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Plastics — Polyols for use in the production of polyurethanes — Determination of degree of unsaturation by microtitration

Plastiques — Polyols pour la production des polyuréthannes — Détermination du degré de non-saturation par microtitrage

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

This second edition cancels and replaces the first edition (ISO17710:2002), of which it constitutes a minor revision.

The changes are as follows:

— the title has been changed to plural form to read: "Plastics — Polyols for use in the production of polyurethanes — Determination of degree of unsaturation by microtitration"

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Standards have been published which deal with the measurement of the degree of unsaturation in polyols used for the production of polyurethane plastics (ASTM D 4671, JIS K 1557, part 6.7). These standards are based on the reaction of mercuric acetate with the unsaturation present in the molecule. The method described in this document relies on the same chemistry, but is a microtitration method which uses less reagent and therefore reduces the disposal problems associated with mercury compounds. It is based primarily on ASTM D 4671.

Plastics — Polyols for use in the production of polyurethanes — Determination of degree of unsaturation by microtitration

WARNING — Persons using this document should be familiar with normal laboratory practice. This document 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 determine applicable national regulatory conditions prior to the application of this document.

1 Scope

This document specifies a microtitration method to measure the degree of unsaturation in polyether polyols used in the production of polyurethanes. It is based on the reaction of mercuric acetate with double bonds in the polyol. It does not apply to compounds in which the unsaturation is conjugated with carbonyl, carboxyl or nitrile groups.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 4787, *Laboratory glassware — Volumetric glassware — Methods for use and testing of capacity*

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.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
unsaturation
property of a compound or polymer distinguished by the presence of a carbon-to-carbon double bond

3.2
polyol
organic compound which contains two or more hydroxyl groups capable of reacting with isocyanates to form polyurethanes

3.3
polyurethane
polymer prepared from the reaction of an organic di- or polyisocyanate with compounds containing two or more hydroxyl groups

4 Principle

Carbon-to-carbon unsaturated compounds in the sample are reacted with mercuric acetate and methanol in a methanolic solution to produce acetoxymercuricmethoxy compounds and acetic acid. The amount of acetic acid released is determined by microtitration with standard alcoholic potassium hydroxide and the result used to calculate the amount of unsaturation originally present. Because the acid cannot be titrated in the presence of excess mercuric acetate, sodium bromide is added to convert the mercuric acetate to the corresponding bromide, which does not interfere with the titration. A suitable correction shall be applied if the sample is not neutral to phenolphthalein indicator. Carbon dioxide shall be excluded from the reaction.

5 Application

Side reactions in polymerizations based on propylene oxide produce small amounts of polymers with only one hydroxyl group per chain. These unsaturated polymers lower functionality and molecular mass, thus changing the overall molecular mass distribution. This test method is suitable for quality control, as a specification test, and for research.

6 Interferences

This test method does not apply to compounds in which the unsaturation is conjugated with carbonyl, carboxyl or nitrile groups. The system shall be essentially free of water and inorganic salts, especially halides. The product being measured shall be essentially dry and free of inorganic salts, especially halides. Acetone in low concentrations does not interfere significantly, although its presence may make the end point less distinct.

7 Reagents

Reagent grade chemicals shall be used in all tests. 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. 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.

7.1 Methanolic mercuric acetate solution, C = 0,05 mol/l.

Dissolve 16 g of mercuric acetate [$Hg(C_2H_3O_2)_2$] into 1 l of reagent grade methanol and add sufficient glacial acetic acid to require a blank titration of 0,5 ml to 1 ml of 0,05 mol/l methanolic KOH for a 2 ml aliquot. Usually several drops of acid are required. Prepare the reagent fresh weekly and filter before using.

WARNING — Mercury compounds are highly toxic. Handle all mercury-containing reagents and waste solutions with care. Handle waste solutions as hazardous materials, and dispose of wastes in accordance with good laboratory practice. Determine any applicable regulations.

7.2 Methanolic potassium hydroxide solution, C = 0,05 mol/l.

Prepare and standardize in accordance with good practice, using potassium acid phthalate as a primary standard.

7.3 Methanolic hydrochloric acid solution, C = 0,05 mol/l.

Prepare by successively diluting concentrated hydrochloric acid with methanol. This will introduce less than 0,5 % water into the titration reagent. Standardize by titrating against 0,05 mol/l methanolic KOH (7.2).

7.4 Sodium bromide (NaBr).

7.5 Methanol.

8 Apparatus

8.1 Autotitrator, capable of determining acidimetric end points, and equipped with a pair of electrodes or a combination glass/calomel electrode, a 5 ml burette and a recorder.

8.2 Analytical balance, capable of weighing samples to 0,1 mg.

8.3 Pipette, 2 ml capacity, conforming to ISO 4787.

8.4 Titration vessel, capable 50 ml to 100 ml capacity.

9 Sampling

Samples shall be drawn from a well-mixed vessel into a thoroughly cleaned and dry borosilicate glass container (soft-glass containers are not acceptable). If drawing from a line or valve, flush the line thoroughly with the product before starting to draw the sample. Seal the sample until taking a test portion for analysis. Care shall be taken to exclude excess moisture and carbon dioxide.

10 Procedure

10.1 This method requires at least a two-fold molar excess of mercury reagent for quantitative reaction of the unsaturated species. If the test portion is too large, the method will give inaccurate (low) results as well as reduced precision. Use no more than 0,033 milli-equivalents (meq) of unsaturated species for the analysis therefore. For samples having 0,033 meq or less of unsaturation per gram of sample, weigh approximately 1 g of sample (weighed to 0,1 mg) into a 100 ml titration flask. If the unsaturation value is not known, determine an approximate value by using a 1 g test portion. Use this approximate value to calculate a correct test portion size that will contain no more than 0,033 meq of unsaturation using Formula (1):

$$m = \frac{0{,}033}{U_A} \tag{1}$$

where

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

U_A is the approximate sample unsaturation, in meq/g.

10.2 Add 2 ml of mercuric acetate solution (7.1) and swirl to dissolve the test portion completely. Cover with a watch glass and allow the solution to stand for 30 min. Add 50 ml of methanol (7.5) followed by 0,25 g of sodium bromide crystals (7.4).

10.3 Titrate using 0,05 mol/l methanolic KOH (7.2) to the end point using an automatic titrator (8.1).

10.4 Titrate a blank using the same procedure, but without adding a test portion.

10.5 To determine the acidity or basicity of the polyol in order to correct the results, prepare a test portion exactly as above, but omit the mercuric acetate. Titrate, as above, with 0,05 mol/l methanolic KOH to the potentiometric end point. If the solution is determined to be already past the end point, repeat this procedure, but titrate with 0,05 mol/l methanolic HCl (7.3).

11 Expression of results

11.1 Calculate the acidity of the sample as shown in Formula (2):

$$A = V_A \times c(\mathrm{KOH}) / m \quad (2)$$

where

A is the acidity, in meq/g;

V_A is the volume of 0,05 mol/l KOH required to neutralize the test portion, in ml;

c(KOH) is the concentration of the methanolic KOH solution, in meq/ml;

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

11.2 Calculate the basicity of the sample as shown in Formula (3):

$$B = V_B \times c(\mathrm{HCl}) / m \quad (3)$$

where

B is the basicity, in meq/g;

V_B is the volume of 0,05 mol/l HCl required to neutralize the test portion, in ml;

c(HCl) is the concentration of the methanolic HCl solution, in meq/ml;

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

11.3 Calculate the degree of unsaturation of the sample, in meq/g, as shown in Formula (4):

$$U = [(V_S - V_B) \times c(\mathrm{KOH}) / m] - A + B \quad (4)$$

where

U is the degree of unsaturation, in meq/g;

V_S is the volume of 0,05 mol/l KOH required for the test portion, in ml;

V_B is the volume of 0,05 mol/l KOH required for the blank, in ml;

c(KOH) is the concentration of the methanolic KOH solution, in meq/ml;

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

B is the basicity, in meq/g;

A is the acidity, in meq/g.

12 Precision and bias

12.1 Precision

Use the following criteria to judge the acceptability of results:

a) Repeatability (single analyst): Duplicate results obtained by the same analyst using the same equipment on the same day shall only be considered different if they differ by more than the *r* value in Table 1 for a similar product.

b) Reproducibility (multilaboratory): Results, each the mean of duplicates run on identical test materials in separate laboratories, shall only be considered different if they differ from that of another laboratory by more than the *R* value in Table 1 for a similar product.

Table 1 — Interlaboratory unsaturation data

Values in meq/g of sample

Sample	Average result	S_r	${}^sR$	r	R	n
A	0,000 7	0,001 1	0,000 6	0,003 1	0,001 7	6
B	0,072 8	0,001 1	0,003 3	0,003 1	0,009 2	6
C	0,036 2	0,000 4	0,001 5	0,001 1	0,004 2	5
D	0,023 1	0,000 8	0,000 7	0,002 2	0,002 0	6
E	0,023 1	0,001 4	0,012 6	0,003 9	0,035 4	6
F	0,035 0	0,000 4	0,001 0	0,001 1	0,002 8	6
G	0,124 0	0,001 8	0,003 7	0,005 0	0,010 4	5

S_r is the within-laboratory standard deviation of the replicates;

${}^sR$ is the between-laboratory standard deviation of the averages;

r is the within-laboratory repeatability limit $(2{,}8 \times S_r)$;

R is the between-laboratory reproducibility limit $\left(2{,}8 \times {}^sR\right)$;

n is the number of laboratories contributing valid data for this material.

NOTE Precision data were determined by an interlaboratory test conducted by seven laboratories using seven different commercially available polyol samples covering an unsaturation range of 0,000 7 meq/g to 0,124 meq/g. Precision values were calculated from experimental data following ASTM Practice E 180. Data can be obtained from ASTM Headquarters (Committee D-20) or from the PURMAC Committee of the American Chemical Council.

Table 2 — Description of interlaboratory samples

Sample A	Polytetramethylene oxide diol, 1 000 g/mol
Sample B	Polypropylene oxide triol with 14 % ethylene oxide, 5 100 g/mol
Sample C	Polypropylene oxide diol, 2 000 g/mol
Sample D	Polypropylene oxide triol with 10 % ethylene oxide, 2 850 g/mol
Sample E	Amine-initiated, 4-functional, polypropylene oxide with 40 % ethylene oxide, 570 g/mol
Sample F	Polypropylene oxide triol with 19 % ethylene oxide, 4 700 g/mol
Sample G	Polypropylene oxide diol, 4 000 g/mol

12.2 Bias

Bias is the difference between the expectation of the test results and an accepted reference value. The bias of this test has not been determined.