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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.

10.3 Measurement

For each test sample, repeat steps 10.2.2 and 10.2.3. The hydroxyl number should be calculated and displayed automatically.

10.4 Illustrative results

Figures A.1 to A.6 in Annex A give illustrative examples of results obtained with six different polyol types.

11 Precision of NIR estimated values

Section 19 of ASTM E1655-05 describes a procedure for the measurement of the precision of hydroxyl numbers of polyols estimated by this method.

12 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary to identify the product analysed (such as manufacturer, product type, batch or notebook number, date of manufacture, as required);

c) the result obtained, expressed as the hydroxyl number (OH#) to the nearest whole number for OH#-values above 100 and to the nearest 0,1 for values less than 100 (the actual precision will depend on the accuracy and precision of the referee method used as well as the results determined by the calibration model used);

d) the date of the analysis;

e) any incident or detail not stipulated in this International Standard which might have influenced the result.

Annex A
(informative)

Illustrative results

Figures A.1 to A.6 show the correlation between hydroxyl values obtained by titration and hydroxyl values obtained by NIR for six different polyol types over a range of hydroxyl numbers for each product. An FT-NIR instrument was used with a disposable glass cell (2 ml or 5 ml, as indicated). Measurements were made at either (110 ± 1) °C or (70 ± 1) °C.

The products tested were as follows:

Figure A.1 Glycerine-based propylene oxide polyol

Figure A.2 Bisphenol-A-based propylene oxide polyol

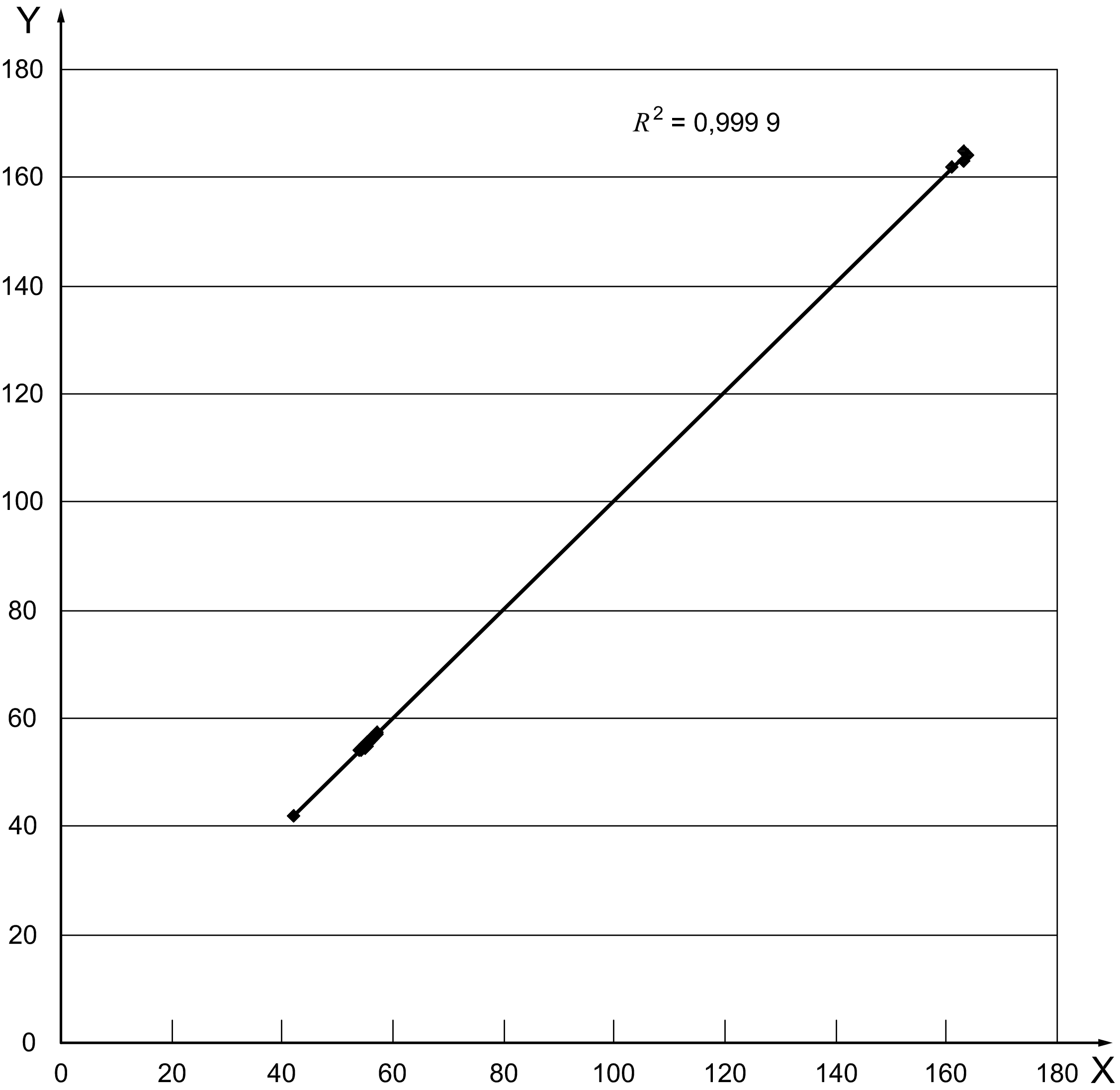
Figure A.3 Polymer polyol

Figure A.4 Pluronic polyol

Figure A.5 Propylene-glycol-based propylene oxide polyol

Figure A.6 Sucrose-based propylene oxide polyol

The coefficient of determination R^2 is given in each figure.



Key

X OH# determined by titration (mg KOH/g)
Y OH# determined by NIR (mg KOH/g)

Figure A.1 — Correlation between titration method and NIR method — Glycerine-based propylene oxide polyol

Table A.1 — Data for Figure A.1

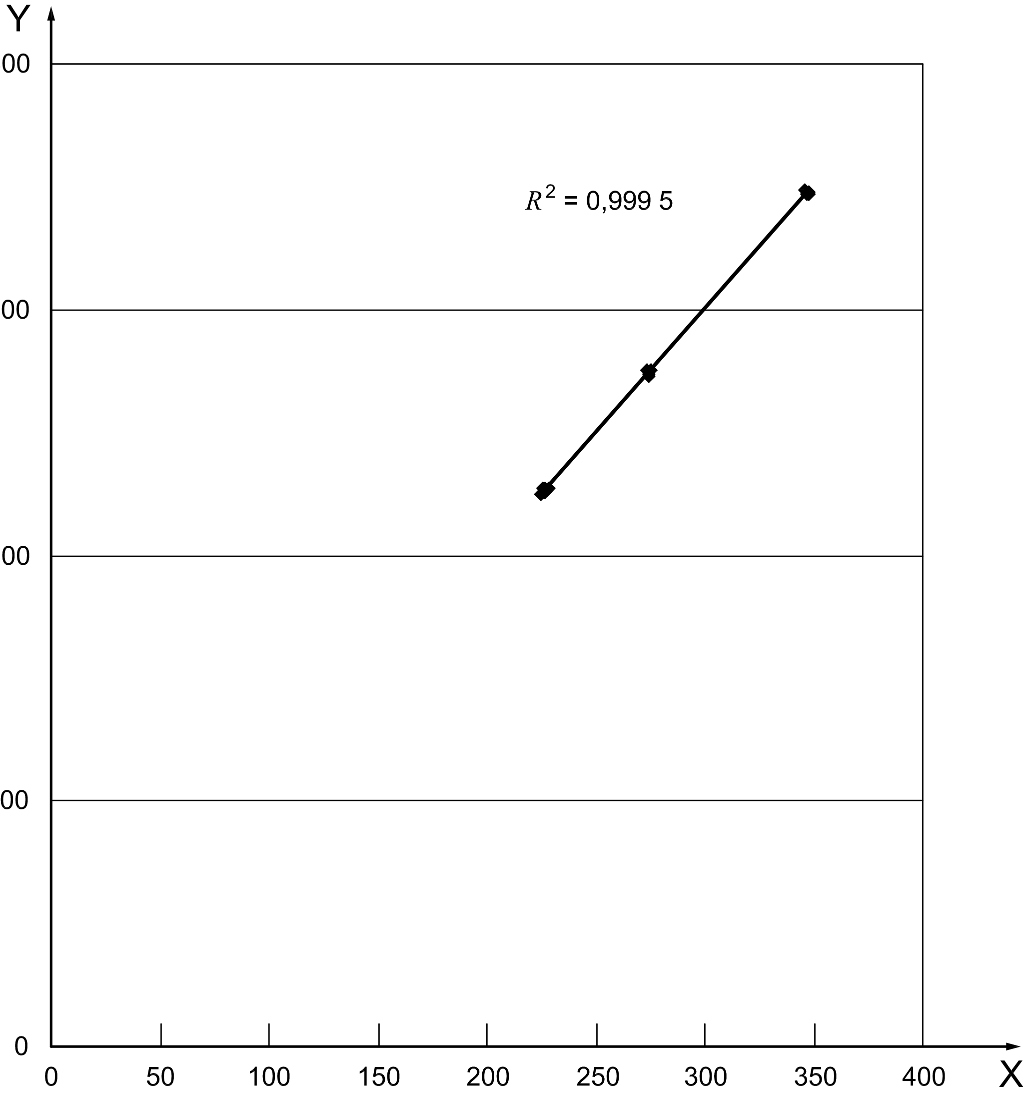
Sample No.	1	2	3	4	5
OH# (av.), mg KOH/g	163	55,8	56	55,2	42,1
Number of replicates	5	4	7	11	2

NOTE 1 All 29 data points plotted in Figure A.1.

NOTE 2 Titration method used: JIS K 1557-1 (pyridine method).

NIR method: FT-NIR apparatus, model MB160 (ABB Bomem Inc., Canada), using a disposable glass cell (ca. 5 ml) at a temperature of (70 ± 1) °C.

NOTE 3 Samples selected randomly and tested in one laboratory by three analysts.



Key

X OH# determined by titration (mg KOH/g)

Y OH# determined by NIR (mg KOH/g)

Figure A.2 — Correlation between titration method and NIR method — Bisphenol-A-based propylene oxide polyol

Table A.2 — Data for Figure A.2

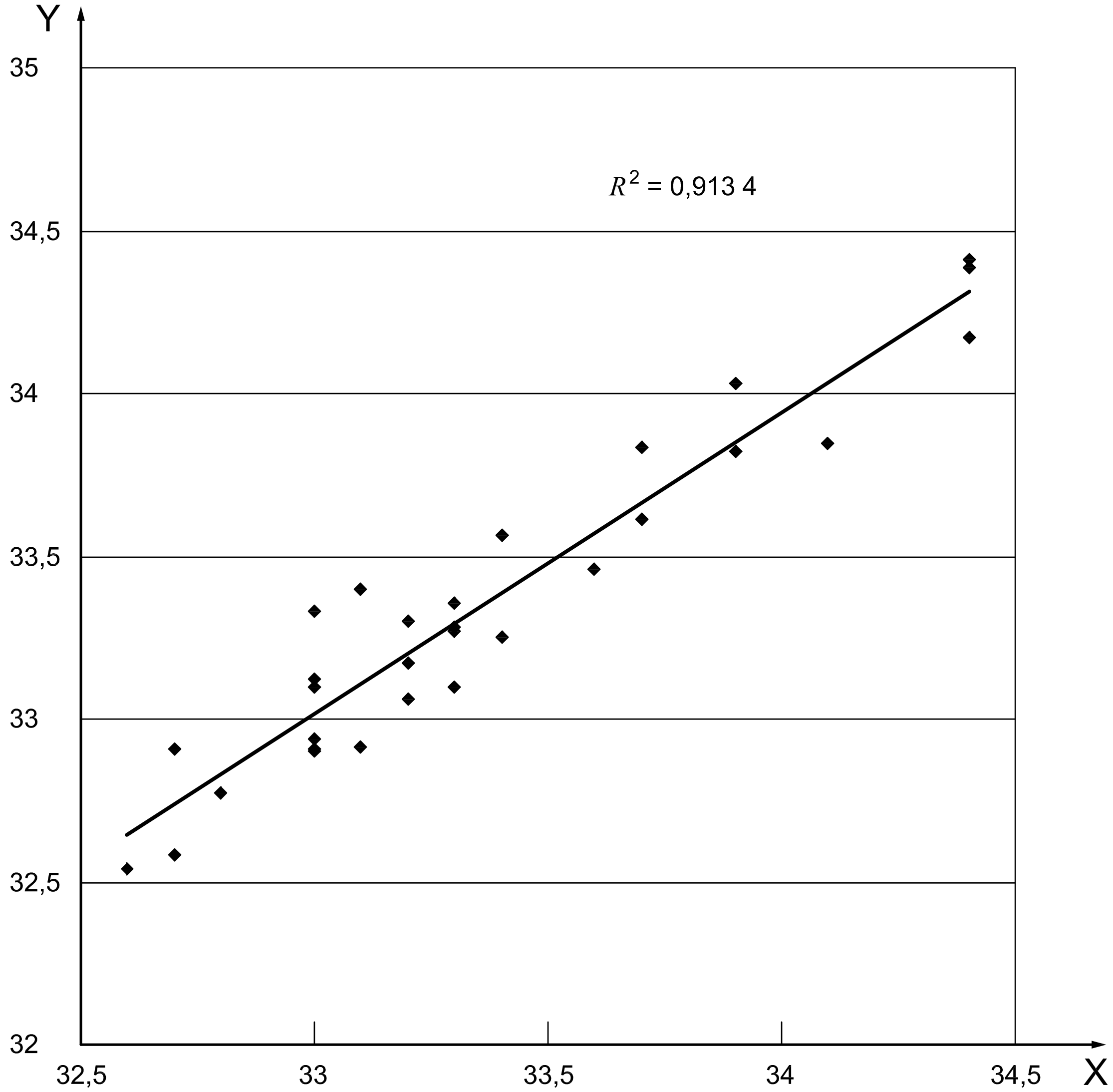
Sample No.	1	2	3
OH# (av.), mg KOH/g	347	274	227
Number of replicates	5	5	7

NOTE 1 All 17 data points were calculated and plotted in Figure A.2.

NOTE 2 Titration method used: JIS K 1557-1 (pyridine method).

NIR method: FT-NIR apparatus, model MB160 (ABB Bomem Inc., Canada), using a disposable glass cell (ca. 2 ml) at a temperature of (110 ± 1) °C.

NOTE 3 Samples selected randomly and tested in one laboratory by three analysts.



Key

X OH# determined by titration (mg KOH/g)

Y OH# determined by NIR (mg KOH/g)

Figure A.3 — Correlation between titration method and NIR method — Polymer polyol

Table A.3 — Data for Figure A.3

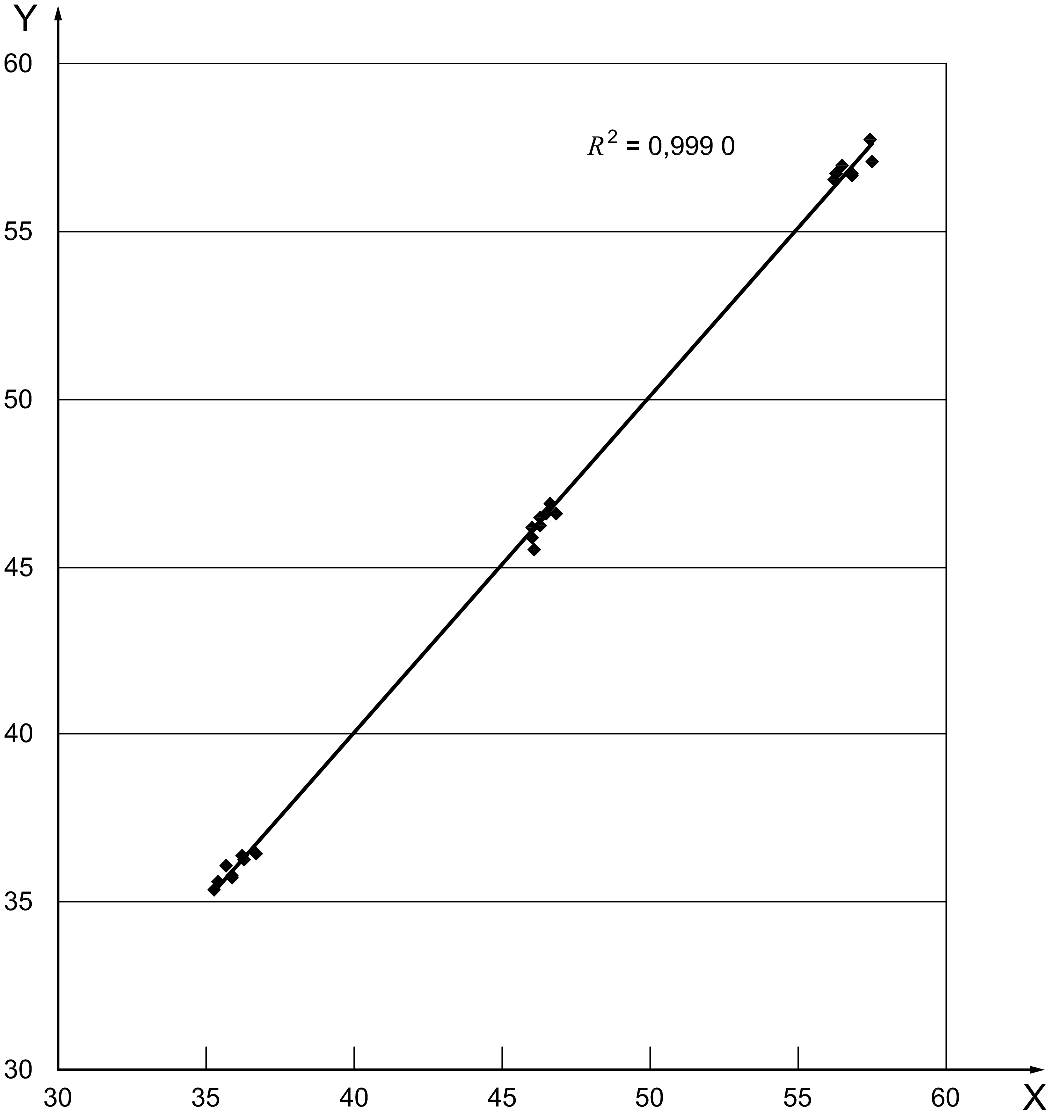
Sample No.	1
OH# (av.), mg KOH/g	33,2
Number of replicates	30

NOTE 1 All 30 data points were calculated and plotted in Figure A.3.

NOTE 2 Titration method used: JIS K 1557-1 (pyridine method).

NIR method: FT-NIR apparatus, model MB160 (ABB Bomem Inc., Canada), using a disposable glass cell (ca. 2 ml) at a temperature of (70 ± 1) °C.

NOTE 3 Samples selected randomly and tested in one laboratory by three analysts.



Key

X OH# determined by titration (mg KOH/g)

Y OH# determined by NIR (mg KOH/g)

Figure A.4 — Correlation between titration method and NIR method — Pluronic polyol

Table A.4 — Data for Figure A.4

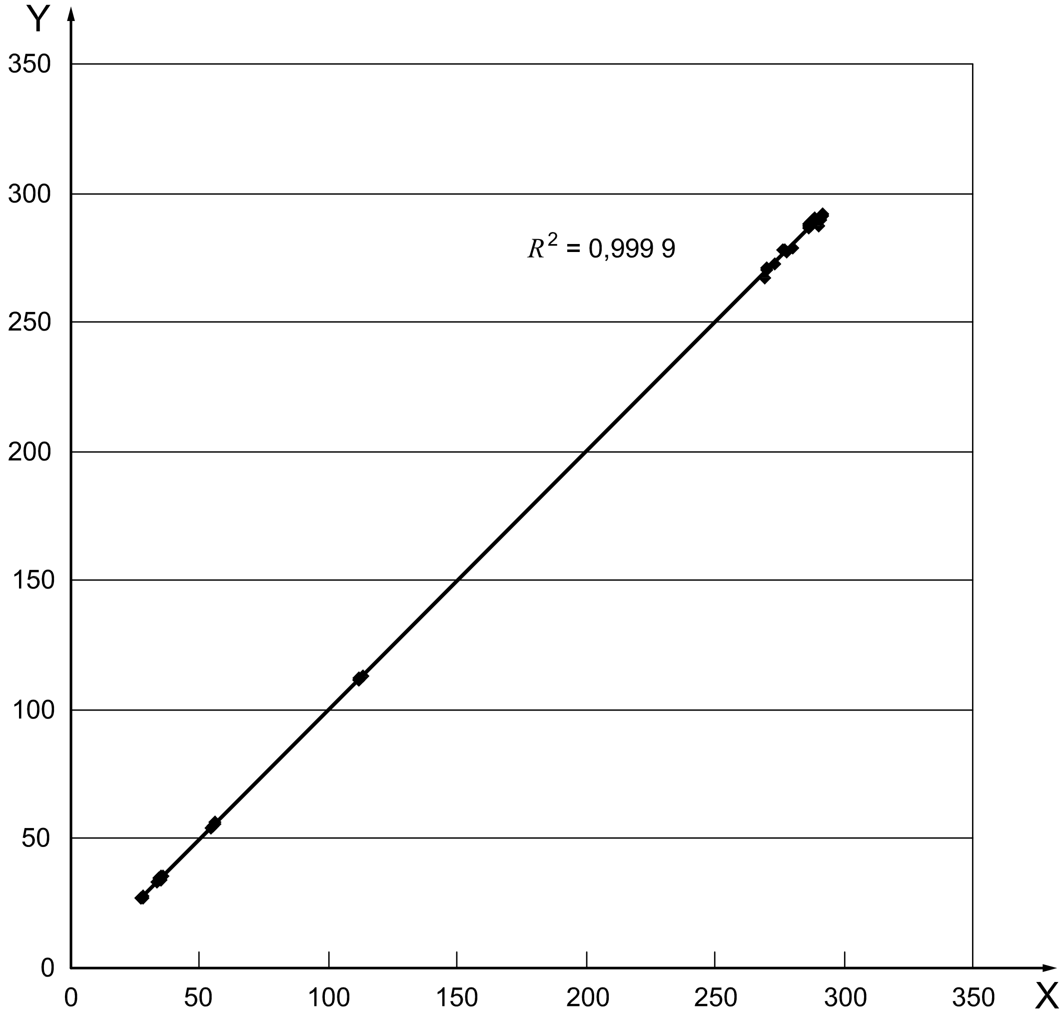
Sample No.	1	2	3
OH# (av.), mg KOH/g	56,5	46,3	35,9
Number of replicates	8	8	8

NOTE 1 All 24 data points were calculated and plotted in Figure A.4.

NOTE 2 Titration method used: JIS K 1557-1 (pyridine method).

NIR method: FT-NIR apparatus, model MB160 (ABB Bomem Inc., Canada), using a disposable glass cell (ca. 2 ml) at a temperature of (70 ± 1) °C.

NOTE 3 Samples selected randomly and tested in one laboratory by three analysts.



Key

X OH# determined by titration (mg KOH/g)

Y OH# determined by NIR (mg KOH/g)

Figure A.5 — Correlation between titration method and NIR method — Propylene-glycol-based propylene oxide polyol

Table A.5 — Data for Figure A.5

Sample No.	1	2	3	4	5	6	7	8
OH# (av.), mg KOH/g	287,4	278	271	112	55,1	35	34,5	27,4
Number of replicates	13	4	4	5	4	6	4	6

NOTE 1 All 46 data points were calculated and plotted in Figure A.5.

NOTE 2 Titration method used: JIS K 1557-1 (pyridine method).

NIR method: FT-NIR apparatus, model MB160 (ABB Bomem Inc., Canada), using a disposable glass cell (ca. 2 ml) at a temperature of (70 ± 1) °C.

NOTE 3 Samples selected randomly and tested in one laboratory by three analysts.

Key

X OH# determined by titration (mg KOH/g)

Y OH# determined by NIR (mg KOH/g)

Figure A.6 — Correlation between titration method and NIR method — Sucrose-based propylene oxide polyol

Table A.6 — Data for Figure A.6

Sample No.	1
OH# (av.), mg KOH/g	456,3
Number of replicates	15

NOTE 1 All 15 data points were calculated and plotted in Figure A.6.

NOTE 2 Titration method used: JIS K 1557-1 (pyridine method).

NIR method: FT-NIR apparatus, model MB160 (ABB Bomem Inc., Canada), using a disposable glass cell (ca. 2 ml) at a temperature of (70 ± 1) °C.

NOTE 3 Samples selected randomly and tested in one laboratory by three analysts.

Annex B
(informative)

NIR spectral measurements

B.1 NIR spectral measurements are based on Beer's law, according to which 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 ratio of the radiant power transmitted by the test sample to the radiant power incident on the sample.

B.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 the instrument. 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 also be filled with a material that has minimal absorption in the spectral range of interest, and the background measurement taken on this. Alternatively, the light beam may be split and one half passed through the test sample and the other half through the space normally occupied by the test sample and holder (i.e. an "empty" space), through an empty cell or through a background material in the cell, or the beam may be passed alternately through the test sample and through an empty space, an empty cell or a background material in the cell. The particular background-referencing scheme that is used might vary among instruments and among applications. It is important, however, that the same sample background-referencing scheme be employed for the measurement of all spectra of calibration materials, validation materials, and unknown test samples. Any differences between the instrumental conditions used for referencing and measurement should be minimized.

B.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.

B.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.

B.5 For definitions and further description of general infrared techniques, refer to ASTM E168.

Annex C
(informative)

Spectrometers

C.1 General

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

C.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 any given time.

C.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.

C.4 Acousto-optic tuneable filter (AOTF) instrument

The AOTF spectrometer 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.

C.5 Light-emitting diode (LED) instrument

In this type of 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.

C.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 converted mathematically 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 than can be achieved, in general, with other types of instrument.

Annex D
(informative)

Sampling systems

D.1 General

Depending upon the application, several different sampling systems can be used in the laboratory or for online instruments, or for both.

D.2 Cuvette

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

D.3 Flow-through cell

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

D.4 Probes

D.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.

D.4.2 Immersion probe

The immersion system uses a bi-directional optical-fibre bundle and variable-pathlength probe for test 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.

D.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- and 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 online analysis. This is an advantage when handling viscous liquids and highly absorbing materials.

Annex E
(informative)

Selection of calibration materials

E.1 Feasibility calibration

E.1.1 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 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 successful feasibility study, the calibration can be expanded and validated.

E.1.2 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 range 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 numbers are not available, it might 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 will have to be taken to avoid changes that might affect the matrix and, ultimately, compatibility with the spectra of the calibration set.

E.1.3 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.

E.1.4 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.

E.1.5 A calibration model is developed using one of several available methods, for example MLR, PCR or PLS regression. The quality of the calibration curve can be tested by any of several statistical tools described in Annex G. The calibration model can be tested using cross-validation procedures (see G.2.5). Other statistical tools can also be used to judge the overall quality of the calibration.

E.1.6 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 ensure a boxcar distribution (an even distribution of values over a defined interval of the hydroxyl number range). A final model can be developed and validated as described in Clause 7.

E.1.7 If the calibration set consists of a range of different types of polyol, and reliable calibration cannot be obtained, it might be necessary to group materials by chemical type and 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.

E.2 Potential sources of variation in calibration materials

E.2.1 The model should exclude all potential sources of variation that can be excluded in the actual applications. If these sources cannot be eliminated, they should be included in the calibration set, if possible. Sources of variation can include the following:

— chemical composition;

— physical characteristics;

— sample handling, temperature and humidity.

E.2.2 The number of materials required to calibrate the NIR model is dependent on the complexity of the samples being analysed. 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 calibration material set to define the relationships between them. On the other hand, complex systems containing several components which vary in concentration will require a large number of calibration materials to define the relationships and to ensure that model development is adequate. If a multivariate model is developed with five or fewer variables (wavelengths in MLR, or factors in PCR or PLS regression), the calibration should contain a minimum of 30 materials after elimination of outliers. If a multivariable model is developed with k (> 5) variables (wavelengths in MLR, or factors in PCR or PLS regression), the calibration set should include a minimum of $6k$ materials after the elimination of outliers.

Annex F
(informative)

Multivariate analysis

F.1 Data pretreatment

F.1.1 Various types of data-preprocessing algorithm 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 International Standard.

F.1.2 Generally, the calibration performance of NIR spectra is improved by a derivative mathematical treatment. Baseline shifts are reduced and the peak shape and resolution of peak positions are improved. There is no single best treatment, but use of the second derivative has proved to be most useful for hydroxyl number determinations. When validating a method, several different mathematical treatments should be used to determine which one produces the best calibration.

F.2 Multilinear regression (MLR)

F.2.1 The simplest algorithm used in NIR spectroscopy is multilinear regression. It provides a solution to Beer's Law equation, which correlates changes in absorbance with changes in the hydroxyl number of the polyol.

F.2.2 The choice of the number of wavelengths to use in MLR is a critical factor in the development of the model. 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.

F.2.3 The choice of specific wavelengths to include in a multilinear regression model is also a critical factor in the development of the model.

F.2.4 Refer to ASTM E1655 for the detailed mathematics of MLR.

F.3 Principal-component regression (PCR)

F.3.1 It is possible to create a set of a few eigenvectors (principal components) that represent the changes in the absorbences that are common to all samples.

F.3.2 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 development of the model. If too few principal components are used, a less precise model will be developed. If too many principal components are used, noise from the calibration samples will be incorporated into the model, leading to unstable estimations.

F.3.3 The optimum number of principal components for a model is related to the number of spectrally distinguishable components in the calibration spectra.

F.3.4 Refer to ASTM E1655 for the detailed mathematics of PCR.

F.4 Partial least-squares (PLS) regression

F.4.1 PLS regression is the method most commonly used as an alternative to MLR and PCR. PLS regression 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 regression actually uses the concentration information during the decomposition process.

F.4.2 The PLS regression method should only be used when there are at least 30 individual calibration materials. When fewer materials are analysed and modelled by the PLS regression algorithm, over-fitting typically occurs. This limits the robustness of the calibration model.

F.4.3 During the calculation, the PLS regression 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.

F.4.4 Generally, the total number of factors that are calculated corresponds approximately to the number of constituents which vary in the sample population. If the polyol samples to be analysed differ in hydroxyl number, moisture and temperature, three to four factors should provide sufficient correlation for hydroxyl number determination.

F.4.5 Refer to ASTM E1655 for the detailed mathematics of PLS regression.

Annex G
(informative)

Statistical tools used to optimize calibration models

G.1 Standard error of calibration

G.1.1 The standard error of calibration (SEC) is defined as follows:

$$\mathrm{SEC} = \left[\frac{\sum \left(Y_{\mathrm{NIR}} - Y_{\mathrm{ref}} \right)^2}{n_{\mathrm{df}}} \right]^{1/2}$$

where

Y_{NIR}	is the value estimated by the model for the calibration material;
Y_{ref}	is the corresponding reference value;
n_{df}	is the number of degrees of freedom in the calibration model.

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

G.1.2 The SEC is used in estimating the expected agreement between values calculated using the calibration model 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 the wrong number of variables, non-linear relationships, etc.)

G.1.3 The SEC is the standard deviation for the difference between reference and calculated NIR values for materials 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.

G.1.4 Additional statistical tests for evaluating the multivariate model can be found in 15.5 of ASTM E1655-05.

G.2 Optimizing the number of variables in a model

G.2.1 Determining how many variables (wavelengths in MLR, or factors in PCR or PLS regression) to use in a model is a critical step in the development of the model. 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 might be unstable. In this case, small changes in the spectrum of the order of the spectral noise might produce statistically significant changes in the estimates.

G.2.2 The maximum number of variables k that should 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.

G.2.3 Models can be built using fewer than k variables, provided that such models exhibit adequate precision and pass validation.

G.2.4 Knowledge of the precision of the reference method is also useful in determining how many variables to include in a model. Comparison of the SEC against the standard deviation calculated from the reference method repeatability provides an indication of the maximum number of variables to include in a model. SECs that are lower than the standard deviation for the reference method indicate over-fitting of the data.

G.2.5 Cross-validation procedures are also used to estimate the optimum number of variables that should be in a model. A detailed description of a suitable cross-validation procedure can found in 15.36.6 of ASTM E1655-05. A PRESS (predicated residual error sum of squares) value can be calculated as follows:

$$\text{PRESS} = \sum \left(Y_{\text{NIR}} - Y_{\text{ref}} \right)^2$$

G.2.6 The standard error of cross-validation (SECV) is calculated as follows:

$$\text{SECV} = \left[\frac{\sum \left(Y_{\text{NIR}} - Y_{\text{ref}} \right)^2}{n} \right]^{1/2}$$

where n is the number of calibration materials.

G.2.7 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 value corresponding to the optimum number of variables in the calibration model. If no minimum occurs, the first point at which the PRESS or SECV value 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.

G.2.8 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 in Clause 7. The number of variables used in a model should ultimately be chosen to produce a model with the desired precision.

G.3 Confidence limits for an estimated value

G.3.1 The confidence limits (CLs) for a hydroxyl number estimated using an MLR or a PLS regression model are given by the following equation:

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

where

t is Student's t-value for the number of degrees of freedom in the model;

D^2 is the Mahalanobis distance statistic defined in 16.2 of ASTM E1655-05.

The confidence limits for an estimated hydroxyl number are often referred to as the confidence bands or confidence intervals for the estimate.

G.3.2 The confidence limits calculated using the above equation are only an approximation since any uncertainty in the spectral data is ignored.

G.4 Determining outliers

G.4.1 During the calibration process, outliers should be identified, and the merit of retaining them in the calibration set should be carefully considered. For a detailed description of outlier statistics, refer to Section 16 of ASTM E1655-05.

G.4.2 Two types of outlier can be identified during the calibration procedure. The first type of outlier is a material 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 outlier can be identified by inspection of data to determine differences in spectra. Outlier statistics are used to identify materials that have unusually high leverage on the multivariate regression.

G.4.3 Remove all outliers which negatively affect the model prior to finalization to avoid erroneous results.

Annex H
(informative)

Sources of calibration and analysis error

H.1 Section 20 of ASTM E1655-05 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.

H.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 ($\mathrm{SEC_{cor}}$) then gives an estimate of the error in the calibration model separate from the error in the primary error.

$$\mathrm{SEC_{cor}} = \mathrm{SEC_{app}} - \frac{\sigma^2 \times n_{\mathrm{df}}}{x^2_{\mathrm{df},\alpha}}$$

where

$\mathrm{SEC_{app}}$	is the SEC calculated for the model;
σ^2	is the variance in the reference method;
n_{df}	is the number of degrees of freedom in the reference value data used to calculate σ^2;
α	is the desired degree of uncertainty in the result;
$x^2_{\mathrm{df},\alpha}$	is the value given in the appropriate standard statistical tables.

Annex I
(informative)

Monitoring the performance of the instrument and calibration model

I.1 Monitoring instrument performance

I.1.1 The instrument used for determining hydroxyl number should be periodically checked using the self-diagnostic functions in the instrument.

I.1.2 The noise level and the wavelength drift over time should be monitored periodically.

I.2 Monitoring calibration model performance

I.2.1 When an 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 calibration materials. This procedure will allow the model to incorporate the current variations (which may be unknown to the operator) that are occurring in new samples as well as variations in the instrument and associated equipment, such as sample cells and other parts of the optical bench.

I.2.2 The materials used for testing and updating of the model should 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 SEC.

I.2.3 If these new calibration materials fall outside the confidence interval used in Clause G.3, consideration should be given to updating the model with the new materials. The instrument should first be checked to make sure its operational performance is within the design test criteria for variables such as wavelength accuracy, light source intensity and signal stability. If all these criteria are within the normal range of operation, the new materials should be used to replace the oldest calibration materials of approximately the same hydroxyl number and the calibration model recalculated.

I.2.4 Calibration materials should be replaced with current materials on a regular basis, even if the new calibration materials fall within the confidence intervals of the test criteria discussed in Clause G.3. 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 the timing or extent of model upgrading. This depends on the number and variety of calibration materials in the model, the frequency of model use and the resources available to do the work. As an average guideline, for a 50-material model that is used daily to measure 10 or more samples, it is suggested that about one calibration material per week be exchanged with a new material so that a new model would be generated yearly. The new reference materials should replace the oldest calibration materials available which are close to the same hydroxyl number. The new spectral data should be acquired in exactly the same manner and time period as the calibration and validation sets.

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