibration value for each test sample.

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

6.3 Determining wavelength regions and pathlength

6.3.1 Wavelength regions

For hydroxyl number determination, two primary wavelength regions may be used: the R-OH combination band (2 000 nm to 2 300 nm) and R-OH first overtone band (1 380 nm to 1 500 nm). Additional spectral regions may be added to the model to correct for interfering absorption.

6.3.2 Pathlength

Before developing a calibration model, it is necessary to determine the optimum pathlength at which to perform the analysis. The optimum pathlength is dependent upon the wavelength(s) chosen for the analysis. To determine the optimum pathlength, the highest hydroxyl number spectrum in the sample set (that is, the test sample that will have the highest maximum absorbance value) is compared for cuvettes with different pathlengths, and the cuvette with a pathlength which gives a maximum absorbance of 1,0 to 1,5 absorbance units is selected.

6.4 Reduction of sources of spectral variation

6.4.1 Test samples may 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 shall be identified. Multiple NIR scans and multiple replicates by the reference method will help to identify the cause of a poor fit.

6.4.2 Analysing duplicate test samples (as opposed to replicate measurement of the same test sample) reveals sampling problems due to heterogeneity. To avoid the possibility of systematic errors, test samples shall be scanned in a random order.

6.4.3 NIR spectra of polyols are affected by temperature. The physical constraints present at the instrument location shall be taken into account when deciding how to deal with these effects when developing the calibration. If the analysis is to be performed in a temperature-controlled laboratory, scan test samples at the standard room temperature after allowing the test sample to come to temperature equilibrium. If room temperature is not stable, a temperature-controlled cell shall be considered. If the hydroxyl number will be analysed at a temperature other than room temperature, it is important to ensure that the temperature of the test sample has stabilized prior to performing an analysis. The time needed to reach temperature equilibrium might vary from sample to sample and is dependent on the temperature and pathlength at which the analysis is to be performed. If the analysis is to be done in a less controlled environment, for example in a warehouse, temperature variations can be built into the calibration model by scanning calibration materials over the range of expected temperatures and including these data in the calibration set. Depending on how tight the production specifications are and how accurate the lab method is, the time to reach an acceptable temperature might be critical. It is necessary to determine the optimum equilibration time for the various products in order to reduce total analysis time or to tighten production specifications.

6.5 Multivariate mathematical treatments

6.5.1 Multivariate mathematics is used to relate the spectra measured for a set of calibration materials to the hydroxyl numbers obtained for this set of materials from a reference test. The resultant multivariate calibration model is then applied to the analysis of unknown materials to provide an estimate of their hydroxyl number.

NOTE Refer to Annex F for a discussion of multivariate analysis.

6.5.2 Three types of regression are commonly used in developing the calibration model: multilinear regression (MLR), principal-component regression (PCR) and partial least-squares (PLS) regression. Generally, if the sample matrices are simple and only one or two analytical wavelengths are needed, MLR is used. If the matrix is complex, or if more than two wavelengths are required for the desired accuracy, PCR or PLS regression is used. All mathematical treatments of multivariate calibration can be found in Section 12 of ASTM E1655-05.

6.6 Evaluating calibration models

Various statistical tools can be used to evaluate and optimize the performance of calibration models.

NOTE Refer to Annex G for details of such tools.

7 Validation of a multivariate calibration model

7.1 A multivariate calibration model shall be validated by predicting analyte concentrations for an independent set of materials with known analyte levels and statistically analysing the model’s response.

7.2 The validation set shall be chosen using the same criteria as those specified for calibration materials (see Clause 6). In addition, the following criteria shall be satisfied:

a) The materials chosen shall span the range of hydroxyl numbers in the calibration set. Any materials which do not fall within the range of the model shall be excluded.

b) The materials shall be evenly distributed throughout the range of hydroxyl numbers to ensure a boxcar distribution.

c) The materials chosen shall have spectra similar to those in the calibration set and shall span the images of all spectral variables. For example, the variability normally encountered during the manufacturing operation, sampling and analysis shall be incorporated.

7.3 Validation spectra shall be collected using the same procedures as were used for the calibration set. The developed model can then be used to predict the analyte concentrations and perform the statistical calculations described in 18.4 to 18.10 of ASTM E1655-05.

NOTE 1 The standard error of validation (SEV) can be calculated as indicated in 18.6 of ASTM E1655-05. The SEV is the standard deviation in the difference between the reference value and the NIR method value for the materials in the validation set.

NOTE 2 Refer to Annex H for details of sources of calibration and analysis error.

8 Calibration transfer

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

8.2 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 shall be tested at least once by performing a full validation of the transferred model.

8.3 Calibration transfer shall be limited to instruments having the same sampling system.

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

9 Calibration quality control

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

NOTE Refer to Annex I for guidance on monitoring the performance of the instrument and calibration model.

10 Procedure

10.1 General

The following procedure is based on the conditions used in laboratory studies carried out by a major polyol producer in Japan. Other procedures based on the principles described in earlier clauses might be suitable if precautions are taken to verify that the results obtained meet the requirements of the analysis.

10.2 Calibration curve

10.2.1 Select 10 or more calibration materials which have similar molecular structures but whose hydroxyl numbers cover the range of interest. Determine the hydroxyl numbers in advance by titration.

10.2.2 Pour one of the materials selected in 10.2.1 into the sample cell. Bring the cell to the desired temperature (about 10 min).

10.2.3 Place the cell in the NIR instrument and record the absorbance across the wavelength region as described in 6.3. Carry out duplicate or triplicate scans as described in 6.4.

10.2.4 Repeat 10.2.2 and 10.2.3 for all samples in the calibration set selected in 10.2.1.

10.2.5 Generate a working curve using the instrument software.