INTERNATIONAL STANDARD

ISO 14896

Third edition
2009-02-15

Plastics — Polyurethane raw materials — Determination of isocyanate content

Plastiques — Matières premières des polyuréthannes — Détermination de la teneur en isocyanate

Reference number
ISO 14896:2009(E)

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Published in Switzerland

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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 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 14896 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

This third edition cancels and replaces the second edition (ISO 14896:2006), of which it constitutes a minor revision, the main purpose of which was to combine the standard with its amendment (ISO 14896:2006/Amd.1:2007), thereby adding a new subclause (12.1.8).

Plastics — Polyurethane raw materials — Determination of isocyanate content

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

This International Standard specifies two methods for the measurement of the isocyanate content of aromatic isocyanates used as polyurethane raw materials. Method A is primarily applicable to refined toluene diisocyanate (TDI), methylene-bis-(4-phenylisocyanate) (MDI) and their prepolymers. Method B is applicable to refined, crude or modified isocyanates derived from toluene diisocyanate, methylene-bis-(4-phenylisocyanate) and polymethylene polyphenylisocyanate. It can also be used for isomer 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. It is not applicable to blocked isocyanates.

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 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — Single-volume pipettes*

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 4788, *Laboratory glassware — Graduated measuring cylinders*

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*

ISO 14898:1999, *Plastics — Aromatic isocyanates for use in the production of polyurethane — Determination of acidity*

3 Terms and definitions

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

3.1
polyurethane
polymer prepared by the reaction of an organic di- or polyisocyanate with compounds containing two or more hydroxyl groups

NOTE Polyurethanes may be thermosetting, thermoplastic, rigid or soft and flexible, cellular or non-cellular.

3.2
assay
percent by mass of a specific isocyanate present in a sample

3.3
isocyanate content
NCO content
percent by mass of the NCO groups present in a sample

3.4
amine equivalent
mass of sample that will combine with 1 gram-equivalent of dibutylamine

4 Principle

4.1 Method A

The isocyanate sample is reacted with an excess of dibutylamine in toluene to form the corresponding substituted urea. After cooling to room temperature, acetone is added as a co-solvent, then the reaction mixture is back-titrated with standardized aqueous HCl using potentiometric or colorimetric end point determination.

4.2 Method B

The isocyanate sample is reacted with an excess of dibutylamine in a toluene/trichlorobenzene solvent to form the corresponding substituted urea. After cooling to room temperature, the reaction mixture is diluted with methanol and back-titrated potentiometrically or colorimetrically with methanolic hydrochloric acid. See also 12.1.8.

5 Application

These test methods can be used for research or for quality control purposes to characterize isocyanates used in polyurethane products.

6 Interferences

Phosgene, the carbamyl chloride of the isocyanate, hydrogen chloride and any other acidic or basic compounds will interfere. In refined isocyanates, these impurities are usually present in such small amounts that they do not affect the determination; however, some crude or modified isocyanates may contain acidities of up to approximately 0,3 %, so the value reported for the NCO content of unrefined isocyanates should preferably be designated as “corrected” or “uncorrected” for acidity.

7 Sampling

Since organic isocyanates react with atmospheric moisture, take special precautions in sampling (see warning). Usual sampling methods (for example, sampling an open drum with a thief), even when conducted rapidly, can cause contamination of the sample with insoluble ureas; therefore, blanket the sample with a dry inert gas (e.g. nitrogen, argon or dried air) at all times.

WARNING — Organic isocyanates are hazardous when absorbed through the skin, or when the vapours are breathed. Provide adequate ventilation and wear protective gloves and eyeglasses.

8 Test conditions

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

9 Reagents

Use reagent-grade chemicals in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of ISO 6353-1, ISO 63535-2 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 3 water as defined in ISO 3696.

9.1 Acetone (method A).

9.2 Toluene, dried over type 4A molecular sieve.

9.3 di-*n*-butylamine solution, 1 mol/l (method A).

Dilute 129 g of di-*n*-butylamine to 1 litre with toluene.

9.4 di-*n*-butylamine solution, 2 mol/l (method B).

Dilute 258 g of di-*n*-butylamine to 1 litre with toluene.

9.5 Aqueous hydrochloric acid, 1 mol/l (method A).

Prepare 1 mol/l aqueous hydrochloric acid and standardize frequently enough to detect changes of 0,001 mol/l.

9.6 Methanolic hydrochloric acid, 1 mol/l (method B).

Prepare 1 mol/l hydrochloric acid in methanol and standardize frequently enough to detect changes of 0,001 mol/l.

NOTE In order to have homogeneous solutions, it is recommended that methanolic HCl be used in this procedure. If desired, aqueous HCl can be used; however, turbidity will be encountered in some titrations. It is recommended that 200 ml to 250 ml of methanol be added to the reacted product to minimize the formation of two layers. Experience has shown that, if the mixtures are agitated vigorously, inhomogeneity can be tolerated without adversely affecting the results.

9.7 Bromophenol blue indicator solution, for colorimetric titration: 0,04 % aqueous solution of bromophenol blue sodium salt, reagent grade, or 0,04 % solution of bromophenol blue in acetone.

9.8 1,2,4-Trichlorobenzene (TCB), dried over type 4A molecular sieve (method B).

9.9 Methanol (method B).

10 Apparatus

10.1 Potentiometric titrator or **pH-meter**, accurate to 0,1 mV or better, equipped with a pair of electrodes or a combination glass-calomel electrode (filled with a 1 mol/l lithium chloride solution in methanol, or an equivalent solution) and a piston burette having a 20 ml capacity.

10.2 Syringes, capacity 2 ml and 5 ml, and **syringes with a large orifice** suitable for weighing viscous prepolymers by difference to the nearest 1 mg.

10.3 Magnetic stirrer.

10.4 Analytical balance, accurate to 0,1 mg.

10.5 Iodine flask, capacity 500 ml, with ground-glass neck (method A).

10.6 Conical flask, capacity 250 ml, with a wide mouth (method B).

10.7 Volumetric pipettes, capacity 25 ml (method A) and 20 ml (method B), conforming to ISO 4787.

10.8 Measuring pipette, capacity 1 ml, conforming to ISO 648.

10.9 Graduated cylinders, capacity 250 ml (method A) and 100 ml (method B), conforming to ISO 4788.

10.10 Beaker, capacity 500 ml.

10.11 Burette, capacity 50 ml, for colorimetric titration, conforming to ISO 385.

11 Method A — Toluene/dibutylamine with aqueous HCl

11.1 Procedure

11.1.1 Using a volumetric pipette (10.7), add 25 ml of 1 mol/l dibutylamine solution (9.3) to an iodine flask (10.5). Rinse the walls of the flask with 10 ml of toluene (9.2).

11.1.2 Weigh a sample of the product to be analysed to the nearest 0,1 mg using a suitable syringe (10.2). The sample used for analysis shall be completely liquid; if it contains crystallized isocyanates, heat it carefully until a homogeneous liquid phase is obtained. Add m_0 grams of the product to the dibutylamine solution in the iodine flask.

The mass (m_0) in grams of the product to be analysed shall contain (15 ± 5) milliequivalents of isocyanate or, in the case of TDI, about 1,5 g or, in the case of MDI, about 2,5 g.

In the event that the isocyanate equivalent is not known, a preliminary test should be run to determine the proper sample size to be used.

11.1.3 After complete dissolution, allow to react for 15 min at ambient temperature. The reaction will cause some warming of the solution. Let the solution stand until it reaches room temperature (an additional 5 min to 10 min).

11.1.4 Using a graduated cylinder (10.9), add 150 ml of acetone (9.1), taking care to rinse the flask walls and stopper.

11.1.5 Titrate the excess dibutylamine using one of the two following procedures:

11.1.5.1 Potentiometric titration (recommended)

Pour the contents of the iodine flask into the titration beaker (10.10), rinsing with 25 ml of acetone (9.1). Place the beaker on the magnetic stirrer (10.3) and stir the contents.

Immerse the electrodes in the reaction mixture and titrate with 1 mol/l aqueous hydrochloric acid (9.5), using the potentiometer (10.1) to determine the equivalence point.

11.1.5.2 Colorimetric titration

Place the iodine flask on the magnetic stirrer and stir the reaction mixture.

Using a graduated 1 ml pipette (10.8), add 0,8 ml of bromophenol blue solution (9.7).

Titrate using the burette containing 1 mol/l aqueous hydrochloric acid until the indicator changes from blue to yellow and remains stable for 15 s. The solution will change from a blue colour at the start of the titration to a bluish-green intermediate colour and to a yellow colour at the end point. Recognition of the end point is a matter of experience, but better defined colour changes are obtained when the acid is titrated rapidly into the solution until the first flash of yellow colour is observed. This flash of colour appears within a few tenths of a millilitre of the end point.

11.1.6 Conduct a blank determination under identical conditions, but omit the test portion.

11.2 Expression of results

11.2.1 Calculate the % NCO as follows:

$$\%\ \mathrm{NCO} = \frac{4{,}202 \times (V_1 - V_2) \times c}{m_0}$$

where

V_1 is the volume of HCl required for titration of the blank, in ml, to the nearest 0,01 ml;

V_2 is the volume of HCl required for titration of the test portion, in ml, to the nearest 0,01 ml;

c is the concentration of the HCl, in mol/l;

m_0 is the mass of the test portion, in g;

4,202 is a constant combining the equivalent mass of NCO (42,02 mg/mequiv), conversion of g to mg, and conversion to 100 %.

11.2.2 The amine equivalent may be calculated as follows:

$$\text{Amine equivalent} = \frac{1000 \times m_0}{(V_1 - V_2) \times c}$$

11.2.3 For isocyanates based on a single isomer or isomer mixture (for example, “pure” TDI or MDI), the assay may be calculated, in %, as follows:

$$\text{Assay} = \frac{(V_1 - V_2) \times c \times E}{1000 \times m_0} \times 100$$

where

V_1 is the volume of HCl required for titration of the blank, in ml, to the nearest 0,01 ml;

V_2 is the volume of HCl required for titration of the test portion, in ml, to the nearest 0,01 ml;

c is the concentration of the HCl, in mol/l;

m_0 is the mass of the test portion, in g;

E is the equivalent mass of the isocyanate, in mg/mequiv (for pure TDI this is 87,08 mg/mequiv, for pure MDI it is 125,13 mg/mequiv);

1 000 is the factor for conversion from g to mg;

100 is the factor for conversion to percent.

11.2.4 The number of equivalents per kilogram (equiv/kg) may be calculated as follows:

$$\text{equiv/kg} = \frac{(V_1 - V_2) \times c}{m_0}$$

where V_1, V_2, c and m_0 have the same meaning as in 11.2.3.

11.2.5 In refined isocyanates, acidic impurities are usually present in such low amounts that they do not affect the determination. Therefore, an acidity correction is not normally necessary.

11.3 Precision and bias

11.3.1 Precision (for refined TDI) [1)]

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 suspect if they differ by more than 0,4 % relative (95 % confidence level) using a colorimetric end-point determination, or by more than 0,2 % relative (95 % confidence level) using a potentiometric autotitrator.

b) Reproducibility (multilaboratory)

Results, each the mean of duplicates run on identical material in separate laboratories, shall only be considered different if they differ by more than 0,8 % relative (95 % confidence level).

11.3.2 Bias

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

11.4 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, date of manufacture, as required);

c) the method of titration used, if other than using a potentiometric autotitrator;

d) the results obtained, including the units in which the results are expressed;

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

f) the date of the analysis.

1) Supporting data are available from the Polyurethane Raw Materials Analysis Committee (PURMAC) of the American Plastics Council.

12 Method B — Toluene/TCB/DBA with methanolic HCl

12.1 Procedure

12.1.1 Introduce 25 ml of TCB (9.8) into a 250 ml wide-mouth conical flask (10.6) that has been rinsed successively with water, alcohol and high-purity acetone, dried at 100 °C, and allowed to cool. Pipette 20 ml of dibutylamine solution (9.4) into the flask. Swirl to mix the contents.

12.1.2 Transfer the approximate amount of sample required, weighed to the nearest 0,001 g, to the flask. The approximate amount of sample required is calculated, in g, from the following equation:

$$\text{Amount of sample} = \frac{84}{\text{Expected \% NCO}}$$

For TDI this is about 1,8 g, for MDI it is about 2,5 g.

12.1.3 Cover the flask and swirl the contents until the solution is homogeneous. The reaction mixture will warm to approximately 40 °C.

12.1.4 Let the reaction mixture stand until it reaches room temperature (20 min to 25 min), then add 100 ml of methanol (9.9).

12.1.5 Titrate potentiometrically with 1 mol/l methanolic HCl (9.6) to the break that occurs near an apparent pH of 4,0.

12.1.6 Prepare a blank exactly as described above, but without adding the test portion. Titrate potentiometrically with 1 mol/l methanolic HCl to the break that occurs near an apparent pH of 4,0.

12.1.7 If a potentiometric titrator is not available, the titration can be performed using a conventional 50 ml burette (10.11) and bromophenol blue indicator, as follows:

Using a graduated 1,0 ml pipette (10.8), add 0,8 ml of bromophenol blue indicator solution (9.7) to each solution to be titrated.

Titrate the blank and test solutions to the first appearance of a stable yellow colour that persists for 15 s. The solution will change from a blue colour at the start of the titration to a bluish-green intermediate colour and to a yellow colour at the end point. Recognition of the end point is a matter of experience, but better defined colour changes are obtained when the acid is titrated rapidly into the solution until the first flash of yellow colour is observed. This flash of colour appears within a few tenths of a millilitre of the end point.

12.1.8 The following variations in the procedure are acceptable:

In general, any other dry aprotic solvent may be used, instead of TCB, as the solvent for the amine which reacts with the isocyanate group to form the corresponding substituted urea. For instance, toluene, xylene, monochlorobenzene, dichlorobenzene, dimethylformamide and *N*-methylpyrrolidone have all been used with success as solvents. If the sample already contains one or more of these solvents to a large extent, addition of solvent can be omitted.

In addition, cyclohexylamine has been used with success, instead of dibutylamine, as the amine.

Instead of methanolic hydrochloric acid, hydrochloric acid in solvents like butanol, 2-propanol, water and acetone has been used with success.

If the expected NCO content of the sample is small and only a limited quantity of sample is available, making it impossible to increase the size of the sample, the concentration of the HCl and dibutylamine solution may be adjusted accordingly. Such low NCO contents may be found in solutions of isocyanates or prereacted isocyanates. Thus 0,2 mol/l or even 0,01 mol/l HCl may be used if lower NCO contents are to be measured.