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Plastics — Polyols for use in the production of polyurethanes — Determination of basicity (total amine value), expressed as percent nitrogen

Plastiques — Polyalcools utilisés pour la production de polyuréthannes — Détermination de la basicité (valeur totale d'amines) en pourcentage d'azote

Reference number
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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information.

The committee responsible for this document is ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

This second edition cancels and replaces the first edition (ISO 25761:2008), which has been technically revised.

Introduction

Polyurethanes are produced by the catalysed reaction of isocyanates with polyols. The basicity of the polyol employed affects the rate of reaction and speed of cure of the product. It is therefore necessary to determine the basicity in order to predict reactivity and monitor product quality.

Plastics — Polyols for use in the production of polyurethanes — Determination of basicity (total amine value), expressed as percent nitrogen

SAFETY STATEMENT — Persons using this document should be familiar with normal laboratory practice, if applicable. 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

The method specified in this International Standard measures the basic constituents in polyols that are soluble in glacial acetic acid and reactive with perchloric acid. Samples containing 0,3 % to 10 % of nitrogen have been evaluated by this method. The method is applicable to amine-based polyols, polyether polyols and polyether polyol blends that are used in polyurethane reactions. The results are measures of batch-to-batch uniformity and may be used to estimate reactivity in polyurethane reactions.

It is also permissible to express the results in equivalents of base per gram of sample.

NOTE This method is technically equivalent to that in ASTM D 6979.

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 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 4788, *Laboratory glassware — Graduated measuring cylinders*

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

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

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

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

3 Terms and definitions

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

3.1
polyol
polymer based on ethylene oxide and/or propylene oxide which contains two or more hydroxyl groups

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

3.3
percent nitrogen
quantity of perchloric-acid-titratable base in a sample, expressed as a mass percentage of nitrogen

3.4
alkalinity
quantity of perchloric-acid-titratable base in a sample, expressed as mg of KOH/g of sample

3.5
total amine value
quantity of perchloric-acid-titratable base in a sample, identified only as amines and expressed as mg of KOH/g of sample

4 Principle

A test portion of the sample is dissolved in glacial acetic acid. The resulting single-phase solution is titrated at room temperature to a potentiometric end point with a standardized solution of perchloric acid in acetic acid. The result is reported as percent nitrogen or mg of KOH/g of sample.

5 Sampling

Draw samples from a well-mixed vessel into a thoroughly cleaned and dry borosilicate-glass container (soft-glass containers are not acceptable). If sampling from a line or valve, flush the line thoroughly with the product before starting to draw the sample. Seal the sample until analysis.

6 Apparatus

6.1 **One-mark volumetric flask**, of capacity 1 000 ml conforming to ISO 1042.

6.2 **Graduated measuring cylinder**, of capacity 100 ml and 500 ml conforming to ISO 4788.

6.3 **Precision balance**, accurate to 0,1 mg or better.

6.4 **Potentiometric titrator**, capable of determining multiple end points, equipped with a pair of electrodes or a combination glass calomel electrode, a 20 ml burette and a recorder.

7 Interference

Any acidic or basic materials inadvertently introduced into the sample will cause errors in the analysis. Any material capable of serving as a buffer may interfere with the analysis by obscuring the titration end point.

8 Reagents

Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of ISO 6353-1, ISO 6353-2 and ISO 6353-3, as applicable. Other grades may be used, however, 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 water as defined in ISO 3696.

8.1 **Glacial acetic acid**.

8.2 **Acetic anhydride**.

8.3 **Perchloric acid**, nominal concentration 70 %.

8.4 Perchloric acid in acetic acid, concentration 0,10 mol/l.

One way of preparing the 0,10 mol/l perchloric acid in acetic acid is as follows. In a 1 000 ml volumetric flask, mix 8,7 ml of perchloric acid (8.3) with 500 ml of glacial acetic acid (8.1). Add 25 ml of acetic anhydride (8.2) and dilute to volume with glacial acetic acid.

WARNING — Perchloric acid is extremely irritating to the skin, eyes and mucous membranes, highly toxic via oral and inhalation routes, and can form explosive mixtures when mixed with carbonaceous material or allowed to dry. Concentrated perchloric acid should only be used in a hood approved for perchloric acid use. Chemically resistant gloves should be worn. In the event of skin contact, wash with soap and water. Goggles or safety glasses with side shields should be worn. In the event of eye contact, flush with copious amounts of water for 15 min. In the event of inhalation, move the victim to an uncontaminated area. In the event of ingestion, do not induce vomiting. For all exposures, seek professional medical advice.

It is strongly recommended that reference articles on perchloric acid safety be consulted to determine safe-handling and clean-up procedures (see References [1] to [6] and references cited therein).

9 Procedure

9.1 Weigh a test portion of the sample into a suitable container, calculating the mass of the test portion as follows:

$$M' = 2/P$$

where

M' is the mass of the test portion, in g;

P is the expected percent nitrogen content of the sample.

For test portion masses below 10,0 g, record the mass to the nearest 0,1 mg; for test portion masses greater than 10,0 g, record the mass to the nearest 0,01 g.

9.2 Add 100 ml of glacial acetic acid and stir gently until the test portion has dissolved completely.

If necessary, the mixture can be heated gently until the test portion has completely dissolved.

9.3 Titrate the test solution potentiometrically using a potentiometric titrator (6.4) with 0,10 mol/l perchloric acid (8.4) through the end point which occurs at about 600 mV.

Colorimetric end point determinations can also be used. Suitable indicators are patent blue VF or crystal violet. Typically, 10 drops of a 0,3 % – 0,5 % (m/v) indicator solution is used.

9.4 Under normal circumstances, the blank value is negligibly small and is not included in the calculation. However, a solvent blank should preferably be evaluated at suitable intervals to confirm that the solvent blank is indeed a negligible value.

NOTE Some laboratories report using this general procedure for lower levels of basicity, employing 0,01 mol/l perchloric acid as the titrant. Better results are reported at low levels with a colorimetric end point determination. No blank is needed since the solvent is neutralized to a green end point before the test solution is added. Precision data reported in this International Standard are based on the range 0,3 % to 10 % nitrogen. Precision data at lower ranges of nitrogen are not available at the current time. Therefore, precision studies will be necessary before the method is applied to ranges below 0,3 % nitrogen.

10 Expression of results

10.1 Calculate the basicity of the sample, as percent nitrogen (% N) as follows:

$$\%\,\mathrm{N} = \frac{V \times F \times 1{,}4}{m \times 1\,000} \times 100$$

where

V is the volume of titrant used to reach the end point of the test solution titration, in ml;

F is the factor for the concentration of the perchloric acid solution used as the titrant (calculated as described in Annex A);

m is the mass of the sample, in g;

1,4 is the product of the atomic mass of nitrogen (14) and the nominal concentration of the perchloric acid (0,1 mol/l);

1 000 is a conversion factor to convert grams to milligrams.

10.2 It is permissible to also report the results as alkalinity in mg of KOH/g of sample, as follows:

$$\text{Alkalinity (total amine value as mg KOH/g)} = \frac{V \times F \times 5{,}61}{m}$$

where 5,61 is the product of the molecular mass of KOH (56,1) and the nominal concentration of the perchloric acid (0,1 mol/l); the other symbols are as defined in 10.1.

11 Precision and bias

11.1 General

Table 1 is based on a round-robin involving seven laboratories and conducted in 2002 in accordance with ASTM E 180. All laboratories used potentiometric titration for the generation of the data used in this study. All of the samples were prepared at one source, but the individual test solutions were prepared at the laboratories that tested them. Each test result was the average of two individual determinations. Each laboratory made duplicate determinations on each material on each of two days.

Table 1 — Round-robin percent nitrogen data

Values in percent nitrogen

Material	Average	s_r	s_R	r	R	DF
A	0,317	0,000 7	0,001 8	0,002 0	0,005 0	5
B	2,51	0,004 6	0,005 3	0,012 9	0,014 8	5
C	5,86	0,007 9	0,013 9	0,022 1	0,039 2	5
D	9,45	0,022 0	0,021 7	0,061 6	0,061 8	5

s_r is the within-laboratory standard deviation from the mean;

s_R is the between-laboratory standard deviation from the mean;

r is the within-laboratory repeatability limit (= $2{,}8 s_r$);

R is the between-laboratory reproducibility limit (= $2{,}8 s_R$);

DF is the number of degrees of freedom in the data.

11.2 Precision

11.2.1 Repeatability, *r*: Comparing two replicate results for the same material, obtained by the same operator using the same equipment on the same day, the two results shall be judged not equivalent if they differ by more than the value of *r* given for that material in Table 1.

11.2.2 Reproducibility, *R*: Comparing two results, each the mean of replicates, for the same material, obtained by different operators using different equipment in different laboratories on different days, the two results shall be judged not equivalent if they differ by more than the value of *R* given for that material in Table 1.

11.2.3 Any judgement in accordance with 11.2.1 or 11.2.2 would have an approximately 95 % probability of being correct.

CAUTION — The explanations of *r* **and** *R* **given above are intended only to present a meaningful way of considering the approximate precision of this test method. The data in Table 1 should not be applied rigorously to the acceptance or rejection of material, as those data are specific to the round-robin and may not be representative of other lots, conditions, materials or laboratories. Users of this test method should apply statistical principles to generate data specific to their laboratory and materials, or to reproducibility between specific laboratories. The principles of 11.2.1 to 11.2.3 would then be valid for such data.**

11.3 Bias

Bias is the difference between the observed test results and an accepted reference value. There are no recognized standards by which to estimate the bias of this test 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, lot or notebook number and date of manufacture, as required);

c) the result obtained, expressed as percent nitrogen to the nearest 0,01 %, or as total amine value to the nearest 0,1 mg of KOH/g of sample;

d) any incident or detail not stipulated in this International Standard which may have influenced the result;

e) the date of the analysis.

Annex A
(informative)

Determination of the factor *F* for 0,1 mol/l perchloric acid in acetic acid

A.1 Procedure

In an agate mortar, crush to a fine powder standard-grade potassium acid phthalate.

Dry the powder for about 60 min at 120 °C.

Cool to room temperature in a desiccator.

Weigh, to the nearest 0,1 mg, 0,5 g to 0,6 g of the dried powder into a 200 ml beaker.

Add 50 ml of glacial acetic acid to the beaker and stir to dissolve.

Potentiometrically titrate the solution with the perchloric acid solution (8.4).

Calculate the factor *F* for the perchloric acid solution as described in Clause A.2.

A.2 Calculation

Calculate the factor *F* as follows:

$$F = \frac{m}{0{,}020\,422 \times V} \times \frac{A}{100}$$

where

F is the factor for the 0,1 mol/l perchloric acid;

m is the mass, in g, of potassium acid phthalate weighed out;

A is the purity of the potassium acid phthalate, in %;

V is the volume of 0,1 mol/l perchloric acid required to titrate the potassium acid phthalate solution;

0,020 422 is the mass, in g, of potassium acid phthalate corresponding to 1 ml of 0,1 mol/l perchloric acid.

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[7] ASTM D 6979, *Standard Test Method for Polyurethane Raw Materials: Determination of Basicity in Polyols, Expressed as Percent Nitrogen*

[8] ASTM E 180, *Standard Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals*

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