Metrohm

Application Bulletin 200/3 e

Acid value, hydroxyl value, and isocyanates in raw materials for the fabrication of plastics

Determination by automatic potentiometric titration according to various standards

Branch

General analytical chemistry; organic chemistry, chemistry; plastics, photographic industry

Keywords

Titration; potentiometric titration; automation; DIS-Cover; acid number; acid value; hydroxyl number; hydroxyl value; isocyanates; branch 1; branch 3; branch 6; ASTM D2572; ASTM D4662; ASTM D5155; ASTM D7253; ASTM E1899; EN ISO 14896; DIN 53240-3

Summary

Polyurethanes are one of the most commonly used types of plastic. They are produced by the reaction of raw polyols with isocyanates. Depending on the starting material a wide variety of plastics can be obtained. The determination of the acid value, hydroxyl value, and isocyanate content plays an important part in the analysis of raw materials for plastics.

The acid number of polyol raw material is usually used in quality control to ensure batch-to-batch uniformity. Additionally it is used as correction factor for calculating the true hydroxyl number. In this Application Bulletin the determination of the acid number according to ASTM D4662 and ASTM D7253 is described.

One raw material for polyurethanes are polyols. Polyols contain multiple hydroxyl groups. Therefore, hydroxyl number of a raw material directly correlates to the amount of polyols present and it is thus an important quality control parameter. In this Application Bulletin the determination of the hydroxyl number according to ASTM E1899 and DIN 53240-3 is described.

As polyols react stoichiometrically with isocyanates, the knowledge of the isocyanate content is an important quality parameter for the production of polyurethanes. In this document the determination according to EN ISO 14896 method A, ASTM D5155 method A and ASTM D2572 is described.

Acid value (AV)

Summary

The acid value corresponds to the amount of carboxylic acid groups in alkyl resins, polyester acrylate resins or mixtures and is given in mg KOH per g sample. It is also used in evaluating plasticizers, in which acid values should be as low as possible.

Instruments

- Sample changer
- Titrator with DET mode
- Buret 20 mL
- Stirrer

Electrodes

Solvotrode easyClean	6.0229.020

Reagents

- Ethanol
- Toluene, dry
- Phenolphthalein

Solutions

Titrant	c(KOH) = 0.1 mol/L in ethanol or methanol If possible this solution should be bought from a supplier.
Solvent mixture	Ethanol / toluene, Φ(EtOH) = 50% (v/v) Neutralized, just before use, with KOH in presence of 0.3 mL phenolphthalein solution per 100 mL solvent mixture.
Phenolphthalein solution	Phenolphthalein in ethanol, β(Phenolphtalein) = 1 g / 100 mL.

Standard

Benzoic acid	Benzoic acid is dried in a desiccator overnight.

Sample preparation

No sample preparation is required.

Analysis

Titer

100 – 120 mg benzoic acid is weighed into the titration vessel and dissolved in 50 mL ethanol. The solution is then titrated using c(KOH) = 0.1 mol/L until after the first equivalence point.

Blank

50 mL solvent mixture is added into a 150 mL beaker. After a pause of 30 s, the solution is titrated until the first equivalence point using alcoholic c(KOH) = 0.1 mol/L.

Sample

An appropriate sample amount is weighed into a 150 mL beaker (see table below). 50 mL solvent mixture is added and the sample dissolved. After a pause of 30 s, the solution is titrated until the first equivalence point using alcoholic c(KOH) = 0.1 mol/L.

Amount of sample depending on the expected acid value

Expected AV / mg KOH / g	Sample amount / g	Accuracy / g
< 7	6 – 8	0.001
7 – 15	2.5	0.001
15 – 75	0.5	0.0001
> 75	0.2	0.0001

Parameters

Titer

Mode	DET U
Signal drift	50 mV/min
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	5
EP recognition	all

Sample

Mode	DET U
Signal drift	20 mV/min
Max. waiting time	38 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	5
EP recognition	all

Calculation

Titer

$$f = \frac{m_S}{V_{EP1} \times c(KOH) \times M_S}$$

f:	Titer of the selected titrant
m_S:	Mass of standard in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c(KOH):	Concentration of the selected titrant in mol/L; here c(KOH) = 0.1 mol/L
M_S:	Molecular weight of the standard; here 122.12 g/mol

Acid value

$$AV = \frac{V_{EP1} \times f \times c(KOH) \times M_A}{m_S}$$

AV:	Acid value of the sample in mg KOH / g
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c(KOH):	Concentration of the selected titrant in mol/L; here c(KOH) = 0.1 mol/L
f:	Correction factor («titer») without unit
M_A:	Molecular weight of KOH; 56.11 g/mol
m_S:	Sample size in g

Example determination

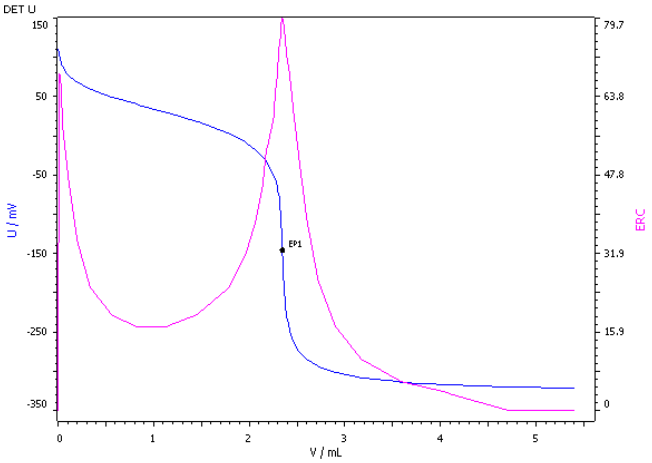

Fig. 1: Determination of the acid value
(blue = titration curve, pink = ERC)

Comments

- For less soluble materials, decrease the sample size or use a solvent mixture of one volume ethanol and three volumes *tert*-butyl methyl ether or toluene. This mixture should also be neutralized.
- ASTM D7253 is similar to ASTM D4662. The differences are:
  - Use of 100 mL isopropanol instead of solvent mixture
  - Use of c(KOH in methanol) = 0.02 mol/L
  - Use of 50 – 60 g sample

References

- ASTM D4662
  Standard Test Methods for Polyurethane Raw Materials. Determination of Acid and Alkalinity Numbers of Polyols.
- ASTM D7253
  Standard Test Method for Polyurethane Raw Materials: Determination of Acidity as Acid Number for Polyether Polyols.

Hydroxyl value (OHV)

Summary

The hydroxyl value is given in mg KOH per g sample and gives information about the degree of esterification within the sample.

Instruments

- Sample changer
- Titrator with DET mode
- 1x Buret 50 mL (acetonitrile)
- 2x Buret 20 mL (reaction solution, titrant)
- 1x Buret 2 mL (deionized water)
- Magnetic stirrer for sample changer
- DIS-Cover

Electrodes

Solvotrode easyClean	6.0229.010

Reagents

- Acetonitrile, HPLC quality
- Toluene-4-sulfonyl-isocyanate (TSI), purum
- Potassium hydrogen phthalate, KHP, pa.

Solutions

Titrant	Tetrabutyl ammonium hydroxide, c(TBAOH) = 0.1 mol/L in isopropanol/methanol, Φ(MeOH) = 50% (v/v) If possible, this solution should be bought from a supplier.
TSI solution	Approximately 250 mL acetonitrile is given into a 500 mL volumetric flask and 20 mL TSI is added. The flask is filled up to the mark with acetonitrile and mixed. The solution reacts vigorously with water, it is therefore recommended to work in a fume hood and under protective gas. The reaction solution is stable for approximately 1 month.

Standard

KHP	KHP is dried in a drying oven for 2 h at 120 °C and allowed to cool down in a desiccator for at least 1 h.

Sample preparation

No sample preparation is required.

Analysis

Titer

60 mL deionized water is added to approximately 180 mg KHP. The suspension stirred for about a minute in order to dissolve the KHP. The solution is then titrated until the first equivalence point using c(TBAOH) = 0.1 mol/L.

Sample

An appropriate amount of sample (see calculation below) is weighed into the titration vessel and dissolved in 10 mL acetonitrile and the solution stirred for 30 s (stirring rate 8). 10.0 mL TSI solution are added, the sample is covered, and the mixture stirred (stirring rate 4). After 5 minutes 0.5 mL deionized water is added, the lid is closed again, and the solution stirred for another 60 s (stirring rate 4). 40 mL acetonitrile is added and the solution is titrated until after the second end point with c(TBAOH) = 0.1 mol/L.

After each titration, the buret and vessel are rinsed first with acetonitrile, then with deionized water, and the electrode is then conditioned for 1 min in deionized water.

$$m_s = \frac{40}{OHV_{expected}}$$

m_s: Sample size in g

$OHV_{expected}$: Expected hydroxyl value

Parameters

Titer

Mode	DET U
Pause	30 s
Signal drift	50 mV/min
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	5
EP recognition	greatest

Sample

Mode	DET U
Pause	30 s
Signal drift	50 mV/min
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	5
EP recognition	all

Calculation

Titer

$$f = \frac{m_s}{V_{EP1} \times c(TBAOH) \times M_S}$$

f: Titer of the selected titrant

m_s: Mass of standard in mg

V_{EP1}: Titrant consumption until the first equivalence point in mL

c(TBAOH): Concentration of the selected titrant in mol/L; here c(TBAOH) = 0.1 mol/L

M_S: Molecular weight of the standard; here 204.22 g/mol

Sample

$$OHV = \frac{(V_{EP2} - V_{EP1}) \times f \times c(TBAOH) \times M_A}{m_S}$$

OHV:	Hydroxyl value of the sample in mg KOH / g sample
V_{EP1}:	Titrant consumption until the first equivalence point in mL
V_{EP2}:	Titrant consumption until the second equivalence point in mL
c(TBAOH):	Concentration of the selected titrant in mol/L; here c(TBAOH) = 0.1 mol/L
f:	Correction factor («titer») without unit
M_A:	Molecular weight of KOH; here 56.11 g/mol
m_s:	Sample size in g

Example determination

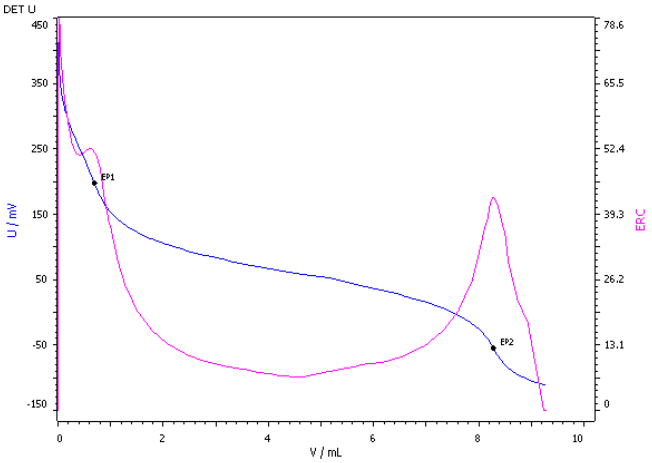

Fig. 2: Determination of the hydroxyl value (blue = titration curve, pink = ERC)

Comments

- The ASTM method is presented here, as it is faster (12 min) than the DIN method (40 min).
- As alcohols react with the TSI, too high results are obtained when using e.g., ethanol for cleaning. Therefore acetonitrile is recommended as solvent. Another possible solvent is acetone.
- Never dab the tip of an electrode with a tissue, as this damages the electrode.
- For samples with an expected hydroxyl value of 2 or less, use 15 to 20 g sample.
- 40 mL instead of 30 mL acetonitrile are added after the preparation in order to ensure the complete immersion of the electrode.
- For information about the automated determination of the hydroxyl value according to the DIN method see Metrohm Application Bulletin No. 332.

References

- ASTM E1899
  Standard test method for hydroxyl groups using reaction with p-toluene sulfonyl isocyante (TSI) and potentiometric titration with tetrabutyl ammonium hydroxide
- DIN 53240-3
  Binders for paints and varnishes - Determination of hydroxyl value - Part 3: Rapid test

Isocyanates content (NCO)

Summary

Diisocyantes are used for manufacturing polyurethanes. The isocyanate (NCO) content is an important quality parameter, as the value indicates the concentration of the active NCO groups in the sample. The NCO content is given in g of isocyanate per 100 g of sample.

Here, the determination according to EN ISO 14896 is described, as in comparison to ASTM D5155 and ASTM D2572, less chemicals are used, making it the more environmental friendly method.

Instruments

- Sample changer
- Titrator with DET mode
- 2x Buret 50 mL (toluene, acetone)
- 2x Buret 20 mL (reaction solution, titrant)
- Magnetic stirrer for sample changer
- DIS-Cover

Electrodes

Solvotrode easyClean	6.0229.010

Reagents

- Toluene (dried over molecular sieve)
- Acetone
- Dibutylamine

Solutions

Titrant	c(HCl) = 1 mol/L aqueous If possible this solution should be bought from a supplier.
Reaction solution	c(dibutylamine) = 1 mol/L in toluene (dried over molecular sieve)

Standard

TRIS	TRIS is dried overnight in a drying oven at 105 °C and allowed to cool down in a desiccator for at least 1 h.

Sample preparation

No sample preparation is required.

Analysis

Titer

About 420 mg TRIS is weighed into a titration vessel. 20 mL deionized water and 50 mL acetone are added. After a pause of 20 s, the solution is titrated with c(HCl) = 1.0 mol/L until the first equivalence point. In between measurements, the electrode membrane is rehydrated for 1 min in deionized water.

Blank

A blank sample is treated and titrated in exactly the same way as the actual sample without sample.

Sample

Weigh out an appropriate amount of the sample (~2 g). Add 30 mL toluene to dissolve it. Add 18.0 mL reaction solution, cover the vessel, and allow reacting for 10 min on the magnetic stirrer. Afterwards 30 mL of acetone is added and the excess of dibutylamine is back titrated with c(HCl) = 1 mol/L.

Parameters

Titer

Mode	DET U
Pause	20 s
Signal drift	20 mV/min
Max. waiting time	38 s
Meas. point density	4
Min. increment	50 µL
Max. increment	off
EP criterion	5
EP recognition	greatest

Blank

Mode	DET U
Signal drift	20 mV/min
Max. waiting time	38 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	5
EP recognition	all

Sample

Mode	DET U
Signal drift	20 mV/min
Max. waiting time	38 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	5
EP recognition	all

Calculation

Titer

$$f = \frac{m_S}{V_{EP1} \times c(HCl) \times M_S}$$

f:	Titer of the selected titrant
m_S:	Mass of standard in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c(HCl):	Concentration of the selected titrant in mol/L; here c(HCl) =1.0 mol/L
M_S:	Molecular weight of the standard; here 121.14 g/mol

Sample

$$CNO = \frac{(V_{BLANK} - V_{EP1}) \times f \times c(HCl) \times M_A}{10 \times m_S}$$

NCO:	Isocyanate content of the sample in g cyanate / 100 g
V_{EP1}:	Titrant consumption until the first equivalence point in mL
V_{blank}:	Used titrant in mL for the Blank back titration
c(HCl):	Concentration of the selected titrant in mol/L; here c(HCl) = 1.0 mol/L
f:	Correction factor («titer») without unit
M_A:	Molecular weight of CNO; here 42.02 g/mol
m_S:	Sample size in g
10:	Conversion factor for %

Example determination

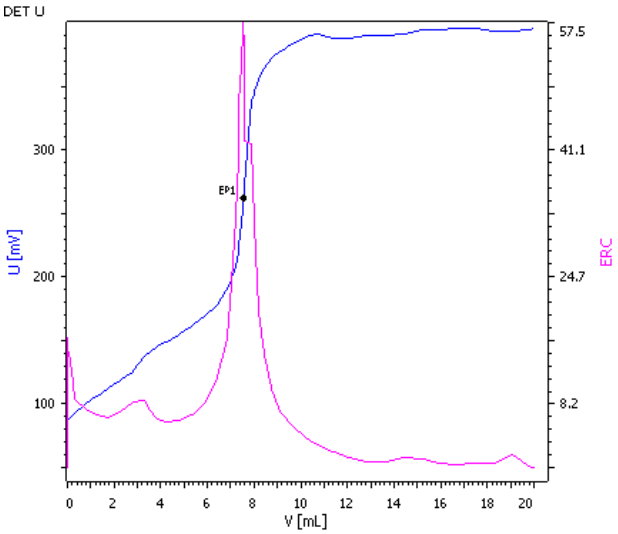

Fig. 3: Determination of the Isocyanate value (blue = titration curve, pink = ERC)

Comments

- Since organic isocyanates react with atmospheric moisture, special precautions in sampling must be taken. Usual sampling methods, even when conducted rapidly, can cause contamination of the sample with insoluble ureas; therefore, cover 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 vapors are breathed in. Provide adequate ventilation and wear protective gloves and eyeglasses.
- Turbidity will be encountered in the titrations. If the mixtures are agitated vigorously, inhomogeneity can be tolerated without adversely affecting the results. Alternatively methanolic HCl could be used as titrant.
- ASTM D5155 is similar to EN ISO 14896. The differences are:
  - Concentration of reaction solution c(dibutylamine) = 2 mol/L
  - Reaction time of 15 min
  - Different amounts of toluene (50 mL) and reaction solution (50 mL) and higher sample size (6.5 – 7 g)
  - Use of isopropanol (225 mL) instead of acetone.

- ASTM D2572 is similar to EN ISO 14896. The differences are:
  - Concentration of reaction solution c(dibutylamine) = 01 mol/L
  - Concentration of titrant c(HCl) = 01 mol/L
  - Reaction time of 15 min
  - Different amounts of toluene (25 mL) and reaction solution (25 mL) and smaller sample size (0.1 g)
  - Use of isopropanol (100 mL) instead of acetone.

References

- EN ISO 14896
  Plastics — Polyurethane raw materials - Determination of isocyanate content
- ASTM D5155
  Standard Test Methods for Polyurethane Raw Materials: Determination of the Isocyanate Content of Aromatic Isocyanates
- ASTM D2572
  Standard Test Method for Isocyanate Groups in Urethane Materials or Prepolymers

Date

May 2019

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