Metrohm

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Automated titration of the hydroxyl number according to ASTM E1899 and EN ISO 4629-2

Branch

General analytical chemistry; organic chemistry; plastics

Keywords

Titration; hydroxyl number; automation; potentiometric titration; polyols; resins; paints; lubricants; ASTM E1899; EN ISO 4629-2; DIN 53240-3; EN 15168; branch 1; branch 3; branch 6

Summary

The hydroxyl group is an important functional group and knowledge of the hydroxyl number, i.e. the hydroxyl group content, is required for the production of intermediate and finished products such as polyols, resins, paint resins and lubricants (petroleum industry). In the method presented here, primary and secondary hydroxyl groups are determined. The hydroxyl number (HN) is defined as the amount of potassium hydroxide in milligrams that is equivalent to the hydroxyl amount of 1 gram of the sample (mg KOH / g sample).

The most frequently described method for determining the hydroxyl number is the reaction with acetic anhydride in pyridine with subsequent titration of the free acetic acid:

However, this method has the following disadvantages:

- The sample must be boiled under reflux for 1 hour (long reaction time and expensive, complicated handling)
- The method cannot be automated
- Small hydroxyl numbers cannot be determined exactly
- Toxic pyridine, which is unpleasant to use, is required

Both standards, ASTM E1899 and EN ISO 4629-2, which replaces DIN 53240-2, describe an alternative method that requires no sample preparation and can therefore be fully automated.

This Application Bulletin demonstrates and discusses a simple analysis method for determining the hydroxyl number according to ASTM and EN ISO using a fully automatic titrimetric system that can be used for numerous industrial samples.

The use of a fully automatic system for this type of analysis is highly recommended, because in this way contact with toxic solvents is minimized.

Additionally, electrode treatment is very important for non-aqueous titrations. An automated system ensures that electrode handling is always carried out in exactly the same way.

The diagram on the following page is intended to summarize the automated analytical steps of the ASTM and DIN methods:

Comparison of the two methods

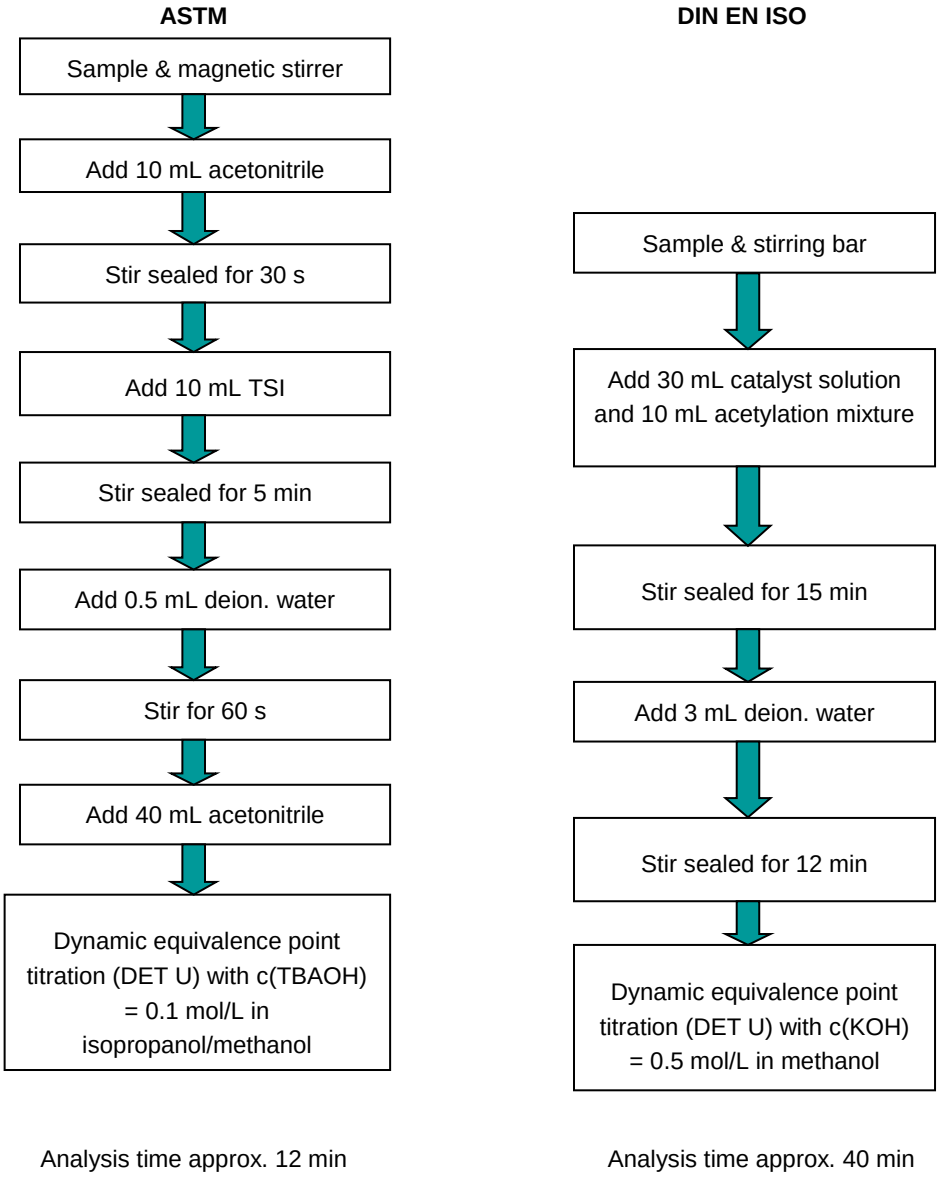

Fig 1: Comparison of the two analysis methods including the approximated titration time for each method.

At the end of the titration, the electrode accessories are automatically rinsed with acetonitrile (dip rinsing) and conditioned in deionized water (see AB-404_1_EN) and instruction leaflet for Solvotrode).

ASTM E1899

Summary

The method described in ASTM E1899 is based on the reaction of the primary and secondary hydroxyl groups with an excess of p-toluenesulfonyl isocyanate (TSI) resulting in an acidic carbamate. This can then be titrated with the strongly basic tetra-n-butylammonium hydroxide solution (TBAOH) under non-aqueous conditions.

The same analysis method is used in the standards EN 15168 and DIN 53240-3.

Instruments

- Sample changer with 2 towers
- Magnetic stirrer for sample changer, 2x
- Titrator with DET mode
- 50 mL buret
- 20 mL buret, 2x
- 2 mL buret
- Titration head with Dis-Cover, 6.9914.158
- Dis-Cover Lids for beakers (6.1459.300), 25x, 6.9920.164

Electrodes

Solvotrode easyClean 2 m cable	6.0229.020

Reagents

This Bulletin contains no information about handling the reagents mentioned; nor does it indicate any safety measures that have to be observed. Please obtain the necessary information from the appropriate regulations and safety data sheets.

- Acetonitrile, purity > 99.5%
- p-Toluenesulfonyl isocyanate (TSI), purity > 95%
- Deionized water
- Tetra-n-butylammonium hydroxide in 2-propanol/methanol, c(TBAOH) = 0.1 mol/L
- Potassium hydrogen phthalate, KHP, p.a.

Solutions

Titrant	c(TBAOH) = 0.1 mol/L in 2-propanol/methanol If possible this solution should be bought from supplier.
TSI reagent	TSI must not become moist (vigorous reaction); working under protective gas (N_2) under a fume hood is strongly recommended. 20 mL TSI is pipetted from a glass volumetric pipet into a dry 500-mL volumetric flask half-full with acetonitrile. The solution is made up to the mark with acetonitrile and thoroughly shaken. The TSI reagent has a shelf life of one month.
Electrolyte	c(TEABr) = 0.4 mol/L in ethylene glycol Metrohm No. 6.2320.000
Electrode rinsing solution	Acetonitrile

Standard

KHP	Potassium hydrogen phthalate is dried at 120 °C for 2 h and cooled down in a desiccator for at least 1 h.

Sample preparation

Previous to the sampling the sample should be homogenized.

Analysis

Titer

Approximately 180 mg dried KHP is weighed into a titration vessel and 60 mL CO_2-free H_2O is added. The solution is then titrated using c(TBAOH) = 0.1 mol/L in 2-propanol/ methanol until after the equivalence point.

Sample

The amount of sample required for the determination according to ASTM depends on the expected hydroxyl number (HN_e). The sample weight m_s is calculated according to the following equation.

$$m_s = \frac{40}{HN_e}$$

m_s:	Sample weight to be used for the analysis in g
40:	Factor for the sample weight calculation
HN_e:	Expected hydroxyl number in mg KOH/g

The manually homogenized sample is weighed out into a 120-mL PP beaker, a stirring bar is added and the beaker is sealed with a Dis-Cover lid. The beaker is placed on the sample changer. When the method has been started, 10 mL acetonitrile is added automatically. After a stirring time of 30 s and dissolution of the sample, 10 mL TSI is added. Then the beaker is resealed and stirred slowly for 5 min.

The chemical reaction is interrupted by opening the lid and adding 0.5 mL deionized water. After stirring for 60 s 40 mL acetonitrile is added and the sample is titrated with c(TBAOH) = 0.1 mol/L in 2-propanol/methanol until after the second equivalence point.

At the end of the titration the Solvotrode easyClean is first immersed in a PP beaker containing acetonitrile. Then the glass membrane (bulp of the electrode) is immersed in deionized water and left there until the next measurement.

At the end of a series of measurements the electrode is automatically stored in a beaker containing acetonitrile until the start of the next analysis.

Parameters

Titer

Mode	DET U
Stirrer	6
Pause	30 s
Signal drift	50 mV/min
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 µL
EP criterion	10
EP recognition	greatest

Sample

Mode	DET U
Stirrer	6
Pause	30 s
Signal drift	50 mV/min
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 µL
Stop EP	2
Volume after EP	1 mL
EP criterion	5
EP recognition	all

Calculation

Titer

$$f = \frac{m_s}{V_{EP1} \times c_{TBAOH} \times M_A}$$

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_A:	Molecular weight of the analyte; here 204.2 g/mol

Sample

$$HN = \frac{(V_{EP2} - V_{EP1}) \times c_{TBAOH} \times f \times M_{KOH}}{m_s}$$

HN:	Hydroxyl number in mg KOH / g sample
V_{EP2}:	Titrant consumption until the second equivalence point in mL
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{TBAOH}:	Concentration of titrant in mol/L
f	Titer of titrant
M_{KOH}:	Molecular weight of potassium hydroxide; 56.106 g/mol
m_S:	Sample weight in g

Example determination

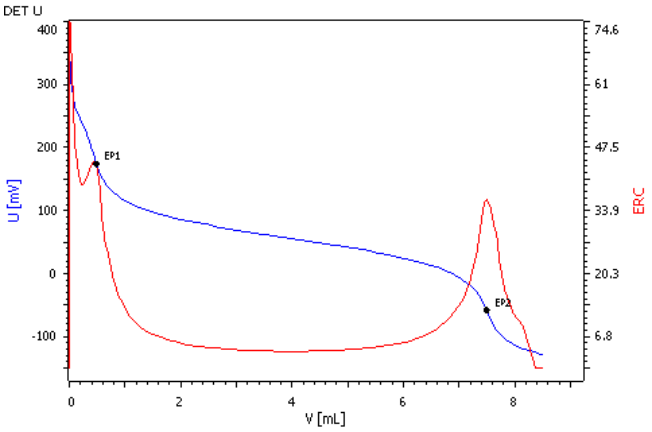

Fig. 2: Titration curve of the hydroxyl number determination according to ASTM E1899 for a polypropylene glycol

Comments

- If the sample cannot be dissolved in acetonitrile, 10 mL THF or 3 mL toluene and 7 mL acetonitrile can be used for the dissolution. However, the best titration curves are obtained with acetonitrile.
- In case the amount of strong acids is too low and no EP1 is found, it is possible to spike the sample with 2 mL c(HCl) = 0.1 mol/L. The c(HCl) = 0.1 mol/L is added instead of the deionized water as it will also quench the TSI.
  The result of the titration is not influenced by the spiking, because the volume difference EP2 – EP1 is taken for the calculation.
- 1-Octanol can be used as reference material, it has a hydroxyl number (HN) of 430.08 mg KOH/g.
- c(TEABr) = 0.4 mol/L in ethyleneglycol is recommended as electrolyte for non-aqueous titrations with alkaline titrants.
- The Solvotrode is usually delivered with c(LiCl) = sat as electrolyte. After changing the electrolyte to c(TEABr) = 0.4 mol/L in ethyleneglycol the Solvotrode is left to adjust to the new electrolyte overnight before using it.
- When not in use for longer periods, the Solvotrode is stored in the electrolyte.
- 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.
- For automation, the acetonitrile addition is increased from 30 mL to 40 mL, in order to ensure that the Solvotrode is immersed to a sufficient depth.
- The standard DIN 53240-3 differs in the following points from the method described here:
  - A mixture of toluene and acetonitrile (3:7 v/v) is used for the dissolution of the sample.
  - 1.5 mL deionized water is used to stop the reaction and the solution is afterwards stirred for 3 min.
  - The sample is dissolved at approx. 30 °C.
  - The TSI reaction is carried out at approx. 30 °C.
- In the standard DIN EN 15168 60 mL THF is added instead of 40 mL acetonitrile prior to the start of the titration.

References

- ASTM E1899
  Standard Test Method for Hydroxyl Groups Using Reaction with p-Toluenesulfonyl Isocyanate (TSI) and Potentiometric Titration with Tetrabutylammonium Hydroxide
- EN 15168
  Surface active agents – Determination of hydroxyl value – p-Toluenesulfonyl isocyanate (TSI) method and potentiometric titration with tetrabutylammonium hydroxide
- DIN 53240-3
  Binders for paints and varnishes - Determination of hydroxyl value - Part 3: Rapid test
- Metrohm Leaflet
  Leaflet for LL Solvotrode, 8.109.8046
- Application Bulletin 404
  Determination of the total acid number in petroleum products

EN ISO 4629-2

Summary

The method proposed in DIN EN ISO 4629-2, which replaces DIN 53240-2, is based on the catalytic acetylation of the hydroxyl group. After hydrolysis of the intermediate product, the remaining acetic acid is titrated with alcoholic KOH solution under non-aqueous conditions.

Instruments

- Sample changer with 2 towers
- Magnetic stirrer for sample changer, 2x
- Titrator with DET mode
- 50 mL buret
- 20 mL buret, 2x
- 2 mL buret
- Titration head with Dis-Cover, 6.9914.158
- Dis-Cover Lids for beakers (6.1459.300), 25x, 6.9920.164

Electrodes

Solvotrode easyClean 2 m cable	6.0229.020

Reagents

This Bulletin contains no information about handling the reagents mentioned; nor does it indicate any safety measures that have to be observed. Please obtain the necessary information from the appropriate regulations and safety data sheets.

- N-Methylpyrrolidone, 1-methyl-2-pyrrolidone, NMP, p.a.
- Acetic anhydride, p.a.
- 4-N-Dimethylaminopyridine, p.a.
- Water, deionized (electrode rinsing solution)
- Potassium hydroxide in methanol, c(KOH) = 0.5 mol/L

Solutions

Titrant	c(KOH) = 0.5 mol/L in methanol If possible this solution should be bought from supplier.
Acetylation mixture	10% acetic anhydride in NMP (v/v). The solution is stored in an amber glass bottle.
Catalyst solution	1% 4-N-Dimethylaminopyridine in NMP (w/v)
Electrolyte	c(TEABr) = 0.4 mol/L in ethylene glycol Metrohm No. 6.2320.000

Standard

KHP	Potassium hydrogen phthalate is dried at 120 °C for 2 h and cooled down in a desiccator for at least 1 h.

Sample preparation

Previous to the sampling the sample should be homogenized.

Analysis

Titer

Approximately 2.5 g dried KHP is weighed into a titration vessel and 150 mL CO_2-free H_2O is added. The solution is then titrated using c(KOH) = 0.5 mol/L in methanol until after the equivalence point.

Blank

A blank determination is carried out as described in the section *Sample* while omitting the sample.

The blank value has to be determined daily.

Sample

The amount of sample required for the determination according to DIN EN ISO depends on the expected hydroxyl number (HN_e). The sample weight m_s is calculated according to the following equation.

$$m_s = \frac{300}{HN_e}$$

m_s: Sample weight to be used for the analysis in g
300: Factor for the sample weight calculation
HN_e: Expected hydroxyl number in mg KOH/g

The calculated amount of sample is weighed out directly into a 120-mL PP beaker. A stirring bar and Dis-Cover lid are added and the beaker is placed on the sample rack. The lid is raised automatically by the magnetic Dis-Cover arm, 30 mL catalyst solution and 10 mL acetylation mixture are added and the beaker is resealed. The sealed sample is stirred for at least 15 min (the reaction time depends on the type of sample). The lid is then again raised automatically and the reaction is interrupted by addition of 3 mL deionized water. The beaker is resealed and stirred for a further 12 min. The titration for determining the hydroxyl number is carried out using c(KOH) = 0.5 mol/L in methanol until after the equivalence point.

At the end of the titration the Solvotrode easyClean is first immersed in a PP beaker containing acetonitrile and then stored until the next measurement with only the membrane immersed in a beaker with deionized water.

At the end of a series of measurements the electrode is automatically stored in a beaker containing acetonitrile until the start of the next analysis.

Parameters

Titer

Mode	DET U
Stirrer	6
Pause	30 s
Signal drift	50 mV/min
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 µL
EP criterion	10
EP recognition	greatest

Sample/Blank

Mode	DET U
Stirrer	5
Pause	30 s
Signal drift	50 mV/min
Min. waiting time	15 s
Max. waiting time	30 s
Meas. point density	4
Min. increment	50 µL
Stop EP	1
Volume after EP	2 mL
EP criterion	5
EP recognition	greatest

Calculation

Titer

$$f = \frac{m_s}{V_{EP1} \times c_{KOH} \times M_A}$$

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_A:	Molecular weight of the analyte; here 204.2 g/mol

Sample

$$HN = \frac{(Blank - V_{EP1}) \times c_{KOH} \times f \times M_{KOH}}{m_s} + AN$$

HN:	Hydroxyl number in mg KOH / g sample
Blank:	Titrant consumption for the blank determination in mL
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{KOH}:	Concentration of titrant in mol/L
f	Titer of titrant
M_{KOH}:	Molecular weight of potassium hydroxide; 56.106 g/mol
m_S:	Sample weight in g
AN:	Previously as per ISO 2114 method A determined partial acid number of the sample (described in AN-T-164)

Example determination

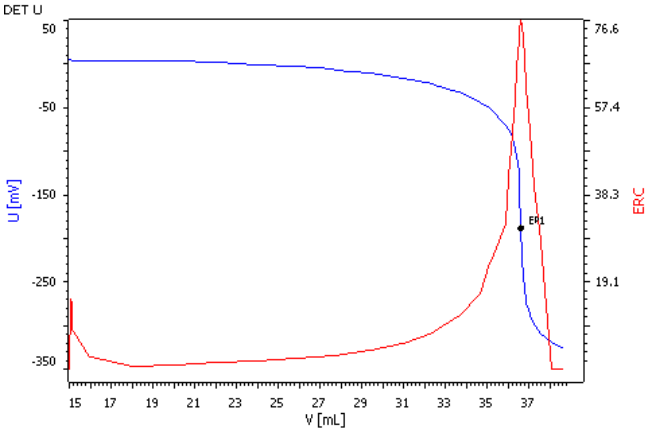

Fig. 3: Titration curve of the hydroxyl number determination according to DIN EN ISO 4629-2 for an oxooil

Comments

- Secondary hydroxyl groups usually need a reaction time of 60 min for the acetylation and 30 min for the hydrolysis after the water addition. Experience has shown that this is also the case for polyols with secondary hydroxyl groups.
- 1-Octanol can be used as reference material, it has a hydroxyl number (HN) of 430.08 mg KOH/g
- c(TEABr) = 0.4 mol/L in ethyleneglycol is recommended as electrolyte for non-aqueous titrations with alkaline titrants.
- The Solvotrode is usually delivered with c(LiCl) = sat as electrolyte. After changing the electrolyte to c(TEABr) = 0.4 mol/L in ethyleneglycol the Solvtrode is left to adjust to the new electrolyte overnight before using it.
- When not in use for longer periods, the Solvotrode is stored in the appropriate electrolyte.

References

- EN ISO 4629-2
  Binders for paints and varnishes - Determination of hydroxyl value - Part 2: Titrimetric method using a catalyst
- AN-T-164
  Partial acid number in unsaturated polyester resin in accordance with EN ISO 2114
- Metrohm Leaflet
  Leaflet for LL Solvotrode, 8.109.8046
- Application Bulletin 404
  Determination of the total acid number in petroleum products

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