Application Bulletin

Of interest to:	General analytical laboratories; Organic chemistry; Plastics	A 1, 3, 6

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

Summary

The determination of the acid number, the hydroxyl number 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.

Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or
  796 Titroprocessor with 700 Dosino or 685 Dosimat
- 2.728.0040 Magnetic Stirrer
- 6.3014.XX3 Exchange Units
- 6.0229.100 LL Solvotrode [reference electrolyte: tetraethylammonium bromide c(TEABr) = 0.4 mol/L in ethylene glycol, Metrohm no. 6.2320.000] with 6.2104.020 electrode cable

1. Determination of the acid number

Reagents

- Titrant: potassium hydroxide solution, c(KOH) = 0.05 mol/L in methanol, CO_2-free
- Solvent A:
  methanol : dist. water = 3 : 1 (volume ratio)
- Solvent B:
  ethanol : toluene = 1 : 1 (volume ratio)
- Benzoic acid, p.a. for the titer determination

Analysis

Weigh 30 … 50 g sample into a glass beaker and add 50 mL solvent, resulting in an homogeneous mixture. Preferably, solvent A is used. If, however, this does not mix well with the sample, solvent B has to be applied (preliminary tests). In this case it is also possible to heat the mixture in order to improve solubility. The sample is then titrated slowly with c(KOH) = 0.05 mol/L using the MET mode.

In the same way the blank of the used solvent has to be determined. This blank consumption is stored as common variable C31 in the titrator.

Upon completion of the titration, rinse the Solvotrode with ethanol and dist. water. When not in use (e.g. over night), store the electrode in dist. water.

Calculation

The acid number is expressed in mg KOH / g sample.

acid number = (EP1 – C31) * C01 * C02 / C00

EP1 = titrant consumption in mL
C00 = 30 ... 50 (sample weight in g)
C01 = 2.8 [= c(KOH) in mol/L * M(KOH) in g/mol = 0.05 * 56.1]
C02 = titer of the titrant (can be determined with benzoic acid)
C31 = blank consumption in mL

2. Determination of the hydroxyl number

Reagents

- Titrant: sodium hydroxide solution, c(NaOH) = 1 mol/L
- Reaction solution: c(phthalic acid anhydride) = 1 mol/L in anhydrous pyridine
- Solvents: pyridine, p.a., anhydrous and dist. water

Analysis

Weigh approx. 2 g sample into an Erlenmeyer flask with standard ground-glass joint and dissolve in 20.0 mL reaction solution. Attach a reflux cooler and heat up to 130 °C for 45 min. After cooling down, rinse the cooler three times with 10 mL pyridine each, then three times with 10 mL dist. water each into the Erlenmeyer flask. Afterwards titrate the formed phthalic acid with c(NaOH) = 1 mol/L.

In order to determine the titrant consumption for the reaction solution and solvents, a blank sample is treated and titrated in exactly the same way as the actual sample. This blank consumption is stored as common variable C31 in the titrator.

The titrations are carried out with a start volume that is approx. 20 mL for the sample and approx. 35 mL for the blank.

Calculation

The hydroxyl number is expressed in mg KOH / g sample.

hydroxyl number = (C31 – EP1) * C01 / C00

EP1 = titrant consumption in mL
C00 = approx. 2 (sample weight in g)
C01 = 56.1 [= c(NaOH) in mol/L * M(KOH) in g/mol]
C31 = blank consumption in mL

Remarks

- The sample must be completely dissolved before heating up.
- For hydroxyl numbers between 100 and 350, the acid number – if it is greater than 0.5 – is added to the hydroxyl number.
- An alternative method (without heating of the sample) is described in standard ASTM E 222-94, method C.

3. Determination of the isocyanates (CNO)

Reagents

- Titrant: hydrochloric acid, c(HCl) = 1 mol/L in methanol
- Reaction solution: c(dibutylamine) = 1 mol/L in toluene
- Solvents: toluene, p.a. and methanol, p.a.

Analysis

Weigh approx. 2 g sample into an Erlenmeyer flask with standard ground-glass joint and, heating slightly if necessary, dissolve in 30 mL toluene. Add 20.0 mL reaction solution, stopper the flask and allow to react for 10 min on the magnetic stirrer. Afterwards add 30 mL methanol and titrate back the excess dibutylamine with c(HCl) = 1 mol/L.

In order to determine the titrant consumption for the reaction solution and solvents, a blank sample is treated and titrated in exactly the same way as the actual sample. This blank consumption is stored as common variable C31 in the titrator.

Calculation

% CNO = (C31 – EP1) * C01 * C02 / C00

EP1 = titrant consumption in mL
C00 = approx. 2 (sample weight in g)
C01 = 42.0 [= c(HCl) in mol/L * M(CNO) in g/mol]
C02 = 0.1 (conversion factor for %)
C31 = blank consumption in mL

Literature

- ASTM D 4662-93
  Standard Test Methods for Polyurethane Raw Materials. Determination of Acid and Alkalinity Numbers of Polyols.
- ASTM E 222-94
  Standard Test Methods for Hydroxyl Groups Using Acetic Anhydride Acetylation.
- DIN 16945 (1976)
  Reaktionsharze, Reaktionsmittel und Reaktionsharzmassen – Prüfverfahren.
- DIN 53188 (1975)
  Anstrichstoffe – Epoxidharze – Prüfung.
- ISO 2114:1996
  Plastics – Unsaturated polyester resins – Determination of partial acid value and total acid value.
- ISO 2554:1997
  Plastics – Unsaturated polyester resins – Determination of hydroxyl value.
- J. G. Pritchard, Y. L. Lang Fung Chung
  Determination of vicinal hydroxyl groups in polyvinylalcohol
  Talanta 23 (1976) 237–239.
- R. Kerker, M. Störi
  Simultanbestimmung von Hydroxyl- und Epoxidgruppen in Epoxidharzen
  Chimia 33 (1979) 84–87.
- S. L. Wellons, M. A. Carey, D. K. Elder
  Determination of hydroxyl content of polyurethane polyols
  Anal. Chem. 52 (1980) 1374–1376.

Figures

```
 'pa
736 GP Titrino          04268   736.0011
date  99-11-09      time  14:03       12
MET  U                   SZ
parameters
>titration parameters
  V step                 0.10 ml
  titr.rate              max. ml/min
  signal drift             15 mV/min
  equilibr.time            43 s
  start V:                OFF
  pause                    60 s
  dos.element:    internal D0
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                abs.
  stop V                    5 ml
  stop U                  OFF mV
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                      30 mV
  EP recognition:    greatest
  fix EP1 at U           OFF mV
  pK/HNP:                OFF
>preselections
  req.ident:              OFF
  req.smpl size:        value
  activate pulse:         OFF
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```

Fig. 1: *Parameter settings on the 736 GP Titrino for the determination of the acid number.*

```
 'fr
736 GP Titrino          04268   736.0011
date  99-11-09      time  14:03       12
U(init)           7 mV  MET U         SZ
smpl size   14.2055 g
EP1           2.280 ml          -215 mV
SZ            0.374 mg/g
stop V reached
          ============


 'cu
736 GP Titrino          04268   736.0011
date  99-11-09      time  14:03       12
start V      0.000 ml  MET  U         SZ
2.0 ml/div      dU=100.0 mV/div
```

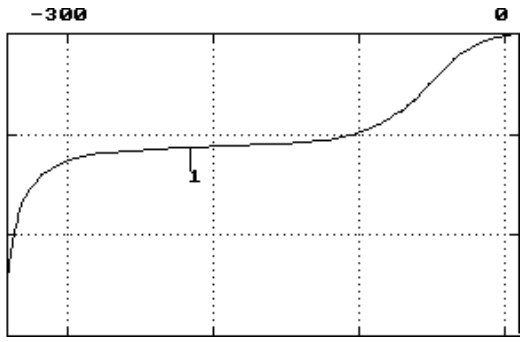


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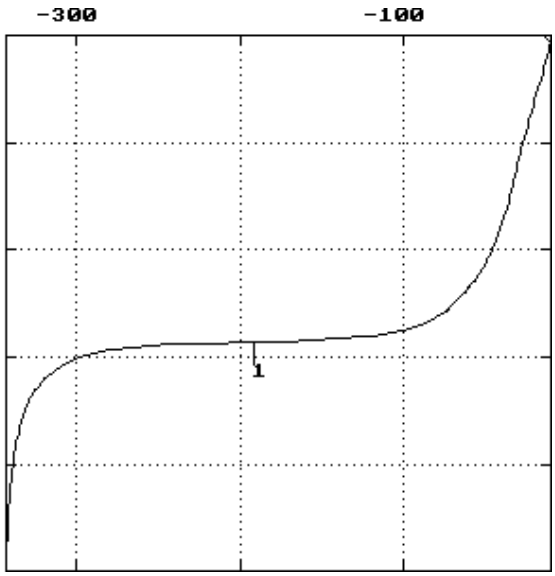
Fig. 2: *Result block and titration curve for the determination of the acid number in a raw material;*
AVG(3) = 0.378 ± 0.001 mg KOH / g sample.

```
 'pa
736 GP Titrino          04268   736.0011
date  99-11-08      time  09:10        1
MET  U                OH-Z
parameters
>titration parameters
  V step                 0.10 ml
  titr.rate              max. ml/min
  signal drift             30 mV/min
  equilibr.time            32 s
  start V:               abs.
  start V                  20 ml
  dos.rate               max. ml/min
  pause                    30 s
  dos.element:    internal D0
  meas.input:               1
  temperature            25.0 °C
>stop conditions
  stop V:                abs.
  stop V                   30 ml
  stop U                  OFF mV
  stop EP                   9
  filling rate           max. ml/min
>statistics
  status:                 OFF
>evaluation
  EPC                      30 mV
  EP recognition:    greatest
  fix EP1 at U           OFF mV
  pK/HNP:                OFF
>preselections
  req.ident:             OFF
  req.smpl size:       value
  activate pulse:        OFF
          ============
```

Fig. 3: *Parameter settings for the determination of the hydroxyl number and isocyanates.*

```
 'fr
736 GP Titrino          04268   736.0011
date  99-11-08      time  09:10         1
U(init)          39 mV  MET U       OH-Z
smpl size    1.9713 g
EP1         25.730 ml           -191 mV
OH-Z         334.1 mg/g
stop V reached
         ============


 'cu
736 GP Titrino          04268   736.0011
date  99-11-08      time  09:10         1
start V     20.000 ml  MET  U       OH-Z
2.0 ml/div      dU=100.0 mV/div
```




```
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```

Fig. 4: *Result block and titration curve for the determination of the hydroxyl number in a raw material;*
AVG(3) = 333.5 ± 0.5 mg KOH / g sample.

```
 'fr
736 GP Titrino          04268   736.0011
date  99-11-10      time  10:23         1
U(init)        -115 mV  MET U         CNO
smpl size    2.0754 g
EP1           4.008 ml             271 mV
CNO           30.96 %
stop V reached
         ============


 'cu
736 GP Titrino          04268   736.0011
date  99-11-10      time  10:23         1
start V      0.000 ml  MET  U         CNO
2.0 ml/div      dU=100.0 mV/div
```

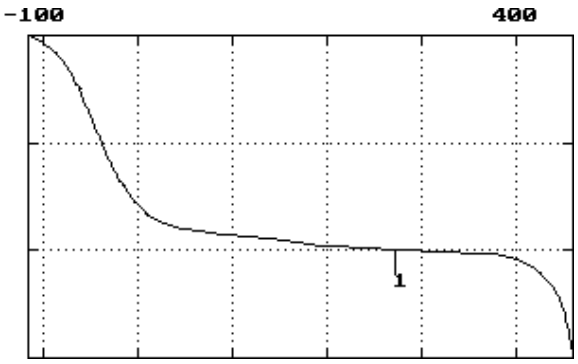


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Fig. 5: *Result block and titration curve for the determination of the isocyanates in a raw material;*
AVG(3) = 31.09 ± 0.09 % CNO.