INTERNATIONAL STANDARD

ISO 9369

First edition
1997-04-15

Plastics — Basic materials for polyurethanes — Pure isocyanates — Analysis of isocyanate groups

Plastiques — Matières de base pour polyuréthannes — Isocyanates purs — Analyse des groupes isocyanates

Reference number
ISO 9369:1997(E)

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.

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 9369 was prepared by Technical Committee ISO/TC 61, *Plastics,* Subcommittee SC 12, *Thermosetting materials.*

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet central@iso.ch
X.400 c=ch; a=400net; p=iso; o=isocs; s=central

Printed in Switzerland

Introduction

The following types of isocyanate are commonly used in the industry as basic materials for polyurethanes:

— isocyanates purified by rectification and their prepolymers (in particular pure TDI — a mixture of the 2,4- and 2,6- isomers of tolylene diisocyanate) to which this International Standard is applicable;

— non-rectified isocyanates such as unrefined MDI [methylene di-(4-phenylisocyanate], or modified isocyanates such as isocyanates containing adducts like carbodiimide adducts (e.g. uretonimine) and phenol adducts for which the method specified will have to be modified. These modifications will depend on the particular products concerned and require agreement between purchaser and manufacturer:

- for some isocyanates, such as modified isocyanates, the temperature of reaction with di-*n*-butylamine will have to be chosen to ensure that complete conversion of the isocyanate groups occurs (the "hot" method);
- for unrefined samples, which generally contain acidic materials, the results must be corrected for any acidic materials present in the unrefined samples since the method involves an acid-base titration.

This page intentionally left blank

Plastics — Basic materials for polyurethanes — Pure isocyanates — Analysis of isocyanate groups

WARNING — Isocyanates shall be handled with care. Inhalation shall be avoided. Persons handling these chemicals shall wear safety glasses and gloves, and the workplace shall be well ventilated.

1 Scope

This International Standard specifies a method for the analysis of the isocyanate groups in pure isocyanates (in particular pure TDI and pure MDI) and their prepolymers.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

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

3 Definitions

For the purposes of this International Standard, the following definitions apply:

3.1 isocyanate concentration: The amount of isocyanate in a product, expressed in one of the following three ways:

3.1.1 isocyanate equivalent: The number of isocyanate (NCO) groups per kilogram of product (for calculation, see 8.1).

3.1.2 isocyanate percentage: The percentage by mass of a specific pure isocyanate compound in a product (for calculation, see 8.2).

3.1.3 isocyanate-group percentage: The percentage by mass of the isocyanate (NCO) groups in a product (for calculation, see 8.3).

4 Principle

The isocyanate groups in a test portion of product are reacted with excess di-*n*-butylamine at room temperature to form the corresponding substituted urea:

$$R-N=C=O + (C_4H_9)_2NH \longrightarrow R-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}-N(C_4H_9)_2$$

The excess amine is then neutralized by titration with hydrochloric acid:

$$(C_4H_9)_2NH + HCl \longrightarrow (C_4H_9)_2-NH_2^+ \ Cl^-$$

and the isocyanate concentration calculated.

5 Reagents

5.1 Toluene, reagent grade or equivalent, kept over a 0,4 nm molecular sieve.

Prior to use, activate the molecular sieve by heating at 400 °C for 4 h. The water content of the toluene shall be less than 1 mg/100 ml as determined by ISO 760.

5.2 Di-*n*-butylamine, approximately 1 mol/l solution in toluene.

Make 129 g of di-*n*-butylamine up to 1 000 ml with toluene (5.1).

5.3 Acetone (or methanol, ethanol or isopropanol), reagent grade or equivalent.

5.4 Hydrochloric acid, approximately 1 mol/l standard volumetric solution standardized to the nearest 0,001 mol/l.

5.5 Bromophenol blue, 1 g/l solution in acetone (or methanol, ethanol or isopropanol) (5.3).

6 Apparatus

6.1 Iodine flask, capacity 500 ml, with a ground-glass stopper.

6.2 One-mark pipette, capacity 25 ml.

6.3 Graduated pipette, capacity 1 ml, or similar dropper suitable for adding indicator to a titration solution.

6.4 Piston-type burette, capacity 20 ml, capable of delivering volumes down to 0,01 ml.

6.5 Graduated cylinder, capacity 250 ml.

6.6 Balance, accurate to 0,1 mg.

6.7 Magnetic stirrer.

6.8 Automatic potentiometric titrator, accurate to 0,1 mV, equipped with a pair of electrodes or a composite glass-calomel electrode (filled with a 1 mol/l lithium chloride solution in methanol or an equivalent solution).

6.9 500 ml beaker.

6.10 Syringes, capacity 2 ml and 5 ml, for non-viscous products or **syringes with a large delivery aperture**, or any other sampling system suitable for viscous prepolymers.

7 Procedure

IMPORTANT — The glassware used in 7.1 and 7.2 shall be dry (for example dried at 110 °C for 1 h).

7.1 Using the one-mark pipette (6.2), introduce 25 ml of 1 mol/l di-*n*-butylamine (5.2) into the iodine flask (6.1). Rinse the walls of the flask with 10 ml of toluene (5.1).

Place a magnetic stirrer bar in the flask, stopper the flask and stir the reaction mixture by means of the magnetic stirrer (6.7) until complete homogenization has occurred.

7.2 Weigh, to the nearest 0,1 mg, a syringe (6.10) filled with the product being analysed. Add, from the syringe, to the di-*n*-butylamine solution in the iodine flask, a quantity of the product containing (15 ± 5) milli-equivalents of isocyanate

— in the case of TDI, this will be about 1,5 g;

— in the case of MDI, this will be about 2,5 g.

Reweigh the syringe to determine the exact amount added.

If the isocyanate equivalent is not known, determine it by carrying out a preliminary test or series of tests.

The sample used for analysis shall be completely liquid. If it contains crystallized isocyanates, heat it carefully until a homogeneous liquid is obtained.

7.3 Dissolve the product completely in the di-*n*-butylamine and leave to react for 15 min at room temperature.

7.4 Using the graduated cylinder (6.5), add 150 ml of acetone (or methanol, ethanol or isopropanol) (5.3), taking care to wash down the iodine flask walls and stopper with the acetone.

7.5 Titrate the excess di-*n*-butylamine using one of the following two procedures:

7.5.1 Colour-indicator

Put the iodine flask on the magnetic stirrer (6.7) and stir the reaction mixture.

Introduce a few (e.g. five) drops of bromophenol blue solution (5.5), using the 1 ml pipette (6.3) or a similar dropper.

Titrate using the burette (6.4) containing 1 mol/l hydrochloric acid (5.4) until the indicator turns from blue to yellow, remaining stable for 15 s.

7.5.2 Potentiometric titration

NOTE 1 Potentiometric titration is the best way to determine the isocyanate content of coloured samples.

Pour the contents of the iodine flask into a 500 ml beaker (6.9), rinsing with 25 ml of acetone (or methanol, ethanol or isopropanol) (5.3). Put the beaker on the magnetic stirrer (6.7) and stir the contents.

Immerse the electrodes in the reaction mixture.

Titrate with 1 mol/l hydrochloric acid (5.4), using the potentiometric titrator (6.8) to determine the equivalence point.

NOTE 2 The titration may also be performed using a 25 ml flow burette graduated at 0,05 ml intervals, instead of the 20 ml piston burette (6.4); in this case, however, the determination is less precise.

7.6 Conduct a blank test under conditions identical to those of the real test, but omitting the product being analysed.

8 Expression of results

8.1 Isocyanate equivalent

The isocyanate equivalent IEq, corresponding to the number of isocyanate groups per kilogram, is calculated using the formula

$$\mathrm{IEq} = \frac{(V_0 - V_1) \times c}{m}$$

where

V_0 is the volume, in millilitres, of hydrochloric acid used for the blank (7.6), to the nearest 0,01 ml (see note 3);

V_1 is the volume, in millilitres, of hydrochloric acid used for the determination (7.5), to the nearest 0,01 ml (see note 3);

c is the concentration, in moles per litre, of the hydrochloric acid used;

m is the mass, in grams, of the test portion taken.

NOTE 3 If a 25 ml flow burette was used instead of a piston burette, V_0 and V_1 will be given to the nearest 0,05 ml.

Express the result to two places of decimals.

8.2 Isocyanate percentage

In the case of a pure isocyanate, it is also possible to calculate the isocyanate percentage I% using the following formula:

$$\mathrm{I\%} = \frac{(V_0 - V_1) \times c \times E}{10m}$$

where

E is the mass, in grams, of pure isocyanate corresponding to one isocyanate group;

the other symbols are as defined in 8.1.

NOTE 4 In the case of pure TDI, E = 87,08, and in the case of pure MDI, E = 125,13.

Express the result to one place of decimals.

8.3 Isocyanate-group percentage

It is also possible to calculate the isocyanate-group percentage NCO% using the following formula:

$$\mathrm{NCO\%} = \frac{(V_0 - V_1) \times c \times 4{,}202}{m}$$

where

the symbols are as defined in 8.1;

4,202 = (42,02 × 100)/1 000,

42,02 being the molecular mass of the NCO group,

100 converting the result to a percentage,

1 000 converting grams to milligrams.

Express the result to one place of decimals.

9 Precision

Interlaboratory tests have shown that, for pure isocyanates, the method described above, using a piston burette and acetone as solvent, has the following precision:

— repeatability $r = \pm 0{,}4$ % (relative);

— reproducibility $R = \pm 0{,}8$ % (relative).

10 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary for identification of the product analysed;

c) the method of titration used;

d) whether a flow burette was used;

e) the results obtained, expressed as specified in clause 8;

f) the date of the analysis;

g) details of any operation not specified in this International Standard, as well as any incident which may have affected the results.