DRAFT FOR COMMENTS ONLY

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BUREAU OF INDIAN STANDARDS
Draft Indian Standard
TOLUENE DIISOCYANATE (TDI-80) — SPECIFICATION

ICS 71.080.99

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Last date for receipt of comment is **01 September 2021**

FOREWORD

(Formal clauses will be added later)

Toluene diisocyanate (TDI) is an organic compound with the formula $CH_3C_6H_3(NCO)_2$. There are two isomers of TDI: 2,4 TDI and 2,6 TDI. TDI is marketed as TDI 80/20 (TDI-80) which is a mixture of 80 percent 2,4-toluene diisocyanate and 20 percent 2,6- toluene diisocyanate and also as TDI 65/35 which contains 2,4-TDI and 2,6-TDI isomers in the ratio of 65:35 respectively.

TDI-80 is available in two types, Type I (for low acidity) and Type II (for high acidity). TDI-80 is mainly used in the production of polyurethane foam and other polyurethane products including elastomers, synthetic leather, coated fabrics, paints and adhesives.

Safety instructions to be followed during testing are given in informative Annex H.

The composition of the Committee, responsible for the formulation of this standard is given at Annex (will be added later).

For the purpose of deciding whether a particular requirement of this standard is complied with the final value, observed or calculated, expressing the result of a test or analysis shall be rounded off in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

Indian Standard

TOLUENE DI-ISOCYANATE (TDI-80) — SPECIFICATION

1 SCOPE

1.1 This *draft* standard prescribes the requirements and the methods of sampling and test for toluene diisocyanate (TDI-80), which is mixture of 80 percent 2,4-toluene diisocyanate and 20 percent 2,6-toluene diisocyanate.

1.2 This standard cover Type I (for low acidity) of toluene diisocyanate (TDI-80).

2 REFERENCES

The following standards contain provisions which through reference in this text, constitute provisions of the standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on these standards are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

IS No.	*Title*
8768 : 2000	Method of measurement of colour in liquid chemical products Platinum-Cobalt scale (*second revision*)
5299 : 2001	Methods of sampling and tests for dye intermediates (*first revision*)

3 REQUIREMENTS

3.1 Description

TDI-80 is a colourless liquid of low viscosity above 15°C. In absence of anti-oxidant, it turns to pale yellow colored liquid upon coming in contact with air.

3.2 The material shall also comply with the requirements given in Table 1 when tested as prescribed in column **5** and column **6** of Table 1.

4 PACKING AND MARKING

4.1 Packing

The material shall be packed in suitable drums, tankers, ISO containers etc, as agreed between purchaser and supplier.

4.2 Marking

4.2.1 Each container shall be securely closed and shall bear the following information:

a) Name of the material;
b) Name of the manufacturer;
c) Month and year of manufacture;
d) Lot or batch number;
e) Nett weight and

f) POISON [red label, printed on white background conforming to IS 1260 (Part I)/ GHS].
g) Any other statutory requirement.

4.2.2 Each container shall bear the minimum cautionary notice worded as under:

KEEP WELL CLOSED AND PROTECTED FROM LIGHT.

TOXIC. AVOID CONTACT WITH SKIN

4.2.3 *BIS Certification Marking*

The product(s) conforming to the requirements of this standard may be certified as per the conformity assessment schemes under the provisions of the Bureau of Indian Standards Act, 2016 and the Rules and Regulations framed thereunder, and the products may be marked with the Standard Mark.

5 SAMPLING

5.1 The method of drawing representative samples of the material and the criteria for conformity shall be as prescribed in **3** of IS 5299.

5.2 Criteria for Conformity

For declaring the conformity of a lot to the requirements of all the other characteristics tested on the composite sample, the test result for each of the characteristics shall satisfy the relevant requirement given in Table 1.

TABLE 1 Requirements for Toluene Di-isocyanate
(*Clause* 3.2 and 5.2)

Sl No.	**Characteristics**	**Requirements**	**Methods of Test, Refer to**	
			Annex No.	**IS**
(1)	**(2)**	**(3)**	**(5)**	**(6)**
i)	Appearance	Clear liquid without any haze or foreign particle.	A	—
ii)	Colour, Pt-Co, *Max*	25	—	8768
iii)	Purity, percent by mass, *Min*	99.5	B	—
iv)	Hydrolyzable Chlorine, percent by mass, *Max*.	0.0080	C	—
v)	Acidity, percent by mass, *Max*.	0.0040	D	—
vi)	Total Chlorine percent by mass, *Max*	0.07	E	—

vii)	Nitro Isocyanates, percent by mass, *Max*.	0.004	F	—
viii)	Isomer Ratio (2,4-TDI: 2,6-TDI), percent by mass	79 – 81.5:18.5-21.0	G	—
ix)	Anti-oxidant or/and Performance Additives[1]	—	—	

NOTE —

1) Name of the Anti-oxidant or/and Performance Additives, their levels and analysis methods shall be provided on mutual agreement between buyer and seller.

ANNEX A

[*Table* 1, *Sl No.* (i)]

TEST METHOD FOR APPEARANCE (VISUAL INSPECTION PROCEDURE)

A-1 PRINCIPLE

The sample is examined visually to detect it is a clear liquid and free from any haze or foreign particles in the sample.

A-2 PROCEDURE

Take a clean and dry 500 ml glass bottle. Visually examine the sample to see if any haze or foreign particles are present. It may be necessary to swirl the sample to stir up any material that has settled to the bottom of the sample bottle.

NOTE — Do not expose the sample to moisture before visual inspection as moisture reacts with toluene diisocyanate to form solids

A-3 REPORT

Report the appearance of the sample as clear liquid, hazy. If foreign particle present, report as foreign particle present.

ANNEX B

[*Table* 1, *Sl No.* (iii)]

TEST METHOD FOR DETERMINATION OF PURITY OF TOLUENE DIISOCYANATE BY GAS CHROMATOGRAPHY

B-1 PRINCIPLE

A sample of TDI is injected on a gas chromatographic capillary column and the results are calculated using the external standard method with area normalization.

B-2 APPARATUS

B-2.1 Gas chromatograph equipped with an FID detector, a split-splitless injector and a suitable electronic integrator/software.

B-2.2 Capillary column, fused silica, with 5 percent phenyl methylpolysiloxane phase.
Length: 50 m;
I.D.: 0.32 mm; and
film thickness: 0.32µm.

B-2.3 Syringe for gas chromatography, volume 10 µl.

B-2.4 Analytical Balance, with least count of 0.1 mg.

B-3 REAGENT

Unless otherwise specified, AR grade chemicals shall be used.

B-3.1 80:20 toluene diisocyanate.

B-3.2 *m*-phenylene diisocyanate.

B-3.3 1,2,4- trichlorobenzene and 1,2,3-trichlorobenzene.

B-3.5 *o*-dichlorobenzene, CP grade.

B-4 SAMPLING

Take a clean and dry 500 ml glass bottle. Do not expose the sample to moisture. Moisture reacts with toluene diisocyanate to form solids.

B-5 GAS CHROMATOGRAPH SETTINGS

Carrier gas	: Hydrogen / Nitrogen / Helium
Pressure at head of column	: 22 psi
Fuel gas & flow rate	: Hydrogen: 40ml, Air: 400ml
Make up flow	: As per the requirement of instrument make/model.
Sample preparation	: Direct (as such sample)
Injection volume	: 1µl. (micro lt.)
Split flow	: 125 ml / min
Detector	: FID

Temperature Programme of Oven, Detector and Injector:

Injector Temperature ,^{o}C	*Detector Temperature,^{o}C*	*Oven*		
		Temperature, ^{o}C	*Hold Time, min*	*Ramp Rate, ^{o}C/min*
250	250	125	2	6
		210	1	20
		240	10	0

B-6 CALIBRATION

Prepare a standard solution containing the components given below, in the expected concentration range. A typical example of standard solution is given below for reference.

Component	**Mass, g**	**Concentration in percent (w/w)**
TDI	70.0000	99.8573
o-dichlorobenzene	0.0250	0.0357
m-phenylene diisocyanate	0.0250	0.0357
1,2,4-Trichlorobenzene	0.0250	0.0357
1,2,3-Trichlorobenzene	0.0250	0.0357

Make sure the GC instrument is adjusted to the conditions stated as above. Inject 1.0 µl of the standard at least three times and obtain the chromatograms. Calculate the calibration correction factor for each component by dividing its concentration by the respective area in its chromatogram. Find the arithmetic mean of the factors calculated for each component. Each factor is calculated to 4 decimal places. When using the factors, the calculation of the concentration of the sample is done using the mean obtained or use suitable software for auto calibration with respect to mass of calibration standard.

B-7 CALCULATION

B-7.1 Sum the areas of all unknown components.

B-7.2 Multiply the area of each component of the sample by its relative response correction factor as mentioned in **B-6**. Obtain the sum of all corrected areas. Normalize each corrected area to 100 percent and report each as mass percent or use suitable software for auto calculation with respect to calibration standard.

NOTES:

1 The above gas chromatographic (GC) conditions are suggestive. However, any GC method having difference in detector, column packing material and type (like packed / capillary, diameter, length, film thickness etc.), calibration technique (internal standard, external standard, area normalization, percent area etc.), carrier gas (He, H_2, N_2) may be used with applicable GC operating parameters, provided standardization and calibration of the components is established after setting GC parameters for the resolution and accuracy level as specified in this standard.

2 Use response correction factor = 1, for the unknown components.

ANNEX C

[*Table* 1, *Sl No.* (iv)]

TEST METHOD FOR DETERMINATION OF HYDROLYZABLE CHLORINE

C-0 GENERAL

This method is used for the determination of hydrolyzable chlorine content of refined 2, 4-toluene diisocyanate, 2,6-toluene diisocyanate and mixture of these toluene diisocyanates. The method is applicable to the determination of hydrolyzable chlorine content in the range of 0 to 0.10 percent.

C-1 PRINCIPLE

The isocyanate containing hydrogen chloride, carbonyl dichloride (CDC), carbamylchlorides, aromatic acid chlorides and chloromethyl compounds is reacted with an aqueous methanol solution to convert the organic chloro compounds to free hydrochloric acid. The liberated HCl is then titrated with silver nitrate solution, potentiometrically.

C-2 SAMPLING

Take a clean and dry 500 ml glass bottle. Do not expose the sample to moisture. Moisture reacts with toluene diisocyanate to form solids.

C-3 APPARATUS

C-3.1 Magnetic stirrer.

C-3.2 Titrator, with a silver electrode versus an Ag/AgCl reference electrode or combine silver ring electrode.

C-3.3 Analytical Balance.

C-3.4 Hotplate/water bath.

C-4 REAGENTS

Unless otherwise specified, AR grade chemicals shall be specified.

C-4.1 Methanol.

C-4.2 Silver Nitrate, 0.014 N standard — Dissolve 2.395 gm silver nitrate in distilled water and make up to 1.0 lt.

C-4.3 1:1 Nitric acid — Take 1 volume of 70 percent HNO_3 and 1 volume of distilled water.

C-5 PROCEDURE

Weigh 13.5 ± 1.5 g of sample using any glass sampling device into a clean, dry 400 ml beaker. Add 125 ml methanol using graduated measuring cylinder and agitate on the magnetic stirrer. When the reaction starts, which is usually within a few seconds, slowly add 100 to 125 ml of chloride free distilled water. Cover with a clean watch glass and agitate for 10 to 15 min. Transfer the beaker from the stirrer to a hot plate or steam bath for 30 min. Wash down the sides of the beaker with distilled water and cool to room temperature by means of an ice bath. Add 10 ml of 1:1 nitric acid to the sample. Titrate the sample with 0.014 N silver nitrate using automatic titrator. From the instrument display, determine the volume of the solution used. Run blanks exactly in a same manner without adding sample.

C-6 CALCULATION

$$\text{Hydrolyzable chlorine, percent} = \frac{(A - B) \times N \times 3.546}{S}$$

where

A = volume $AgN0_3$, or sample titration, ml;
B = volume $AgN0_3$ for blank titration, ml;
N = normality of $AgNO_3$ solution; and
S = sample weight, g.

ANNEX D

[*Table* 1, *Sl No.* (v)]

TEST METHOD FOR DETERMINATION OF ACIDITY

D-1 PRINCIPLE

The isocyanates are reacted with excess n-propanol to form urethanes. The acidic components released are absorbed in the reaction mixture and titrate potentiometrically with methanolic potassium hydroxide.

D-2 SAMPLING

Take a clean and dry 500 ml glass bottle. Do not expose the sample to moisture. Moisture reacts with toluene diisocyanate to form solids.

D-3 APPARATUS

D-3.1 Automatic titrator, complete with reference and glass electrodes.

D-3.2 Buffer solutions, *p*H 4 and 7.

D-3.3 Beaker, 250 ml.

D-4 REAGENTS

Unless otherwise specified, AR grade chemicals shall be used.

D-4.1 Potassium Hydroxide, 0.01 N methanolic, standardized to ± 0.0001 N — Take 0.66 g Potassium Hydroxide (assay-85 percent) in dry 1.0 lt volumetric flask and dilute to mark with methanol. Stir thoroughly for 15 min.

D-4.2 Hydrochloric acid, 0.01 N, standardized — Take 1.042 gm hydrochloric acid (assay-35 percent) in dry 1.0 lt volumetric flask and dilute to mark with methanol. Stir thoroughly for 15 minutes.

D-4.3 *n*-Propanol.

D-5 PROCEDURE

Add 100 ml of *n*-propanol to 250 ml glass beaker. Prepare the titrator according to its operation manual. If necessary, standardize instrument to *p*H 4 with buffer solution, while the solution is gently agitated. Immerse electrodes in n-propanol. Adjust solution to a *p*H of 5.0 with either 0.01 N alcoholic potassium hydroxide or 0.01 N hydrochloric acid carefully. Remove electrodes from the solution. Add 10 ml of the TDI sample into beaker while agitating using volumetric pipette. Cover with a watch glass and continue agitation for 10 min. Immerse electrodes in sample solution and titrate with 0.01 N alcoholic potassium hydroxide, till the end point is reached. The equivalence point will occur in the range of about 5.50 to 7.00 *p*H units.

D-6 CALCULATION

$$\text{Acidity as percent HCl} = \frac{A \times N \times 3.647}{S}$$

where

A = volume of potassium hydroxide solution required, ml;
N = normality of potassium hydroxide solution; and
S = mass of sample, g (= sample volume, ml x 1.22).

D-7 Report results to nearest 0.001 percent.

ANNEX E

[*Table* 1, *Sl No.* (vi)]

TEST METHOD FOR DETERMINATION OF TOTAL CHLORINE IN TOLUENE DI-ISOCYANATE

E-1 PRINCIPLE

The organic matter in the sample is destroyed by combustion with oxygen, converting the organically combined chlorine to ionic chloride. The concentration of chloride ion is then determined by potentiometric titration with dilute standard silver nitrate solution.

E-2 APPARATUS

E-2.1 Oxygen Bomb apparatus.

E-2.2 Automatic Titrator.

E-2.3 Electrode, reference and silver indicating or combine silver ring electrode.

E-2.4 Micro burette, 5 ml capacity, 0.01 ml graduation.

E-2.5 Weighing bottle, suitable for weighing a liquid sample by difference to the nearest 0.5 mg.

E-2.6 Nicrome fuse wire for ignition.

E-4 REAGENTS

Unless otherwise specified, AR grade chemicals shall be used

E-4.1 Sodium Carbonate, 10 percent aqueous solution — Take 100 gm sodium carbonate powder in a 1.0 lt. volumetric flask and make up to the mark with distilled water.

E-4.2 Oxygen, pure grade

E-4.3 Nitric Acid, 1:1 — Take 1 volume of 70 percent HNO_3 and 1 volume of distilled water

E-4.4 Silver Nitrate, 0.014 N standard — Dissolve 2.395 gm silver nitrate in distilled water and make up to 1.0 lt.

E-4.5 Sulfuric Acid, concentrated.

E-4.6 Emery Polishing Paper Grit No. 2/0.

E-4.7 Chromic Oxide.

E-4.8 Ethyl Alcohol, absolute (*free from chloride*)

E-4.9 Methyl Red Indicator — Take 0.1 gm methyl red powered and dissolves in 100 ml ethanol.

E-5 SAMPLING

Take a clean and dry 500 ml glass bottle. Do not expose the sample to moisture. Moisture reacts with toluene diisocyanate to form solids.

E-6 PROCEDURE

Check to be sure that the bomb, oxygen lines, and fittings are free of oil and grease. Small quantities of either may cause violent rupture of the equipment. Weigh 0.9 to 1.0 g (accurately upto 0.0005 g) sample using any glass sampling device into the combustion capsule.

Add 1.0 ml of absolute ethyl alcohol into the combustion capsule. Fit a 10 cm length of firing Nichrome wire onto the two electrodes. Place the combustion capsule in place on the loop electrode and adjust the fuse wire so that it is under the surface of the sample in the capsule but does not touch the capsule at any point.

Take 10 ml sodium carbonate solution in a measuring cylinder. By means of a rubber policeman wet the interior surface of the bomb including the head as thoroughly as possible. Put the bomb head in the bomb cylinder, the contact ring on top of the bomb head, and screw the cap down finger tight. Close the outlet valve securely, with the special wrench provided for the purpose and open the main oxygen cylinder valve slightly.

Place the bomb in the holder mounted on the bench and secures the bomb in place by tightening the holder bolt with a wrench. Attach the union on the oxygen-filling connection to the inlet valve of the bomb. Admit oxygen slowly until 20 – 25 atmospheric of oxygen is admitted. Close the operating valve of the oxygen cylinder and observe the pressure on the gauge. If the pressure drops over 1 atmosphere refill and again check. Continual loss indicates a leak. Do not continue until the bomb satisfactorily holds pressure between 20 – 25 atmospheric.

Close the valves on the cylinder and bomb. Open the valve in the intervening line to release the oxygen pressure. Disconnect the bomb from the oxygen-filling system. Put the cap on the inlet valve to the bomb. Pull the plug to the bomb ignition unit. Fill the bomb ignition receptacle 3/4 full with de-ionized water. Submerge the bomb in the center of the receptacle and visually inspect for leaks in the bomb. Do not fire the bomb until all leaks have been corrected.

Connect the terminal at the top of the ignition receptacle to the terminal on the top of the bomb. Connect the plugs to the cooling receptacle, insert the plug to the ignition unit and fire the bomb. Pull the plug. Allow the bomb to cool at least 10 min. Remove it from the receptacle and shake to wet the sides of the bomb.

After all the oxygen pressure has been released, and before opening the bomb, rinse the head and entire outside of the bomb with deionized water. Open the bomb and examine the contents. Traces of unburned sample or sooty material indicate incomplete combustion and the test must be repeated. Carefully wash the bomb head, the electrodes, the capsule, and the cylinder walls with deionized water. Transfer the washings to a 250 ml beaker. The total volume of washings is normally about 75 ml.

Cool to less than 30°C and acidify the solution to methyl red by dropwise addition of nitric acid (1:1). Add 1 dropper full of the nitric acid in excess. Add 75 ml of ethanol to cover the electrode tips and cool the solution to 30°C. Turn the set switch to “Titrate” and allow the titrator to proceed automatically to a little past the end point. From the instrument display, determine the volume of the solution used.

Run a blank on all reagents (including oxidation) and obtain a titer value for the blank. If the blank titer exceeds 0.1 ml repeat the bomb cleaning procedure.

E-7 CALCULATION

$$\text{Total Chlorine, percent} = \frac{(A - B) \times N \times 3.55}{S}$$

where

A = volume, silver nitrate, required to titrate sample, ml;
B = volume, silver nitrate required to titrate blank, ml;
N = normality of the silver nitrate solution; and
S = mass of sample, g.

E-8 Report results to nearest 0.005 percent.

ANNEX F

[*Table* 1, *Sl No.* (vii)]

TEST METHOD FOR DETERMINATION OF NITRO ISOCYANATES (NIC), BY POLAROGRAPH

F-0 GENERAL

This is a method for the determination of trace amounts (up to 1000 ppm) of mono nitro mono Isocyanates- toluene (NIC) in purified toluene diisocyanate (TDI). The method can be used for refined (80-20) TDI.

F-1 PRINCIPLE

The NIC is extracted from the precipitated urethane with methanolic sodium hydroxide which serves as supporting electrolyte for subsequent polarographic analysis of the extract with a dropping mercury electrode. The nitro group is irreversibly reduced at a half-wave potential of approximately - 0.9 Volt and a well formed wave is obtained.

F-2 SAMPLING

Take a clean and dry 500 ml glass bottle. Do not expose the sample to moisture. Moisture reacts with toluene diisocyanate to form solids.

F-3 APPARATUS

F-3.1 Polarograph.

F-3.2 Working Electrode — Dropping Mercury electrode (DME).

F-3.3 Auxiliary Electrode — Platinum.

F-3.4 Reference Electrode —Ag/AgCl/KCl (3mol/L).

F-3.5 Flask, stoppered, for spent mercury storage.

F-3.6 Centrifuge.

F-3.7 Centrifuge tubes, 50 or 100 ml.

F-3.8 Water/ice bath.

F-4 REAGENT

Unless otherwise specified, AR grade chemicals shall be used.

F-4.1 Methanol.

F-4.2 Potassium Chloride, saturated aqueous solution — Dissolve 22.37 g of potassium chloride into 100 ml of distilled water.

F-4.3 Nitrogen, oxygen-free.

F-4.4 Surfactant, 0.2 percent aqueous — Dissolve 0.2 gram of surfactant into 100 ml of distilled water.

F-4.5 Base Electrolyte — Take 40 gram sodium hydroxide pallet in 250 ml glass beaker and add 80 ml distilled water. Stir the material using glass rod until the all sodium hydroxide pallet dissolved. Cool the material to room temperature. After cooling, material transfer the 1.0 lt volumetric flask and add methanol up to the mark.

F-4.6 Nitrotoluene Diisocyanate.

F-5 SAMPLE PREPARATION

Take 6 g of sample in a clean 250 ml beaker using glass sampling device Add 20 ml of methanol and keep for 15 minutes for complete precipitation. Add 75 ml of electrolyte solution and 1 ml of surfactant and centrifuge for 10 minutes at 2500 rpm. Take supernatant liquid from the centrifuge tube in glass vessel for polarographic analysis.

F-6 SAMPLE ANALYSIS

20 ml of prepared sample is taken in a voltametric vessel. Sample is purged for 5 minutes with nitrogen and the analysis started using polarograph software.

F-7 POLAROGRAPH PARAMETER

Working electrode	DME
Drop size	4
Stirrer speed	2000 rpm
Mode	DP
Initial purge time	300
Equilibration time	10 s
Start potential	-0.6 V
End potential	-1.4 V
Pulse amplitude	0.05 V
Pulse time	0.04 s
Voltage step	0.006 V
Voltage step time	0.4 s
Sweep rate	15 mV/s
Peak potential NIC	-1.1 V

F-8 CALIBRATION

Using toluene diisocyanate (TDI) which is free of nitro Isocyanates (NIC), prepare standards containing 10, 20, 30, 40 and 50 ppm NIC, on a weight of NIC to volume of TDI basis. Analyse each standard according to the above procedure. Measure the current of peak at half wave potential 0.9 V ± 0.1. Plot a calibration curve of ppm NIC versus current. Calibration curve is generated automatically using software with respect to concentration of standard vs current.

F-9 CALCULATION

F-9.1 Using software of the polarograph, report NIC ppm with respect to calibration curve.

F-9.2 Alternatively, calculate as under:

$$\text{NIC, ppm} = \frac{\text{Current in nA x Factor x 100 x 10000}}{\text{1000 x Sample Size}}$$

where

Current Factor in nA = Value of current display on software of half wave potential of NIC peak.
Current 1nA = mg NIC derived from calibration data.

F-9.3 Report result in percent by converting the ppm value in to percent by mass.

ANNEX G

[*Table* 1, *Sl No.* (viii)]

TEST METHOD FOR DETERMINATION OF ISOMER RATIO BY INFRARED SPECTROSCOPY.

G-0 GENERAL

This method is applicable to samples of TDI containing 17 to 25 percent of the 2, 6-TDI isomer and 75 to 83 percent of the 2, 4-TDI isomer.

G-1 PRINCIPLE

This method is based on a quantitative intensity measurement of absorption bands arising from out-of-plane C-H deformation vibrations of the aromatic ring (12.35 mm and 12.8 mm). Since the system shows apparent deviations from Beer´s law, it is necessary to construct calibration curves for the procedure. The method is carried out by dissolving the sample in cyclohexane and running the spectrum in the 12 to 13 mm region (840 nm to 760 nm), measuring the absorbance, calculating the absorbance ratio and converting the value obtained to a corresponding mass composition by the use of a previously established equation or calibration curve.

G-2 SAMPLING

The sample shall be taken in a clean, dry, 500 ml glass bottle. Do not expose the sample to moisture. Moisture reacts with toluene diisocyanate to form solids.

G-3 APPARATUS

G-3.1 Spectrophotometer — Any Single or double beam Infrared (IR) spectrophotometer having sufficient resolution to distinguish between the two peaks of the 2,4-TDI isomer doublet at 810 nm is adequate for use with this method.

G-3.2 Cells — Sodium chloride (NaCl) sealed liquid absorption cells having a thickness of 0.2 mm are required. The actual thickness of the cells should be known to within ± 0.002 mm.

G-3.3 Volumetric flasks, 25 ml, glass stoppered.

G-3.4 Vials, about 10 ml, also glass stoppered.

G-4 REAGENTS

Unless otherwise specified, AR grade chemicals shall be used.

G-4.1 Cyclohexane, this solvent should be stored over some adequate desiccant to remove traces of moisture (recommended desiccants are: silica gel and molecular sieve type 5A).

G-4.2 Diisocyanate Standards, certified reference material of pure 2,4-toluene diisocyanate and 2,6-toluene diisocyanate.

NOTES:

1 Since these diisocyanate will react with moisture and may discolor in the presence of air, they should be stored and handled under dry nitrogen.

2 The diisocyanate should be free of each other. It will be desirable to run a GC analysis on each of the two isomers to make sure they are sufficiently pure.

G-5 CALIBRATION

G-5.1 Take six dry, 10 ml glass stoppered flasks and prepared a calibration blend y weighing into them the amounts of pure 2,4-TDI and 2,6-TDI as given in the following table:

percent 2,4-TDI	percent 2,6-TDI	2,4-TDI, g	2,6-TDI, g
75	25	2.6250	0.8750
77	23	2.6960	0.8050
79	21	2.7650	0.7350
80	20	2.8000	0.7000
81	19	2.8350	0.6650
83	17	2.9050	0.5950

G-5.2 Swirl each flask to mix its contents very well.

G-5.3 Now weigh 1.0000g of each of the above standards into dry 25 ml volumetric flasks.

G-5.4 Dilute to volume with dry cyclohexane and mix thoroughly.

G-5.5 Using the 0.2 mm sealed liquid absorption cells, fill both the reference and sample cells with cyclohexane and record the solvent spectrum from 840 nm to 760 nm three times.

G-5.6 Empty the sample cell and fill it with the standard solution. Record the spectrum superimposing it over the previously recorded solvent spectrum.

G-5.7 Repeat steps **G-5.6** for each standard solution.

G-5.8 Measure the absorbance of each of the calibration solutions at the following wavelengths, starting from the solvent blank absorption spectrum:

2,4-TDI at 810 nm; and

2,6-TDI at 782 nm

G-5.9 Calculate now the absorbance ratios and the mass ratios as follows:

$$\textbf{Absorbance ratio: } \frac{\text{Absorbance of 2,4-TD at 810 nm}}{\text{Absorbance of 2,6-TD at 782 nm}}$$

$$\textbf{Mass Ratio: } \frac{\text{Mass of 2,4-TDI taken for blend preparation}}{\text{Mass of 2,6-TDI taken for blend preparation}}$$

G-5.10 Obtain a calibration curve by plotting the absorbance ratios on the y- axis versus the mass ratios of 2,4-TDI to 2,6-TDI in each solution on the x-axis.

G-6 PROCEDURE FOR SAMPLES OF 80/20 TDI

G-6.1 Weigh 1.0000 gm. of the TDI sample using lung ray pipette or any glass sampling device into a dry 25 ml glass stoppered volumetric flask.

G-6.2 Dilute to volume with dry cyclohexane and mix thoroughly.

G-6.3 Fill two 0.2 mm cells with pure solvent and obtain its spectrum from 840 to 760 nm.

G-6.4 Fill 0.2 mm cell of IR spectro with sample and take the spectrum of sample and note down the absorbance at 810 nm and 782 nm.

G-6.5 Take a blank run of cyclohexane solvent and subtract the absorbance of respective wavelength from sample run absorbance.

G-7 CALCULATION

G-7.1 Absorbance ratio of 2, 4-TDI & 2,6-TDI

$$= \frac{\text{Sample Absorbance at 810nm} - \text{Blank Absorbance at 810 nm.}}{\text{Sample Absorbance at 782nm} - \text{Blank Absorbance at 782 nm}}$$

G-7.2 Obtain the mass ratio using calibration curve of Absorbance ratio vs Mass ratio as per **G-5.10**.

G-7.3 Calculate 2,4-TDI percent and 2,6 TDI percent as bellow:

2,6-TDI percent = 100 / (R+1)

2,4-TDI percent = 100 – (2,6-TDI percent)

where

R = Mass ratio found out as per **G-7.2**.

ANNEX H

(*Informative Annex*)

H-1 SAFETY INSTRUCTIONS TO BE TAKEN DURING TESTING

H-1.1 General Instructions

Isocyanates, may cause local skin irritation and care must be taken to avoid contact. If a spill is encountered, wash the affected area promptly with soap and water. Use adequate ventilation to keep the vapor concentration at a minimum.

H-1.2 Instructions for test method for determination of purity of toluene diisocyanate by gas chromatography

Work under a fuming hood so as to avoid inhaling their vapors and use adequate gloves wherever possible to avoid contact with the skin.

H-1.3 Instructions for test method for Determination of Hydrolyzable Chlorine in Toluene Diisocyanate

a) Nitric acid is extremely corrosive to the skin. Any spills must be washed off immediately with cold water.

b) Methanol is flammable. Keep sparks and flames away.

H-1.4 Instructions for test method for determination of Total Chlorine in Toluene diisocyanate

a) The bomb must be pressure tested periodically at 13.78951 MPa (2000 psi).

b) The pressure gauge must be tested periodically for accuracy at the pressure used in the bomb [3.10264 MPa (450 psi)]. It also shall withstand the pressure permitted by the safety disc [4.82633 MPa (700 psi)].

c) Before admitting oxygen to the bomb make sure that the bomb with fittings including the valve packing and the oxygen line with fittings are free of oil and grease to prevent a violent rupture of the equipment.

d) Other safety precautions are written into the procedure. It must be remembered that the oxygen bomb combustion is a hazardous operation. Deviation from the accepted safety standards can result in a serious explosion. Contact supervision concerning any unfamiliar operation or situation before proceeding.

e) Nitric acid and sulfuric acid are both severely corrosive. Use rubber gloves, an apron, and goggles when handling these reagents.

f) Ethanol is flammable. Keep sparks and flames away.

H-1.5 Instructions for test method for determination of nitro isocyanate (nic), by polarograph

a) Avoid skin contact and do not inhale fumes.

b) Use the vacuum trap to suck up spills immediately and transfer to the bottle for discarding mercury.

c) Take normal precautions with methanol and strong bases, such as the base electrolyte. Do not allow the base electrolyte to contact the eyes.

d) Do not open the centrifuge while the rotor is spinning. Never try to break the rotor by applying pressure on the spindle.