Fully automated potentiometric determination of the hydroxyl number (HN) according to ASTM E 1899-08 and DIN 53240-2

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Titration

Introduction

Hydroxyl is an important functional group and knowledge of its content is required in many intermediate and end-use products such as polyols, resins, lacquer raw materials and fats (petroleum industry). The test method to be described determines primary and secondary hydroxyl groups. The hydroxyl number is defined as the mg of KOH equivalent to the hydroxyl content of 1 g of sample.

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

$$H_3C\text{-}CO\text{-}O\text{-}CO\text{-}CH_3 + R\text{-}OH \longrightarrow R\text{-}O\text{-}CO\text{-}CH_3 + CH_3COOH$$

However, this method suffers from the following drawbacks:

- The sample must be boiled under reflux for 1 h (long reaction time and laborious, expensive sample handling)
- The method cannot be automated
- Small hydroxyl numbers cannot be determined exactly
- Pyridine has to be used, which is both toxic and foul-smelling

Both standards, ASTM E 1899-08 and DIN 53240-2, offer alternative methods that do not require manual sample preparation and therefore can be fully automated:

- The method suggested in **ASTM E 1899-08** is based on the reaction of the hydroxyl groups attached to primary and secondary carbon atoms with excess toluene-4-sulfonyl-isocyanate (TSI) to form an acidic carbamate. The latter can then be titrated in a non-aqueous medium with the strong base tetrabutyl-ammonium hydroxide (TBAOH).
- The method suggested in **DIN 53240-2** is based on the catalyzed acetylation of the hydroxyl group. After hydrolysis of the intermediate, the remaining acetic acid is titrated in a non-aqueous medium with alcoholic KOH solution.

The present work demonstrates and discusses an easy way to determine the hydroxyl number according to ASTM E 1899-08 or DIN 53240-2 with a fully automated titrimetric system for a great variety of industrial oil samples.

Instrumentation

- 814 USB Sample Processor
- 809 Titrando
- 800 Dosino
- Solvotrode
- ***tiamo***™ software

Analytical procedure

The appropriate amount of sample (defined by ASTM and DIN) is weighed accurately into a titration beaker that is equipped with a stirring bar and lid. The beaker is placed on the rack of the system and the following steps are carried out fully automatically:

ASTM E 1899-08

- Add 10 mL acetonitrile
- Stir under cover for 30 s
- Add 10 mL TSI
- Stir under cover for 5 min
- Add 0.5 mL ultrapure water
- Stir under cover for 60 s
- Add 40 mL acetonitrile
- Dynamic equivalence point titration (DET U) with c(TBAOH) = 0.1 mol/L in isopropanol/methanol

DIN 53240-2

- Add 30 mL catalyst and 10 mL acetylation mixture
- Stir under cover for 15 min
- Add 3 mL distilled water
- Stir under cover for 12 min
- Dynamic equivalence point titration (DET U) with c(KOH) = 0.5 mol/L in methanol

After the titration, the electrode and the cell equipment are automatically rinsed; subsequently, the electrode is conditioned in ethanol and distilled water.

Calculation

$$HN_{ASTM} = \frac{(EP2 - EP1) \times Conc. \times 56.106 \times Titer}{Sample\ size}$$

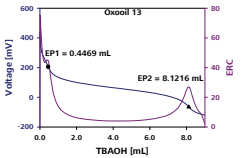
$$HN_{DIN} = \frac{(Blank - EP1) \times Conc. \times 56.106 \times Titer}{Sample\ size} + TAN$$

HN:	Hydroxyl number in mg KOH per g sample	56.106:	Molecular weight of KOH in g/mol
EP1:	Titrant consumption up to the first endpoint in mL	Titer:	Titer of the titrant used (dimensionless)
EP2:	Titrant consumption up to the second endpoint in mL	Sample size:	Sample size in g
Blank*:	Blank value of solvent and reagents	TAN:	Previously determined total acid number (TAN) in mg KOH per g sample
Conc.:	Concentration of the titrant used		

*The blank value is extremely important for the calculation and has an approximate value of 40 mL. It has to be verified daily.

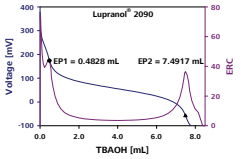
Results

ASTM E 1899-08



Oxooil 13*						
Sample size [g]	0.322	0.296	0.296	0.308	Mean*	RSD
HN_{ASTM} [mg KOH/g]	128	132	134	127	130.0	2.54%

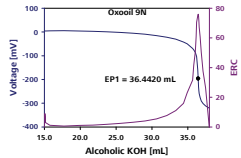
*expected value: 120...130 mg KOH/g



Lupranol® 2090*						
Sample size [g]	1.274	1.332	1.253	1.303	Mean*	RSD
HN_{ASTM} [mg KOH/g]	29.8	29.9	29.9	29.7	29.6	1.39%

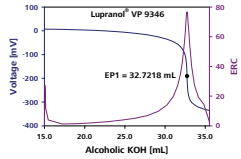
*expected value: 30 mg KOH/g; registered trade mark of BASF group in many countries

DIN 53240-2



Oxooil 9N*						
Sample size [g]	1.306	1.226	1.111		Mean*	RSD
HN_{DIN} [mg KOH/g]	102	104	103		103	0.97%

*expected value: 100 mg KOH/g



Lupranol® VP 9346*						
Sample size [g]	0.535	0.538	0.430		Mean*	RSD
HN_{DIN} [mg KOH/g]	446	448	451		448	0.56%

*expected value: 400...450 mg KOH/g; registered trade mark of BASF group in many countries

Comparison of the different techniques

ASTM E 1899-08	DIN 53240-2
+ Reaction at room temperature	+ Reaction at room temperature
+ Covered reaction in an automated run	+ Covered reaction in an automated run
+ Small hydroxyl numbers are easy to determine	+ Small hydroxyl numbers are easy to determine
+ No more heating or boiling under reflux	+ No more heating or boiling under reflux
+ Easy procedure – only one single titration. No blank titration necessary	+ Very good standard deviation and recovery
+ Short reaction time	

Conclusion

The presented titration system can be used for the fully automated determination of the hydroxyl number (HN) according to ASTM or DIN. The method allows, for example, the determination of polyols and oxooils without boiling under reflux or other sample preparation and is therefore a big benefit for laboratories that have to analyze a great number of these samples per day.

References

(1) ASTM E 1899-08, Standard test method for hydroxyl groups using reaction with p-toluene-sulfonylisocyanate (TSI) and potentiometric titration with tetrabutylammonium hydroxide.
(2) DIN 53240-2, Determination of hydroxyl value – Part 2: method with catalyst.

Acknowledgements

The authors thank BASF SE, Ludwigshafen, Germany, for providing the Oxooil and Lupranol® samples.

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