

JAPANESE
INDUSTRIAL
STANDARD

Translated and Published by
Japanese Standards Association

JIS K 1556 : 2006

(JURA/JPIF/JSA)

**Polyurethane raw materials—
Testing methods for toluene
diisocyanate**

ICS 71.080.10

Reference number : JIS K 1556 : 2006 (E)

PROTECTED BY COPYRIGHT

Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of Economy, Trade and Industry through deliberations at the Japanese Industrial Standards Committee as the result of proposal for revision of Japanese Industrial Standard submitted by Japan Urethane Raw Materials Association (JURA)/The Japan Plastic Industry Federation (JPIF)/Japanese Standards Association (JSA) with the draft being attached, based on the provision of Article 12 Clause 1 of the Industrial Standardization Law applicable to the case of revision by the provision of Article 14.

Consequently **JIS K 1556**:1968 is replaced with this Standard.

Attention is drawn to the possibility that some parts of this Standard may conflict with a patent right, application for a patent after opening to the public, utility model right or application for registration of utility model after opening to the public which have technical properties. The relevant Minister and the Japanese Industrial Standards Committee are not responsible for identifying the patent right, application for a patent after opening to the public, utility model right or application for registration of utility model after opening to the public which have the said technical properties.

Date of Establishment: 1968-08-01

Date of Revision: 2006-12-20

Date of Public Notice in Official Gazette: 2006-12-20

Investigated by: Japanese Industrial Standards Committee
Standards Board
Technical Committee on Chemical Products

JIS K 1556:2006, First English edition published in 2007-05

Translated and published by: Japanese Standards Association
4-1-24, Akasaka, Minato-ku, Tokyo, 107-8440 JAPAN

In the event of any doubts arising as to the contents,
the original JIS is to be the final authority.

© JSA 2007

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from the publisher.

Printed in Japan

PROTECTED BY COPYRIGHT

Contents

	Page
Introduction	1
1 Scope	1
2 Normative references	1
3 Definitions	2
4 Sampling method	2
5 Test terms	3
6 Testing method	3
6.1 Hazen units	3
6.2 Density	3
6.3 Solidifying point	3
6.4 Isomer rate	5
6.5 Total amount of chlorine	10
Annex 1 (informative) Testing method of isocyanate-group content	14
Annex 2 (informative) Testing method of acidity of aromatic isocyanates	22
Annex 3 (informative) Testing method of hydrolysable chlorine	28
Bibliography	31

Polyurethane raw materials— Testing methods for toluene diisocyanate

Introduction This Japanese Industrial Standard was established in 1968 and becomes what to this day. The revision of this time is to respond the addition or alteration of test terms, improvement of testing method or the like.

In addition, testing methods of isocyanate-group content, acidity and hydrolysable chlorine are shown in Annex 1, Annex 2 and Annex 3 respectively for reference. The determination of isocyanate content is going to be established as the Japanese Industrial Standard based on **ISO 14896:2000** *Plastics—Polyurethane raw materials—Determination of isocyanate content*, the determination of acidity based on **ISO 14898:1999** *Plastics—Aromatic isocyanates for use in the production of polyurethane—Determination of acidity*, and the determination of hydrolysable chlorine based on **ISO 15028:2004** *Plastics—Aromatic isocyanates for use in the production of polyurethanes—Determination of hydrolysable chlorine*, respectively.

WARNING Persons using this 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 Standard specifies the testing methods for toluene diisocyanate (hereafter referred to as “TDI”) used in the production of polyurethane.

2 Normative references The following standards contain provisions which, through reference in this text, constitute provisions of this Standard. If the indication of the year of publication is given to these referred standards, only the edition of the indicated year constitutes the provision of this Standard but the revision and amendment made thereafter do not apply. The normative references without the indication of the year of coming into effect apply only to the most recent editions (including amendments).

- JIS B 7410 *Liquid-in-glass thermometers for testing of petroleum product*
- JIS B 7411 *Solid-stem general purpose liquid-in-glass thermometers*
- JIS K 0061 *Test methods for density and relative density of chemical products*
- JIS K 0071-1 *Testing methods for colour of chemical products—Part 1: Estimation of colour in Hazen units (platinum-cobalt scale)*
- JIS K 0113 *General rules for methods of potentiometric, amperometric, coulometric, and Karl Fischer titrations*
- JIS K 1101 *Oxygen*
- JIS K 8001 *General rule for test methods of reagents*
- JIS K 8034 *Acetone*
- JIS K 8464 *Cyclohexane*
- JIS K 8541 *Nitric acid*

JIS K 8891 *Methanol*

JIS R 3505 *Volumetric glassware*

JIS Z 8401 *Guide to the rounding of numbers*

JIS Z 8802 *Methods for determination of pH of aqueous solutions*

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

3 Definitions For the purposes of this Standard, the following definitions apply.

- a) **isomer rate** rate of two isomers respectively expressed by percentage so that the sum of the mass percentage (%) or mol percentage (%) of 2,4-TDI and 2,6-TDI as the isomer of TDI is 100 %
- b) **amount of hydrolysable chlorine** amount of chloride expressed in mass percentage (%) of chlorine which is the organic and inorganic chloride possible to be contained in sample as impurities produced during manufacturing of TDI and generates hydrogen chloride by reacting with methanol under test condition
- c) **total amount of chlorine** amount of chloride expressed in mass percentage (%) of chlorine in sample which is produced by making sample combusted in oxygen
- d) **polyurethane** polymer obtained by reacting organic diisocyanate or organic polyisocyanate with the compound having bifunctional or more hydroxyl groups
- e) **isocyanate-group content** mass percentage (%) of isocyanate group (hereafter referred to as “NCO-group”) existing in sample
- f) **amine equivalent** mass (g) of sample combined with one gram equivalent of di-*n*-butylamine
- g) **acidity** strength of acid of sample indicated as the amount of HCl in µg/g or %

4 Sampling method⁽¹⁾ The sample shall be taken from a production lot so as to be representative of the quality. The sampling shall cautiously be made in winter since TDI is liable to freeze or deposit crystals at low temperature. If the deposition of crystals is observed, the content to be sampled shall be warmed at a temperature 40 °C or lower until it is completely dissolved.

Note (1) When the sampling is carried out, a protecting devices (gloves, goggles, gas-mask, etc.) shall be worn under adequate ventilation.

Sampling shall be made in nitrogen atmosphere protecting from moisture.

The sample shall be stored tightly in a suitable container sealed with nitrogen or dry air at a cold dark place.

If the sample comes in contact with the skin, it shall be washed promptly with soap water.

If the sample is disposed after use, it shall be stored in an open vessel filled with water for two days until it has been decomposed completely.

The used apparatus shall be immersed overnight in methanol, washed and dried for the reuse.

5 Test terms

- a) **Hazen units**
- b) **Density**
- c) **Solidifying point**
- d) **Isomer rate**
- e) **Total amount of chlorine**

6 Testing method

6.1 Hazen units The hazen units shall be measured in accordance with **JIS K 0071-1**. The hazen units colorimetric solutions shall be in accordance with table 1.

Table 1 Hazen units colorimetric solutions

Standard colorimetric solution number	Dilution ratio	
	Standard colorimetric stock solution ml	Water ml
5	1.0	99.0
10	2.0	98.0
15	3.0	97.0
20	4.0	96.0
25	5.0	95.0
30	6.0	94.0
40	8.0	92.0
50	10.0	90.0

6.2 Density The density shall be measured in accordance with **JIS K 0061**.

6.3 Solidifying point

6.3.1 Outline The sample is slowly cooled under stirring at a specified speed, and the solidifying point is obtained by preparing the solidifying curve. When solidification begins, the temperature rise is confirmed; however after this, the temperature of which the indication of thermometer for measurement becomes constant shall be read and taken as the solidifying point.

6.3.2 Apparatus and instruments (see figure 1)

- a) **Sample container** 25 mm $\pm$ 1 mm in inside diameter, 280 mm $\pm$ 6 mm in length and made of glass.
- b) **Air jacket** 50 mm $\pm$ 1 mm in outside diameter, 175 mm $\pm$ 4 mm in length and made of glass.
- c) **Dewar's bottle** 85 mm $\pm$ 2 mm in outside diameter and 180 mm $\pm$ 4 mm in length.

- d) **Holding box** 138 mm $\pm$ 3 mm in inside diameter and 205 mm $\pm$ 5 mm in height.
- e) **Thermometer for measurement** Type SOP57 thermometer for solidifying point specified in **JIS B 7410**.
- f) **Coolant thermometer** Thermometer with immersion line specified in **JIS B 7411** with proper temperature range.
- g) **Stirring wire** About 1 mm diameter with a loop end about 18 mm outside diameter.
- h) **Absorbent cotton or equivalent**

6.3.3 Procedure Pour the sample into the dried container (A) as deep as the mark. Insert the thermometer for measurement (E) and stirring wire (G) and stopper⁽²⁾. Then insert the assembly into the air jacket (B) and place in the Dewar vessel (C) which is filled with the coolant kept at a temperature about 10 °C lower than the anticipated solidifying point. When the sample is cooled to a temperature about 5 °C higher than the anticipated solidifying point, the stirring wire (G) shall be moved slowly up and down at a rate of 30 cycles per minute and the readings of the thermometer for measurement (E) shall be plotted on a section paper at the intervals of 30 s. The stirring of the sample shall be continued even after the sample begins to solidify and the temperature rises, then read the temperature down to 0.01 °C when at least five consecutive readings agree each other.

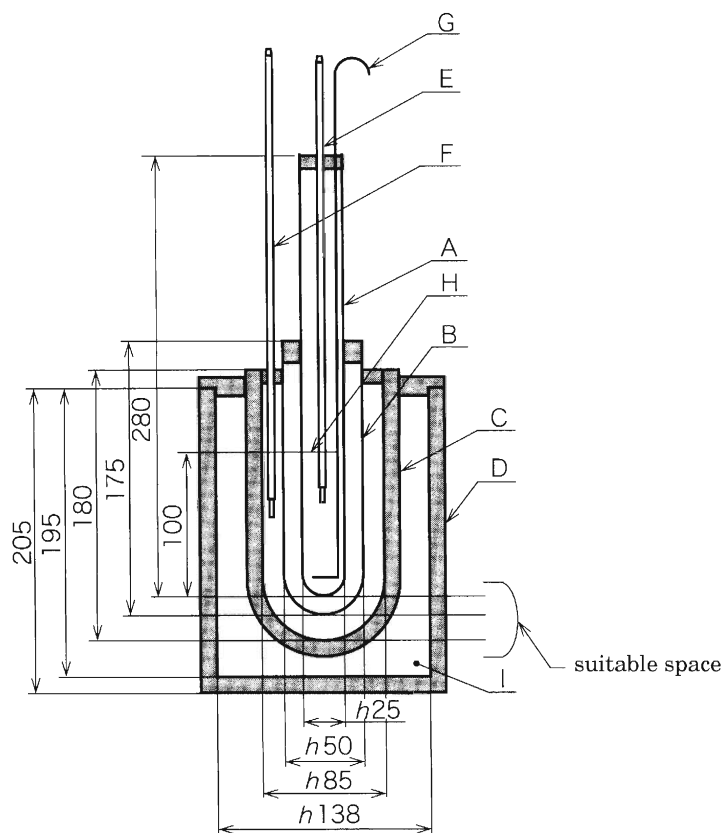
Note ⁽²⁾ The thermometer for measurement shall be inserted in the container in such position that the mercury bulb locates in the middle of the sample.

6.3.4 Precision Use the index shown below to determine the validity of the test result.

	Same operator and same apparatus	Different operator and different apparatus
Tolerance (°C)	0.2	0.6

6.3.5 Report The solidifying point shall be reported in the average of two measurement results rounded to one decimal place according to **JIS Z 8401**.

Unit: mm



- A: sample container
- B: air jacket
- C: Dewar vessel
- D: holding box
- E: thermometer for measurement
- F: coolant thermometer
- G: stirring wire
- H: mark (100 mm above the bottom)
- I: absorbent cotton or equivalent thereof

Figure 1 Example of apparatus

6.4 Isomer rate

6.4.1 Outline The measurement of isomer rate shall be divided into two methods one of which is that 2,6-isomer rate is over 5 % up to and including 95 % (method A) and the other is that the rate is 0 % or over to and including 5 % (method B). The absorbancy of the absorption maximum around 810 cm^{-1} ($12.35\text{ }\mu\text{m}$) and 780 cm^{-1} ($12.80\text{ }\mu\text{m}$) arising from out-of-plane C-H vibration of the aromatic ring by the infra-red spectrophotometer shall be measured for each test solution diluted by cyclohexane, then the respective isomer rate is calculated using the calibration curve.

6.4.2 Apparatus and instruments

- a) **Infrared spectrophotometer** Any single-beam or double-beam distributed infrared spectrophotometer or Fourier transform infrared spectrophotometer (FT-IR) having sufficient resolution to distinguish absorption maximum around 810 cm^{-1} ($12.35\text{ }\mu\text{m}$) for 2,4-isomer and 780 cm^{-1} ($12.80\text{ }\mu\text{m}$) for 2,6-isomer may be used.

NOTE : Various types of infrared spectrophotometer are available. If this test is carried out under a condition other than specified, any other method can be applied providing that the precision by that method is equivalent to precision of this method.

- b) **Cells** Sodium chloride sealed cell having the thickness of 0.2 mm (method A) and 0.1 mm (method B) are used. The thickness of the cells shall be determined by the interference fringe method.
- c) **Ground-stoppered volumetric flask**⁽³⁾ 25 ml or 50 ml.

Note ⁽³⁾ All glass apparatus should be dried completely prior to tests as the sample will easily react with the moisture remained in the apparatus.

6.4.3 Reagents

- a) **Cyclohexane** Cyclohexane specified in **JIS K 8464**. Mass percentage of water is less than 0.02 % and having the permeability more than 70 % when measured at a wavelength 830 cm^{-1} to 770 cm^{-1} ($12\text{ }\mu\text{m}$ to $13\text{ }\mu\text{m}$) by use of a 0.2 mm cell.
- b) **Standard sample** Pure 2,4-isomer and 2,6-isomer standard samples shall be prepared by phosgenating the corresponding pure amine and vacuum distilling the product⁽⁴⁾.

Note ⁽⁴⁾ Since pure 2,4-isomer and 2,6-isomer react with moisture in air they should be stored and handled under dry nitrogen.

6.4.4 Procedure

a) Method A

- 1) **Preparation of calibration curve and determination of absorptivity** Weigh pure 2,4-isomer and pure 2,6-isomer standard samples to the nearest 0.01 g accurately according to table 2 and dilute them in dried 25 ml or 50 ml volumetric flask with cyclohexane to the mark with precision. Six standard solutions of different concentrations for each isomer, twelve in total, shall be prepared.

Table 2 Standard solutions by method A

2,4-isomer standard solution concentration g/ml	Pure 2,4-isomer mass g	Final volume of standard solution prepared by solvent dilution ml
0.040	1.0	25
0.024	0.60	25
0.016	0.40	25
0.008 0	0.20	25
0.004 0	0.10	25
0.002 0	0.10	50
0.040	1.0	25
0.024	0.60	25
0.016	0.40	25
0.008 0	0.20	25
0.004 0	0.10	25
0.002 0	0.10	50

By filling the standard solution in sequence to the 0.2 mm cell, the spectrum of wavenumber range 870 cm^{-1} to 740 cm^{-1} (wavelength range $11.5\text{ }\mu\text{m}$ to $13.5\text{ }\mu\text{m}$) shall be traced upon the spectra of standard solution alone⁽⁵⁾. Then, obtain the absorbancy of the absorption maximum around 810 cm^{-1} ($12.35\text{ }\mu\text{m}$) for 2,4-isomer and 780 cm^{-1} ($12.80\text{ }\mu\text{m}$) for 2,6-isomer for these spectrum diagram, plot the relation between the concentration and the absorbancy on diagram, and prepare the calibration curve by the least-square method. The absorptivity shall be obtained by the following formula using this calibration curve.

$$\xi_a = \frac{A}{c_a \cdot d}$$

where, ξ_a : absorptivity [$\text{ml}/(\text{g} \cdot \text{mm})$]

A : absorbancy of standard solution ($\log_{10} I_0/I$)

I_0 : light intensity (before permeation)

I : light intensity (after permeation)

c_a : concentration of the solution (g/ml)

d : thickness of the cell (mm)

Note (5) Do not perform the adjustment of the infrared spectrophotometer during a series of the operation.

- 2) **Measurement** Weigh the sample accurately about 1 g, dilute in dried 25 ml volumetric flask with cyclohexane and prepare the test solution. By filling this test solution to the 0.2 mm cell, the spectrum of wavenumber range 870 cm^{-1} to 740 cm^{-1} (wavelength range $11.5\text{ }\mu\text{m}$ to $13.5\text{ }\mu\text{m}$) shall be recorded under the same condition as in preparation of calibration curve.

b) **Method B**

- 1) **Preparation of calibration curve and determination of absorptivity** Weigh pure 2,4-isomer and pure 2,6-isomer standard samples to the nearest 0.001 g accurately according to table 3 and admixture.

Table 3 Standard solutions by method B

2,6-isomer rate %	Pure 2,4-isomer mass g	Pure 2,6-isomer mass g
0.00	4.000	0.000
0.50	3.980	0.020
1.00	3.960	0.040
2.00	3.920	0.080
3.00	3.880	0.120
4.00	3.840	0.160
5.00	3.800	0.200

Using the 0.1 mm thickness cell, spectrum of wavenumber range 830 cm⁻¹ to 740 cm⁻¹ (wavelength range 12.0 μm to 13.5 μm) of standard solutions above shall be traced. Then, obtain the absorbancy of the absorption maximum around 780 cm⁻¹ (12.80 μm) for 2,6-isomer by the baseline method, plot the relation between the concentration and the absorbancy on diagram, and prepare the calibration curve by the least-square method. The absorptivity shall be obtained by the following formula using this calibration curve.

$$\xi_b = \frac{A \times 100}{c_b \times d}$$

where, ξ_b : absorptivity (mm⁻¹)

A : absorbancy of standard solution ($\log_{10} I_0/I$)

I_0 : light intensity (before permeation)

I : light intensity (after permeation)

c_b : 2,6-isomer rate (%)

d : thickness of the cell (mm)

- 2) **Measurement** By filling the sample used in 1) to the 0.1 mm cell, the spectrum of wavenumber range 830 cm⁻¹ to 740 cm⁻¹ (wavelength range 12.0 μm to 13.5 μm) shall be recorded in the same way as in preparation of calibration curve.

6.4.5 Calculation

- a) **Method A** The absorbancy of each component shall be obtained in accordance with the method in 6.4.4 a) 1). For the compensation of a slight overlap of the absorbent bands of two isomers, the corrected absorbancy of 2,4-isomer and 2,6-isomer shall be calculated.

$$A_{2,6} = A_{780} - 0.043A_{810}$$

$$A_{2,4} = A_{810} - 0.024A_{780}$$