### Abstract

Measurement of isocyanate content is standardized by the below quoted test methods.

Sample liquid after dissolved in dry toluene reacts with excessive di-n-Butylamine, and back titrate residual di-n-Butylamine with hydrochloric acid up to the endpoint. The content of Isocyanate is calculated from titration volume.

### Reference

1. JIS K 7301-1995 Test Method for Tri-range Isocyanic Prepolymer for Heat-curable Urethane Elastomer
2. JIS K 1603-1985 Test Method for Polymethylene Polyphenyl Polyisocyanate
3. JIS K 1556-2006 Test Method for Tolunediisocyanate — Polyurethane raw materials (Appendix 1)
4. ISO 14896-2006 Plastics -- Polyurethane raw materials -- Determination of isocyanate content

### Cautions in measurement

1. Repeated measurement lowers sensitivity of glass electrode, and regeneration process of electrode is required each time a measurement is finished.
   To regenerate the electrode, dip it in solvent once for cleaning, and then in pure water for 10 to 60 min. (depends on how much contaminated)
2. Handle chemicals in a well ventilated room or use a draft.
3. Note that organic cyanate is harmful when its fume is absorbed through skin or inhaled. Wear protective gloves and glasses, and work in a well ventilated room.
4. Isocyanate reacts with ambient moisture. Keep room humidity as low as possible, preferably below 50% RH.
4. Post-measurement care

After a series of measurements for the day is over, be sure to regenerate the electrode according to the preceding “3. Cautions in measurement”.

5. Test equipment

Main unit: Automatic potentiometric titrator (Standard preamplifier STD —)
Electrode: Combination glass electrode

6. Reagent

Titrant: 1mol/L Hydrochloric acid (f = 1.00)
Solvent: Dry Toluene + Isopropyl alcohol
Reagent: 2mol/L di-n-Butylamine

7. Measurement procedure

—Measurement—
1) Prepare 3g sample in a 200mL conical flask.
2) Add 20mL Toluene to dissolve the sample.
3) Add 20mL of 2mol/L di-n-Butylamine.
4) Shake to make it even, and leave it for more than 20 minutes.
5) Add 100mL of Isopropyl alcohol.
6) Titrate with 1mol/L Hydrochloric acid up to the endpoint.
7) Likewise, perform blank test.

8. Formula

Isocyanate content = ( SIZE / ( ( BL1 - EP1 ) × FA1 ) ) × K2

 EP1 : Titration volume (mL)  
 BL1 : Blank level (39.888mL)  
 FA1 : Titant factor (1.00)  
 K2 : Coefficient (1000)  
 SIZE : Sample size (g)
9. Example of measurement

— Ambient condition —

<table>
<thead>
<tr>
<th>Room temperature</th>
<th>Humidity</th>
<th>Weather</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 °C</td>
<td>41 %</td>
<td>Fair</td>
</tr>
</tbody>
</table>

- Titrination parameter -

Model : AT-400
Method No. : 18
Titr.mode : Auto
Intermit
Titr.form : EP Stop

[TITR. PARA]
Form : EP Stop
Buret No. : 1
Preamplifier : STD
Detector No. : 1
Dimension : pH
Max. Vol. : 60.0mL
W.Time : 0s
Direction : Auto

[CALCU. PARA]
Sample Measurement
Conc1 CalcuNo. : 7
Conc1 Dim. : [ ]
Conc1 EP Position : 1
Data : [f(EP2-EP1)]
T.Type : [Back]
Blank : 39.888mL
Common T.Factor : K2 1000
Temp. Comp. : [Off]

[CTRL. PARA]
End Point No. : 1
S(dE) : 50
S(E/mL) : 100
O.Titr : 0mL
Gain : 1
S.Pot : 4.0mV
Stab. : 0.5mV/s
Delay Time : 1s
L.Time : 30s
M.Unit : 0.5mL
Separation : Off
A.Simulation : Off

(The above printout data were obtained from titration by AT-400)

≪TITR. PARA: titration parameter≫
Form: of titration / Buret No.: the burette used in titration / Detector No.: the detector used in titration
Dimension: potential unit / Max.Vol: of titration / W.Time: before titration starts
Direction: of titration

≪CTRL. PARA: control parameter≫
End Point No.: number of EPs / S(dE): EP potential (difference) / S(E/mL): EP potential (differential)
O.Titr: over-titration / Gain: sensitivity of detection signal / S.Pot.: potential change of sampling signal
M.Unit: titration volume of data sampling / Separation: of potential / A.Simulation: redetection of EP

≪CALCU. PARA: calculation parameter≫
Conc.1 formula 1 / Conc1 Dim. Unit of conc 1 / Data: calculation formula of titration volume
T.Type: normal or back titration / Blank: blank level / Common T.Factor: selection of factor
Temp. Comp.: temperature compensation / K2(mg/mL): concentration conversion at EP1
K2: unit conversion coefficient / Conc1 EP Position: EP position at concentration 1

Method 18
No. 01-01
Date 98/07/18 11:43
I.LeV 10.56 pH
F.Vol 23.7250mL
F.LeV 2.74 pH
D.Vol 10.0000mL
Time 00:00:29
Size 3.0793 mL
Conc-1 184.96
Conc-2 22.719%
EP-1 23.2391 mL
5.03 pH
### Measurement results

<table>
<thead>
<tr>
<th>n</th>
<th>Sample (g)</th>
<th>Titration (mL)</th>
<th>Isocyanate content</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0793</td>
<td>23.2391</td>
<td>184.96</td>
</tr>
<tr>
<td>2</td>
<td>3.0545</td>
<td>23.4141</td>
<td>185.41</td>
</tr>
<tr>
<td>3</td>
<td>3.0105</td>
<td>23.6911</td>
<td>185.87</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Statistics of results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
</tr>
<tr>
<td>185.41</td>
</tr>
<tr>
<td>SD</td>
</tr>
<tr>
<td>0.46</td>
</tr>
<tr>
<td>RSD</td>
</tr>
<tr>
<td>0.25 %</td>
</tr>
</tbody>
</table>

*The above results were obtained by 3 tests of the same sample.
* Red underline shows the data from page 3/4.

### 10. Summary

Urethane is dehydrated compound of amino group and alcohol group via carbonyl, and Ethyl carbamate or Polyurethane (Urethane resin) is popularly called Uretahne. The chemical compound Isocyanate having chemical structure of \(\text{−N}=\text{C}=\text{O}\) is also called Isocyanic ester, which is important material for polyurethane. The above sample test shows a good repeatability of 0.25% relative standard deviation as the automated potentiometry is the most reliable measurement technique. The analysis of urethane can be easily and precisely made by any of the following titration systems manufactured by Kyoto Electronics (KEM).

- **AT-610**
  - Awarded Product of Supreme Technology from Kyoto City
  - Easy key entry by touch panel of large color LCD (8-inch wide)
  - Simultaneous titration in parallel
  - Both potentiometric and Karl Fischer moisture titration (coulometric・volumetric) can be performed at a time.

- **AT-510**
  - Compact and cost performance model
  - PC card expands data memory for convenience and versatility.

- **AT-500N-1**
  - Low cost and high performance
  - Easy view with back light LCD
  - GLP/GMP conformed model

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