INTERNATIONAL STANDARD

ISO
14898

First edition
1999-10-15

Plastics — Aromatic isocyanates for use in the production of polyurethane — Determination of acidity

Plastiques — Isocyanates aromatiques utilisés pour la production de polyuréthanne — Détermination de l'acidité

Reference number
ISO 14898:1999(E)

Contents

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet iso@iso.ch

Printed in Switzerland

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.

International Standard ISO 14898 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

Introduction

No International Standard dealing with the analysis of polymeric isocyanates and their prepolymers for acidity has been published. Method A of this International Standard is used to determine moderate to high (> 100 µg/g) levels of acidity in aromatic isocyanates. The method is based on ASTM D 4876 and related work carried out by the Polyurethane Raw Materials Analysis Committee of The Society of the Plastics Industry in the USA. Method B of this International Standard was adapted from ASTM D 5629, and is applicable to the determination of acidity in low-acidity (< 100 µg/g) aromatic isocyanates and prepolymers.

Plastics — Aromatic isocyanates for use in the production of polyurethane — Determination of acidity

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 methods for the measurement of the acidity of aromatic isocyanates and prepolymers used as polyurethane raw materials. Method A is a straightforward titration without a blank and is primarily applicable to products derived from crude or modified methylene-bis-(4-phenylisocyanate), polymethylene polyphenylisocyanates and toluene diisocyanate having moderate to high (> 100 µg/g) levels of acidity. Method B is applicable to refined, crude or modified isocyanates derived from methylene-bis-(4-phenylisocyanate), polymethylene polyphenylisocyanate and toluene diisocyanate having low (< 100 µg/g) levels of acidity, and a blank is employed. These methods can also be used for isomeric mixtures of toluene diisocyanate, methylene-bis-(4-phenylisocyanate) and polymethylene polyphenylisocyanate. Other aromatic isocyanates may be analysed by this method if precautions are taken to verify suitability.

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

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

ISO 4787:1984, *Laboratory glassware — Volumetric glassware — Methods for use and testing of capacity.*

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

3.2
acidity
the acid strength of a sample, expressed as micrograms of HCl per gram of sample

4 Principle

4.1 Method A: A test portion of isocyanate is reacted with an excess of methanol and a cosolvent to form the corresponding urethane. Acid from the test portion is released into the solvent system during urethane formation. The acid is then titrated potentiometrically with methanolic KOH, and the acidity value is calculated from the titre.

4.2 Method B: A test portion of isocyanate is reacted with an excess of acidified *n*-propanol and a cosolvent. Additional acid due to the test portion is released into the solvent system during urethane formation. The acid is then titrated potentiometrically with methanolic KOH. The same procedure is performed with a blank solution, and the difference in titre is used to calculate the acidity present in the isocyanate sample.

5 Application

These test methods can be used for research or for quality control purposes to characterize isocyanates and prepolymers used in the preparation of polyurethane products.

6 Interference

These test methods were developed to determine those acidic components which are readily released under the comparatively gentle reaction conditions used in the initial reaction with an alcohol. This acidity is due primarily to hydrogen chloride. Excessive reaction time or heating may cause other chlorine-containing compounds to react and release HCl, giving falsely high results. Although unlikely to be present in an isocyanate, basic materials would interfere with the titration. Acidic or basic materials inadvertently introduced by contaminated reagents or equipment may interfere with the titration step.

7 Test conditions

Since isocyanates react with moisture, keep the laboratory humidity low, preferably below 50 % relative humidity.

8 Reagents

Use reagent-grade chemicals in all analyses. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of ISO 6353, parts 1, 2 and 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 water as defined by ISO 3696:1987.

8.1 Potassium hydroxide, 0,02 mol/l methanolic solution (1,12 g KOH/1 000 ml methanol), for method A, standardized with potassium acid phthalate (KHP).

8.2 Potassium hydroxide, 0,01 mol/l methanolic solution (0,56 g KOH/1 000 ml methanol), for method B, standardized with KHP.

8.3 Toluene, for method A and method B, dried over type 4A molecular sieve.

8.4 1,2,4-Trichlorobenzene (TCB), for method A and method B, dried over type 4A molecular sieve.

8.5 Methanol, anhydrous.

8.6 Tetrahydrofuran, for method A and method B.

8.7 *n*-Propanol, acidified, for method B.

Acidify with 120 µl of concentrated hydrochloric acid per 4 litre bottle.

8.8 Ethanol, anhydrous.

May be substituted for methanol (8.5) or *n*-propanol (8.7). Denatured ethanol may be used if it has been demonstrated that the particular formulation used does not affect the results of the test.

9 Apparatus

9.1 Potentiometric titrator, accurate to 0,1 mV or better, equipped with a pair of suitable electrodes or a combination glass-calomel electrode (see 9.2 and 9.3) and a magnetic stirrer.

9.2 Reference electrode: calomel electrode, with a double-junction sleeve-type diaphragm, having LiCl/ethanol solution in both chambers.

9.3 Measurement electrode: glass pH electrode.

9.4 Analytical balance, accurate to 1 mg or better.

9.5 Magnetic stirrer.

9.6 Adjustable dispenser, or **one-mark pipettes** of capacity 20 ml and 100 ml conforming to ISO 648.

9.7 Beakers, of capacity 250 ml.

9.8 Graduated cylinders, of capacity 50 ml and 100 ml, conforming to ISO 4788.

9.9 Weighing pipette, or other suitable device for weighing a liquid sample by difference to the nearest 1 mg.

10 Method A: aromatic isocyanates with moderate to high acidity ($>$ 100 µg/g)

10.1 Procedure

10.1.1 Weigh, to the nearest 1 mg, approximately 10 g of sample into each of two clean, dry 250 ml beakers (9.7).

10.1.2 Add 50 ml of toluene (8.3) to each beaker and stir with a magnetic stirrer to dissolve the sample.

NOTE If the sample does not dissolve readily, TCB (8.4) may be substituted for toluene. If this method is used for prepolymers, tetrahydrofuran (8.6) may be substituted for toluene to aid dissolution. With refined-TDI (toluene diisocyanate) samples, toluene is not required and may be omitted, and the test portion added directly to the anhydrous methanol in step 10.1.3.

10.1.3 Add 100 ml of anhydrous methanol (8.5) to each beaker (see 8.8 for alternative solvents).

10.1.4 Cover with a watchglass and stir for 20 min.

10.1.5 Using the titrator (9.1), titrate each test portion with 0,02 mol/l methanolic KOH (8.1) through the titration end point between apparent pH 4 and 9.

10.2 Expression of results

Calculate the acidity, as µg of HCl/g of sample, as follows:

$$\text{Acidity } (\mu\text{g/g}) = \frac{VcF}{m}$$

where

V is the volume of KOH solution needed for the test portion, in ml;

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

F is 36 455 [= 36,455 (molar mass of HCl)] × [1 000 (factor to change mg/g to µg/g)];

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

10.3 Precision and bias

10.3.1 General

The following criteria shall be used to judge the acceptability of results:

NOTE The precision data are based on studies conducted by the Polyurethane Raw Materials Committee (PURMAC) of the Society of The Plastics Industry using the protocol of ASTM E 691 (see bibliography). Copies of the research report may be obtained from SPI headquarters (1801 K Street NW, Washington, DC 20006, USA).

10.3.2 Repeatability (single analyst)

Duplicate results obtained by the same analyst on the same day shall be considered suspect if they differ by more than 5 µg of HCl/g of sample (95 % confidence level).

10.3.3 Reproducibility (interlaboratory)

Results, each the mean of duplicates, obtained with the same material in separate laboratories, shall be considered different if they differ by more than 21 µg of HCl/g of sample (95 % confidence level).

10.3.4 Bias

Bias is the difference between the expectation of the test results and an accepted reference value. There are no recognized standards by which to estimate the bias of this test method.

10.4 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary for complete identification of the sample analysed (such as manufacturer, product type, lot or notebook numbers, date of manufacture, as required);

c) the method used (i.e. A or B);

d) the results obtained, reported as the average of duplicates and expressed as µg of HCl/g of sample, to the nearest 1 µg;

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

f) the date of the analysis.

11 Method B: aromatic isocyanates with low acidity (< 100 µg/g)

11.1 Procedure

11.1.1 Calibrate the electrodes using aqueous pH 4 and pH 7 buffers.

11.1.2 Make blank determinations in conjunction with each series of test portions. Prepare blanks in the same manner as a test portion, but omitting the test portion. All test portions and blanks shall be prepared in duplicate.

11.1.3 Weigh, to the nearest 1 mg, approximately 20 g of sample into a 250 ml beaker (9.7).

11.1.4 Add 50 ml of toluene (8.3).

NOTE If the test portion does not dissolve readily, TCB (8.4) or tetrahydrofuran (8.6) may be substituted for toluene. With refined-TDI samples, toluene is not required and may be omitted, and the TDI added directly to the alcohol in step 11.1.5.

11.1.5 With a pipette (9.6), introduce 100 ml of acidified *n*-propanol (8.7) into the solution (see 8.8 for alternative solvents).

With refined TDI, when toluene is omitted, add an additional 20 ml of acidified *n*-propanol (8.7).

11.1.6 Add a stirrer bar, cover with a watchglass, and stir for 20 min.

Test solutions shall be at room temperature before titration.

11.1.7 Titrate the mixture with 0,01 mol/l methanolic KOH (8.2) through the titration end point as determined potentiometrically. Continue the titration through an apparent pH of 8.

If the results indicate a drift in the readings or a slow electrode response, clean the pH electrode by soaking in a 2:1 sulfuric:nitric acid mixture for 10 min, followed by soaking in water for 20 min and then rinsing with acetone.

11.1.8 Record the titrant volume for the potentiometric end point. If more than one potentiometric end point is found, record the one at the highest apparent pH below 7. The point of inflection is typically at an apparent pH between 4 and 5.

11.2 Expression of results

Calculate the acidity, as µg of HCl/g of sample, as follows:

$$\text{Acidity } (\mu\text{g/g}) = \frac{(V_\text{S} - V_\text{B})cF}{m}$$

where

V_S is the volume of KOH solution needed for the test portion, in ml;

V_B is the volume of KOH solution needed for the blank, in ml;

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

F is 36 455 [= 36,455 (molar mass of HCl)] × [1 000 (factor to change mg/g to µg/g)];

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

11.3 Precision and bias

NOTE The following precision data are based on a round robin conducted in 1993 in accordance with ASTM E 691. Nine laboratories were involved in the study.

Table 1 — Round-robin acidity data

Values in µg/g,expressed as HCl

Product	Average	Repeatability limit, r	Reproducibility limit, R
Refined TDI (sample A)	39,47	4,03	11,98
Refined TDI (sample B)	73,81	8,79	21,84
TDI polyether prepolymer	23,58	2,77	11,20
MDI polyether prepolymer	3,37	2,30	6,36
Modified MDI homopolymer	1,12	4,28	6,75
Refined MDI	1,07	2,07	7,08

11.3.1 Repeatability (single analyst)

Duplicate results obtained by the same analyst with the same equipment on the same day shall be considered suspect if they differ by more than the r value for that type of material.

11.3.2 Reproducibility (interlaboratory)

Results, each the mean of duplicates, obtained with identical test material in separate laboratories, shall be considered different if they differ by more than the R value for that type of material.

11.3.3 Bias

Bias is the difference between the expectation of the test results and an accepted reference value. There are no recognized standards by which to estimate the bias of this test method.

11.4 Test report

The test report shall be drafted as in 10.4.

Bibliography

[1] ASTM D 4876:1993, *Standard Test Method for Polyurethane Raw Materials — Determination of Acidity of Crude or Modified Isocyanates.*

[2] ASTM D 5629:1994, *Standard Test Method for Polyurethane Raw Materials — Determination of Acidity in Low-Acidity Aromatic Isocyanates and Polyurethane Prepolymers.*

[3] ASTM E 691:1992, *Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method.*

ICS 83.080.10

Price based on 7 pages