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

*Plastiques — Polyols pour la production du polyuréthane —
Détermination de l'indice d'hydroxyle*



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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 14900 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 unsaturated-polyester resins (ISO 2554), non-ionic surface active agents (ISO 4326, ISO 4327), binders for paints and varnishes (ISO 4629) and industrial polyglycols (ISO 6796). The two methods in this document are improved versions of imidazole-catalysed procedures specifically tailored to the determination of the hydroxyl number of many types of polyol, including those used in the production of polyurethanes. Method A is especially suited to the determination of the hydroxyl number of polyether polyols that may have steric hindrance, or are otherwise difficult to determine by phthalation. Method B is a general method based on phthalation and is applicable to a wide range of polyol types. Both of these methods are similar to procedures found in ASTM D 4274.

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Plastics — Polyols for use in the production of polyurethane — Determination of hydroxyl number

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 to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies two methods for the measurement of the hydroxyl number of polyols used as polyurethane raw materials. It is necessary to know the hydroxyl content of polyols to properly formulate polyurethane systems. Method A is primarily applicable to readily esterified polyether polyols. It is also recommended for polyols which have significant steric hindrance, such as those based on sugars. Method B is recommended for polyether polyols, polymer polyols and amine-initiated polyols, but may give low results for sterically hindered polyols. Other polyols may be analysed by these methods if precautions are taken to verify applicability. These methods can be used for research and for quality control and specification purposes.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements*.

ISO 648:1977, *Laboratory glassware — One-mark pipettes*.

ISO 760:1978, *Determination of water — Karl Fischer method (General method)*.

ISO 835-1:1981, *Laboratory glassware — Graduated pipettes — Part 1: General requirements*.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*.

ISO 4788:1980, *Laboratory glassware — Graduated measuring cylinders*.

ISO 6353-1:1982, *Reagents for chemical analysis — Part 1: General test methods*.

ISO 6353-2:1983, *Reagents for chemical analysis — Part 2: Specifications — First series*.

ISO 6353-3:1987, *Reagents for chemical analysis — Part 3: Specifications — Second series*.

3 Terms and definitions

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

3.1

polyurethane

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

3.2

hydroxyl number

hydroxyl value

the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of a test portion

4 Principle

4.1 Method A: A test portion is refluxed in a solution of acetic anhydride in pyridine to acetylate the hydroxyl groups present; the reaction is catalysed by imidazole. The excess reagent is hydrolysed with water and the resulting acetic acid is titrated with standardized sodium hydroxide solution. The hydroxyl content is calculated from the difference in titration of the test portion and a blank solution.

CAUTION — Acetic anhydride and pyridine are toxic and flammable. In addition, acetic anhydride is corrosive. Take proper precautions when handling these reagents.

4.2 Method B: The hydroxyl groups in a test portion are esterified by refluxing with a solution of phthalic anhydride in pyridine; the reaction is catalysed by imidazole. The excess anhydride is hydrolysed with water and the phthalic acid formed is titrated with standardized sodium hydroxide solution. The hydroxyl content is calculated from the difference in titration of the test portion and a blank solution.

5 Interferences

5.1 Excess water will interfere by destroying part of the esterification reagent. If the sample contains more than 0,2 % water, dry the sample with a reagent that will not add acidity or basicity to the sample.

5.2 Primary and secondary amines and long-chain fatty acids react with the reagent to form stable compounds that will be included in the result.

6 Reagents

Reagent-grade chemicals shall be used in all determinations. Unless otherwise indicated, it is intended that all reagents conform to the specifications of ISO 6353-1, ISO 6353-2 and ISO 6353-3, although other grades may be used provided that it is first determined that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Unless otherwise indicated, references to water shall be understood to mean grade 2 reagent water as defined by ISO 3696:1987.

6.1 Acetylation reagent (for method A).

Mix 127 ml of acetic anhydride with 1 000 ml of dry pyridine (6.7). Add 16 g of imidazole (6.3) and swirl carefully to dissolve. Prepare the reagent fresh daily and keep it in a dark bottle. Do not use it if it is darker than pale yellow.

NOTE Some laboratories have reported that dark, resinous solids have formed when the mixture of pyridine and esterification reagent is heated. In that event, it has been found that preparing the acetylation reagent with the addition of 0,4 %

water in the pyridine (6.8) will correct the problem. However, care has to be taken that sufficient reagent is present to complete the reaction quantitatively. See also 8.1.2.

CAUTION — Acetic anhydride and pyridine are eye, skin, and respiratory irritants. Avoid bodily contact with these reagents and use only in a well-ventilated area.

6.2 Phthalation reagent (for method B).

Weigh 116 g of phthalic anhydride into a 1 litre brown bottle. Add 700 ml of pyridine (6.7) and shake vigorously until dissolved. Add 16 g of imidazole and swirl carefully to dissolve. The reagent shall stand overnight before use. Avoid prolonged exposure of the reagent to moisture in the air. Discard reagent that develops a colour. In the blank titration as described in the procedure for method B, exactly 25 ml of this reagent shall consume between 95 ml and 100 ml of 0,500 mol/l sodium hydroxide.

6.3 Imidazole, reagent grade or equivalent.

6.4 Hydrochloric acid, standard solution, 0,1 mol/l.

Prepare and standardize to four significant figures in accordance with good practice, using potassium acid phthalate (6.6) as a primary standard. Determine and record the temperature at which the standardization was performed. The concentration of the solution shall be corrected to the temperature at which the determination is performed, as described in 6.9. This solution is required only if a correction is to be applied for the presence of strong base in the sample being analysed.

6.5 Phenolphthalein indicator solution, 10 g/l.

Prepare a solution of 1 g of phenolphthalein in 100 ml of pyridine (6.7).

6.6 Potassium acid phthalate.

Use a certified primary standard.

6.7 Pyridine, reagent grade, containing less than 0,1 % water.

If purification is required, distil from phthalic anhydride, discarding the fraction boiling below 114 °C to 115 °C.

6.8 Pyridine, containing from 0,30 % to 0,45 % water (used for special cases: see the note to 6.1).

Determine the water content of the pyridine using ISO 760. Add the required amount of water. The required volume of water to add per litre of pyridine may be calculated as follows:

$$\text{Water to add, in ml} = 4,0 - 9A$$

where A is the percent water already in the pyridine.

6.9 Sodium hydroxide, standard solution, 0,5 mol/l.

Prepare and standardize to four significant figures in accordance with good practice. Determine and record the temperature at which the standardization was performed. The factor for thermal expansion of this solution is 0,00014. For calculation of the hydroxyl content, the concentration of the solution shall be corrected to the temperature at which the determination was performed by the following:

$$c_{\theta_2} = c_{\theta_1} + F(\theta_1 - \theta_2)$$

where

c_{θ_1} is the concentration of the solution when standardized, in mol/l;

c_{θ_2} is the concentration during analysis of samples, in mol/l;

θ_1 is the temperature of solution during standardization, in °C;

θ_2 is the temperature of the solution during analysis of samples, in °C;

F is the factor to correct for thermal expansion of the solution.

7 Apparatus

7.1 Potentiometric titrator or pH-meter, accurate to 0,1 mV or better, equipped with a pair of electrodes or a combination glass-calomel electrode and a piston burette having a 100 ml capacity or capability for multiple automatic refilling.

7.2 Syringes, 2 ml, 5 ml and 10 ml, with an orifice suitable for handling viscous polyols.

7.3 Magnetic stirrer.

7.4 Analytical balance, accurate to 0,1 mg.

7.5 Volumetric pipette, 20 ml, conforming to ISO 648.

7.6 Measuring pipette, 1 ml, conforming to ISO 835-1.

7.7 Graduated cylinder, 100 ml, conforming to ISO 4787.

7.8 Beakers, 250 ml, 500 ml.

7.9 Burette (for colorimetric titration), 100 ml total capacity, range of graduated portion 50 ml, with 0,1 ml graduations, and conforming to ISO 385-1. If a 100 ml burette is not available, the first 50 ml of titrant may be added by pipette and the titration completed with a 50 ml burette.

7.10 Conical flasks, 300 ml, with standard-taper 24/40 joint.

7.11 Condenser, West type, 400 mm, drip-tip, standard taper 24/40 joint with cooling extending to the joint.

7.12 Oil bath, maintained at $115\text{ °C} \pm 2\text{ °C}$.

8 Method A — Acetylation

8.1 Procedure

8.1.1 If the sample does not contain an appreciable amount of water, determine the test portion size required using one of the following equations:

$$\text{Test portion size, in g} = \frac{561 \times 0,98}{\text{Expected hydroxyl number}}$$

or

$$\text{Test portion size, in g} = \frac{0,009\ 8 \times M_r}{n}$$

where

M_r is the molecular mass of the hydroxyl-containing compound;

n is the number of hydroxyl groups in the molecule.

NOTE In each case, the calculation is based on the assumption that a maximum of 9,8 meq of hydroxyl is present.

Since the calculated test portion size will be near the maximum permitted by the method, adhere closely to the amount calculated.

If the sample contains an appreciable amount of water, the test portion size shall be adjusted to accommodate this interference. In this case, determine the test portion size using one of the following equations:

$$\text{Test portion size, in g} = \frac{0,1701 \times 0,98}{0,0094R + [0,01S \times (n \times 17,01)/M_r]}$$

or

$$\text{Test portion size, in g} = \frac{550}{\text{Expected hydroxyl number} + (31,2 \times R)}$$

where

R is the water in the sample, in mass %;

S is the purity of the sample, in mass %;

M_r is the molecular mass of the hydroxyl-containing compound;

n is the number of hydroxyl groups present in the molecule.

Precision and accuracy may be decreased when appreciable amounts of water are present because of the required decrease in test portion size.

8.1.2 Having calculated the appropriate size, weigh the test portion into a clean, dry conical flask (7.10).

8.1.3 Pipette 25,0 ml of the acetylation reagent (6.1) into each flask (7.10) used for test portion and blank determinations, using a uniform drainage time for all aliquots. If necessary, swirl the test portion flask to dissolve the test portion. Connect each flask to a condenser (7.11) (if the surrounding atmosphere is humid, connect the condenser to a drying trap containing 2-mesh, indicating-type calcium chloride), seal the joint with 1 or 2 drops of pyridine, and place on a hotplate. Heat at the reflux temperature for 30 min, regulating the hotplate so that the vapours condense gently near the bottom of the condenser. Note that, for some polyol types, a longer period of reflux may be necessary. Check that the time used is sufficient to reach a constant value for the hydroxyl number.

8.1.4 After the reflux period, allow the flask to cool, then rinse the condenser with 25 ml of water. Remove the condenser and rinse the joint of the condenser and the flask with water, collecting the rinsings in the flask.

8.1.5 Titrate the solution by one of the following two procedures:

8.1.5.1 Potentiometric titration

Quantitatively transfer the solution to a 250 ml beaker, rinsing the flask with a small portion of water.

Place on the automatic titrimer (7.1) and stir with a magnetic stirrer (7.3).

Immerse the titrimer electrodes in the solution and titrate with 0,5 mol/l sodium hydroxide solution (6.9) until the equivalence point is reached. If the volume of 0,5 mol/l NaOH solution required for the titration of the test portion is less than 80 % of that required for the blank, the test portion was too large and the analysis shall be repeated with a smaller test portion.

Record the temperature of the 0,5 mol/l NaOH solution.

8.1.5.2 Colorimetric titration

Add 0,5 ml of phenolphthalein indicator solution (6.5) and a magnetic stirrer bar to the test portion solution.

Titrate, while stirring, with 0,5 mol/l sodium hydroxide solution to the first faint pink end point that is permanent for 15 s.

Read the volume to 0,02 ml. If the volume of 0,5 mol/l NaOH solution required for the titration of the test portion is less than 80 % of that required for the blank, the test portion was too large and the analysis shall be repeated with a smaller test portion.

Record the temperature of the 0,5 mol/l NaOH solution.

8.1.6 If the sample contains significant acidity or alkalinity, correct the result as follows:

8.1.6.1 Weigh into a 300 ml conical flask the same amount of sample used for the hydroxyl determination. Add to the flask 75 ml of pyridine (6.7), 75 ml of water, and 0,5 ml of phenolphthalein indicator solution.

8.1.6.2 Acidity correction: If the solution in 8.1.6.1 is colourless, titrate with standard 0,1 mol/l NaOH using potentiometric or colorimetric end point detection. Conduct a blank determination on the reagent mixture described in 8.1.6.1, leaving out the test portion. The acidity correction, in milligrams of KOH per gram, is calculated as follows:

$$\text{Acidity correction} = \frac{(V_1 - V_2)c \times 56,1}{m}$$

where

V_1 is the volume of NaOH solution required for titration of the test portion, in ml;

V_2 is the volume of NaOH solution required for titration of the blank, in ml;

c is the concentration of the NaOH solution, in mol/l;

m is the mass of the test portion, in g.

8.1.6.3 Alkalinity correction: If the solution in 8.1.6.1 is pink, titrate potentiometrically to the equivalence point (or, if colorimetric end point determination is used, titrate to the disappearance of the pink colour), using 0,1 mol/l HCl. Then add 1,0 ml excess of 0,1 mol/l HCl. Back-titrate with standard 0,1 mol/l NaOH to the equivalence point (or, if colorimetric, to a pink end point that persists for at least 15 s). Using standard 0,1 mol/l NaOH, titrate a blank containing exactly the same total amount of added 0,1 mol/l HCl and the reagent mixture used previously, but omitting the test portion. The alkalinity correction, in milligrams of KOH per gram, is calculated as follows:

$$\text{Alkalinity correction} = \frac{(V_2 - V_1)c \times 56,1}{m}$$

in which the symbols are as defined in 8.1.6.2.

8.2 Expression of results

8.2.1 Calculate the hydroxyl number, in milligrams of KOH per gram of sample, as follows:

$$\text{Hydroxyl number} = \frac{(V_4 - V_3)c \times 56,1}{m}$$

where

V_3 is the volume of NaOH solution required in 8.1.5.1 or 8.1.5.2 for titration of the test portion, in ml;

V_4 is the volume of NaOH solution required in 8.1.5.1 or 8.1.5.2 for titration of the blank, in ml;

c is the concentration of the NaOH solution, in mol/l;

m is the mass of the test portion, in g.

8.2.2 If the sample contains free acidity or alkalinity as measured in 8.1.6, correct the result as follows:

Hydroxyl number (corrected) = Hydroxyl number + acidity

or

Hydroxyl number (corrected) = Hydroxyl number – alkalinity

8.3 Precision and bias

8.3.1 Precision data were determined from round-robin tests conducted by laboratories associated with the Polyurethane Raw Materials Analytical Committee (PURMAC) in the U.S. ASTM E 180 was used to calculate precision values. Data from the round robin may be obtained from ASTM Committee D-20 or from the PURMAC committee of the American Plastics Council.

Use the criteria given in 8.3.2 and 8.3.3 to judge the acceptability of results.

8.3.2 Repeatability (single analyst): Duplicate results obtained by the same analyst using the same equipment on the same day should only be considered suspect if they differ by more than the value of r shown in Table 1 for the same, or similar, material.

8.3.3 Reproducibility (multilaboratory): Results, each the mean of duplicates, obtained in separate laboratories should only be considered different if they differ by more than the value of R shown in Table 1 for the same, or similar, material.

Table 1 — Precision data for hydroxyl number by acetylation

Test material	Mean value of OH number	s_r	s_R	r	R
PTME glycol	111	0,7	2,8	2,0	7,8
Glycerine-based polyol, p.o./e.o. capped	33,4	0,3	0,7	0,8	2,0
Glycerine-based polyol, p.o./e.o. capped	54,5	0,6	2,8	1,7	7,8
Sucrose/glycerine-based propoxylated polyol	492,6	1,5	3,9	4,2	10,9
s_r is the within-laboratory standard deviation of replicates; s_R is the between-laboratory standard deviation of averages of duplicates; r is the within-laboratory repeatability limit ($2,8 \times s_r$); R is the between-laboratory reproducibility limit ($2,8 \times s_R$).					

8.3.4 Bias: The bias for this test method has not been determined.

8.4 Test report

The test report shall include the following:

- a) a reference to this International Standard;
- b) the corrected hydroxyl number, to the nearest 0,1;
- c) all details necessary to identify the product analysed (such as manufacturer, product type, lot or notebook numbers, date of manufacture, as required);
- d) the method of titration used (potentiometric autotitrator or colorimetric);
- e) any incident or detail not stipulated in this International Standard which may have influenced the result;
- f) the date of the analysis.

9 Method B — Phthalation

9.1 Procedure

9.1.1 Weigh into a conical flask (7.10), using a syringe (7.2) or other suitable equipment, an amount of sample calculated as follows:

$$\text{Test portion size, in g} = \frac{561}{\text{Expected hydroxyl number}}$$

No material shall be allowed to touch the neck of the flask.

Record the test portion size to the nearest milligram.

Since the calculated mass will be near the maximum permitted by the method, adhere closely to the mass calculated.

9.1.2 Accurately pipette 25 ml of the phthalation reagent (6.2) into each flask used for test portion and blank determinations. Swirl the test portion flask to dissolve the test portion. Connect each flask to a condenser (7.11), and place the flasks in the oil bath (7.12), maintained at $115\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$, for 30 min.

NOTE Some laboratories prefer to maintain the oil bath at $100\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$. This variation may be used if it is demonstrated that quantitative reaction is obtained with the particular product being tested.

9.1.3 After the heating period, remove the assembly from the bath and cool to room temperature. Wash down the condenser with 30 ml of pyridine and remove the condenser. Quantitatively transfer the solution to a 250 ml beaker using 20 ml of pyridine to rinse the flask.

9.1.4 Titrate the solution by one of the following two procedures:

9.1.4.1 Potentiometric titration

Place on the automatic titrimer (7.1) and stir with a magnetic stirrer (7.3).

Immerse the titrimer electrodes in the solution and titrate with 0,5 mol/l sodium hydroxide solution (6.9) until the equivalence point is reached. If the volume of 0,5 mol/l NaOH solution required for the titration of the test portion is less than 80 % of that required for the blank, the test portion was too large and the analysis shall be repeated with a smaller test portion.

Record the temperature of the 0,5 mol/l NaOH solution.