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**NATIONAL STANDARD OF THE
PEOPLE'S REPUBLIC OF CHINA**

GB/T 12008.3-2009

**Plastics -- Polyether polyols -- Part 3: Determination of hydroxyl
number**

塑料 聚醚多元醇 第3部分：羟值的测定

(English Translation)

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1 Scope

1.1

This Part of GB/T 12008 specifies two methods for the determination of the hydroxyl value of polyether polyols.

1.2

Method A is phthalic anhydride method. It is recommended for polyether polyols, polymer polyols and polyols with ammonia as initiator. But for polyols with steric hindrance, the result shall be lower. If corrective measures can be taken, other polyols can also apply this method.

1.3

Method B specifies the determination of hydroxyl value in polyether polyols by near infrared spectroscopy. It describes the steps of sample selection, data collection, establishment and verification of calibration models.

2 Normative references

The provisions in following documents become the provisions of this Part of

GB/T 12008 through reference in this Part. For dated references, the subsequent amendments (excluding corrigendum) or revisions do not apply to this Part, however, parties who reach an agreement based on this Part are encouraged to study if the latest versions of these documents are applicable.

For undated references, the latest edition of the referenced document applies.

GB/T 601-2002, Chemical Reagent - Preparations of Standard Volumetric

Solutions

GB/T 2035-2008, Terms and definitions for plastics (ISO 472:1999, IDT)

GB/T 6682-2008, Water for analytical laboratory use - Specification and test methods (ISO 3696: 1987, MOD)

ASTM D7253:2006, Standard Test Method for Polyurethane Raw Materials

4.5.1 Use a syringe (4.4.2) or other suitable sampling equipment to sample into

the Erlenmeyer flask (4.4.10). The mass of test material, m , is calculated by dividing 561 by the estimated hydroxyl value, in grams.

Do not touch the sample to the bottleneck. record the mass of test material, to the nearest of milligrams. Since the calculated mass of test material may be close to the maximum value allowed by the method, the mass of test material shall be close to the calculated value.

4.5.2 Accurately pipette 25mL of phthalic anhydride acylation reagent (4.3.3)

into each test material and blank Erlenmeyer flask. Shake the flask until the test material dissolves. Each Erlenmeyer flask is connected to an air condenser (4.4.11). Put it in the $(115 \pm 2)^{\circ}\text{C}$ oil-bath (4.4.12) for 30min.

NOTE: Some laboratories prefer to maintain the oil bath temperature at $(100 \pm 2)^{\circ}\text{C}$. If it can be proved that the special product can complete the quantitative reaction, then this temperature is OK.

4.5.3 After heating, take the device out of the oil bath and cool to room temperature. Use 30mL of pyridine (4.3.2) to rinse the condenser and remove the condenser tube. Quantitatively transfer the solution to a 250mL beaker (4.4.8). Use 20mL of pyridine to rinse the Erlenmeyer flask.

4.5.4 Titrate the solution in one of the following methods:

4.5.4.1 Potentiometric titration method

Place the beaker on the automatic titrator (4.4.1). Use a magnetic stirrer (4.4.3) to stir.

Immerse the titrator electrode in the solution. Use 0.5mol/L sodium hydroxide standard titration solution (4.3.5) to titrate to the end point. If the volume of sodium hydroxide standard titration solution consumed for titrating the test material is less than 80% of the blank volume, the mass of the test material is too large. Reduce the mass of the test material and re-measure.

4.5.4.2 Colorimetric titration

Add 0.5mL phenolphthalein indicator solution (4.3.6) and magnetic stir bar.

Under stirring, use 0.5mol/L sodium hydroxide standard titration solution to titrate to the light pink end point and keep it for 15s.

Read the volume, to the nearest of 0.02mL. If the volume of sodium hydroxide standard titration solution consumed for titrating the sample is less than 80% of the blank volume, the mass of the test material is too large. Reduce the mass it is necessary to understand the chemical structure, interference, any non- linear relationships, the influence of temperature, and the interaction of the analyte with other components such as catalysts, moisture and other polyols, so as to simulate these uncontrollable factors.

5.3.2.2 The calibration is only valid for the NIR instrument that specifically generates the calibration table. Calibration and analysis using different instruments (even manufactured by the same manufacturer) shall seriously affect the accuracy and precision of the hydroxyl value of the test. Calling the calibration table between instruments is problematic. These processes require complete verification and error statistical analysis on the new instrument.

5.3.2.3 The analysis result is only statistically valid within the hydroxyl value range used for calibration. The extrapolated hydroxyl value is too low or too high shall increase the error and reduce the accuracy. Similarly, the analysis results are only valid for samples of the same chemical composition used in the calibration set. Significant changes in composition or contamination can also affect the results. Outlier detection is a tool that can be used to detect the possible problems mentioned above.

5.4 Selection of calibration samples

5.4.1

The samples of the calibration set shall be selected according to the following guidelines as far as possible.

5.4.1.1

Sample selection includes all components expected to appear in the sample of interest.

5.4.1.2

The selected sample includes a range of hydroxyl values beyond the expected.

5.4.1.3

The hydroxyl value of the sample is evenly distributed throughout the calibration range. Provide a "box" distribution of samples (evenly distributed over the entire range of interest).

5.4.1.4

The number of selected samples shall be large enough to statistically define the relationship between the spectral variables and the number of hydroxyl values.

5.4.1.5

The spectra of all samples shall be similar to avoid wrong modeling. For example, use the same path length for all samples; the baseline, peak maximum, and peak minimum shall be similar.

5.4.2

The model shall eliminate all potential sources of variables that can be eliminated during actual testing. If these sources cannot be eliminated, they shall be included in the sample set. Sources of variables can include:

Perform one-to-one correspondence between the hydroxyl value (raw data) of the polyether polyol in the sample set and the scanned spectrum. The blank value shall be registered in the table.

5.5.3 Model establishment

Build a model according to the operating requirements of the instrument manual.

Optimize the variables in the model. In the process of model calibration, use mathematical and statistical methods to identify outliers. And remove all outliers before the model is finalized. Correct the model. The calibrated model is called calibration model.

Simultaneously generate a calibration table for the model.

5.5.4 Model verification

Model verification is done by predicting the concentration of the analyte in the independent sample set and the known analyte concentration, and statistically analyzing the response of the model. Select the validation set samples according to the same conditions as the calibration set samples. In addition, the following conditions must be observed:

5.5.4.1

The sample selection shall be within the range of the calibration set hydroxyl value. Any samples that are not within the scope of the model shall be discarded.

5.5.4.2

The sample shall be evenly distributed throughout the hydroxyl value range to ensure a "box" distribution.