Metrohm

Application Bulletin 200/3 e

Determination of the acid value, hydroxyl value, and isocyanates in raw materials for the fabrication of plastics by automatic potentiometric titration

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, edible fat; branch 1; branch 3; branch 6; ASTM E1899-08; ASTM D 4662-93; ISO 14896/3

Summary

The determination of the acid value, the hydroxyl value, and the isocyanates plays an important part in the analysis of raw materials for plastics. The present bulletin describes the determination of these characteristic values by automatic potentiometric titration. The acid and hydroxyl value are measured according to ASTM, the isocyanate value is measured according to ISO.

Determination of the 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
- Burette 20 mL
- Stirrer

Electrodes

Solvotrode easyClean	6.0229.020

Reagents

- Ethanol
- Diethyl ether, peroxide-free
- 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 / diethyl ether, 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.

Sample

An appropriate sample amount is weighed into a 150 mL beaker (see table below). 50 to 100 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

Expected AV / mg KOH / g	Sample amount / g	Accuracy / g
0 – 1	20	0.05
1 – 4	10	0.02
4 – 15	2.5	0.01
15 – 75	0.5	0.001
> 75	0.2	0.001

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 112.12 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

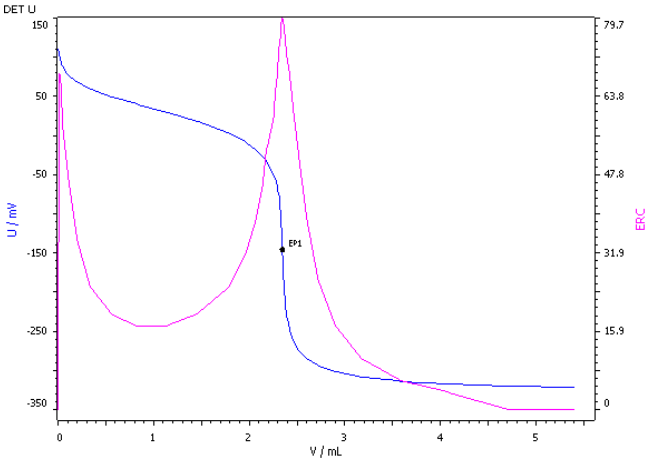

Figure 1: Determination of the acid value
(blue = titration curve, pink = ERC)

Comments

- For less soluble materials, a solvent mixture of one volume ethanol and three volumes *tert*-butyl methyl ether or toluene is recommended. This mixture should also be neutralized.

References

- ASTM D 4662-93
Standard Test Methods for Polyurethane Raw Materials. Determination of Acid and Alkalinity Numbers of Polyols.
- ISO 2114:1996
Plastics – Unsaturated polyester resins – Determination of partial acid value and total acid value.

Determination of the hydroxyl value (OHV) according to ASTM E1899-08

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 Burette 50 mL (acetonitrile)
- 2x Burette 20 mL (reaction solution, titrant)
- 1x Burette 2 mL (dist. H_2O)
- Magnetic stirrer for sample changer
- DIS-Cover

Electrodes

Solvotrode easyClean	6.0229.010

Reagents

- Acetonitrile, HPLC quality
- Toluene-4-sulfonyl-isocyanate (TSI), purum
- Ethanol
- 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

To approximately 180 mg KHP 60 mL dist. H_2O is added and 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 and the sample is covered and the mixture stirred (stirring rate 4). After 5 minutes 0.5 mL dist. H_2O is added, the lid is again closed, 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 burette and vessel are rinsed first with ethanol, then with dist. H_2O and the electrode is then conditioned for 1 min in dist. H_2O.

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

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

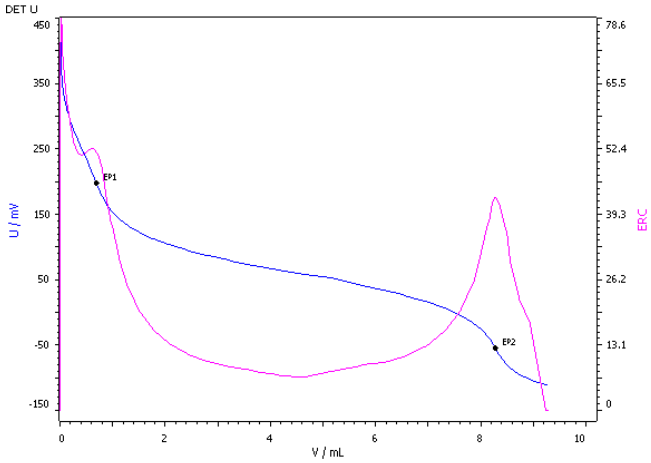

Figure 2: Determination of the hydroxyl value (blue = titration curve, pink = ERC)

Comments

- The ASTM method is presented here, as it is faster (12 min) than the DIN method (40 min).
- 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 covering 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 53240-2

  Determination of the hydroxyl value – part 2: method with catalyst

Determination of the isocyanates (NCO)

Summary

The isocyanate content is given in g of isocyanate per 100 g of sample. This value indicates the concentration of the active NCO groups of the sample.

Instruments

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

Electrodes

Solvotrode easyClean	6.0229.010

Reagents

- Toluene (dried over molecular sieve)
- Methanol
- 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 methanol 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 (~2g). 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 methanol 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

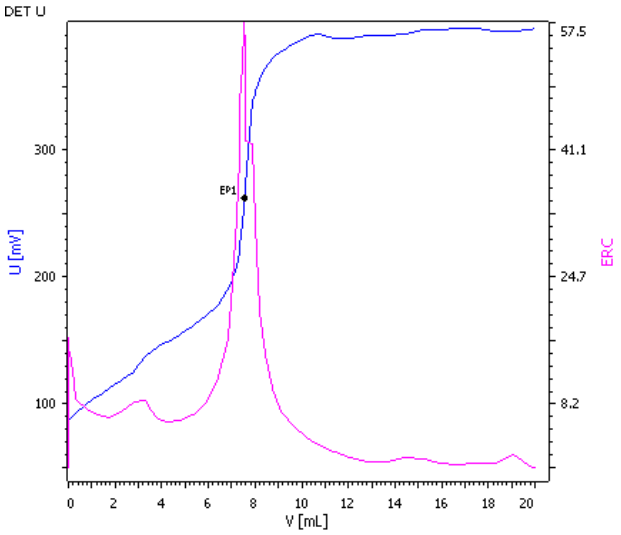

Figure 3: Determination of the Isocyanate value (blue = titration curve, pink = ERC)

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.

References

- ISO 14896/3
  Plastics — Polyurethane raw materials - Determination of isocyanate content

Author

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