

Acid Value in Polyester Resins and Binders for Paints and Varnishes

The acid number is the amount of potassium hydroxide used to neutralize acidic components in different samples (mg KOH/g). Here the determination of the acid value according to DIN EN ISO 2114 (2000) is presented.

Sample	Resin glue
Compound	Acidic components
Chemicals	50 mL solvent mixture toluene:ethanol:acetone 4:2:3 (v:v:v)
Titrant	KOH in ethanol: $c(\text{KOH}) = 0.1 \text{ mol/L}$
Standard	Benzoic acid, 70 – 120 mg
Indication	DGi113-SC
Chemistry	$\text{OH}^- + \text{H}^+ = \text{H}_2\text{O}$
Calculation	Blank determination (m084B): $R1 = Q$ stored as blank value B[Blank M084] Acid value determination (m084A): $R1 = (Q1 - B[\text{Blank M084}]) \cdot C/m$ $C = 56.1$
Waste disposal	Organic solvent waste
Author, Version	Daniel Widmer MSG Anachem, March 2008

Preparation and Procedures

1) The titer determination is performed by titrating approx. 0.1 g benzoic acid in 50 mL deionized water (see M534). The titer can also be determined using potassium hydrogen phthalate.

2) Solubility check of the sample:
The solvent mixture according to DIN EN ISO 2114 is toluene:ethanol 2:1 (v:v) or, if sample is not soluble, toluene:ethanol:acetone 4:2:3 (v:v:v). Stir vigorously. Speed and stirring time can be adapted according to the viscosity or the low solubility of the sample.
If the dissolution of the sample is not straight-forward, heating or ultrasonic irradiation may be applied.

3) A blank value is determined for every new batch of solvent mixture (method m084B) and stored as B[Blank M084].

4) Depending on the acid value of the sample, different sample amounts and titrant concentrations are requested, i.e. $c(\text{KOH}) = 0.1 \text{ mol/L}$ and 5 g of sample for expected 5 mg KOH/g.

Remarks

This application describes the determination of the acid value of resins, polymers, binders, oils, fats, fatty acids, solvents, and softeners.
It is not applicable to phenolic resins.

The method has been developed according to DIN EN ISO 2114 (2000), which replaces DIN 53402 (1973) and DIN EN ISO 3682 (1998).

The regulation DIN EN ISO 2114 (2000) describes two methods: Method A for partial acid value und method B for total acid value. In method A all carboxyl-terminated groups and free acids plus 50% of the free acid anhydrides are neutralized. In method B a different solvent is used to neutralize the remaining 50% of the anhydrides. This application refers to method A described in DIN EN ISO 2114 (2000).

Instruments

Titration Excellence T50 / T70 / T90
Rondolino Sample Changer with PowerShower™
LabX Titration Software

Accessories

Balance XS205
Olivetti Printer JobJet 210

Results**All results**

Method-ID	m084A
Sample	resin glue (1/6)
R1 (Acid Value)	5.191 mg KOH/g
Sample	resin glue (2/6)
R1 (Acid Value)	5.163 mg KOH/g
Sample	resin glue (3/6)
R1 (Acid Value)	5.160 mg KOH/g
Sample	resin glue (4/6)
R1 (Acid Value)	5.166 mg KOH/g
Sample	resin glue (5/6)
R1 (Acid Value)	5.149 mg KOH/g
Sample	resin glue (6/6)
R1 (Acid Value)	5.175 mg KOH/g

Statistics

Method-ID	m084A
R1	Acid Value
Samples	6
Mean	5.167 mg KOH/g
s	0.014 mg KOH/g
srel	0.278%

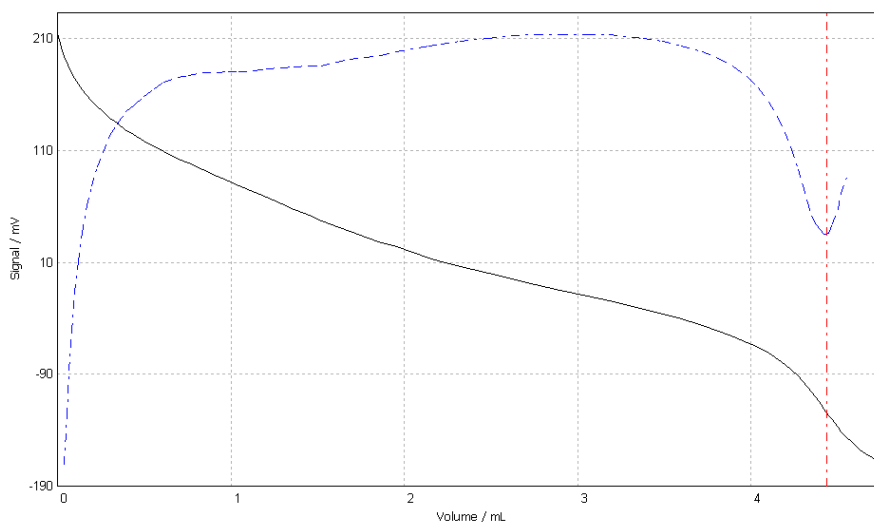
Titration curve

Table of measured values

	Volume mL	Increment mL	Signal mV	Change mV	1st deriv. mV/mL	Time s	Temperature °C
	0.000	NaN	208.4	NaN	NaN	0	25.0
	0.005	0.005	203.5	-4.9	NaN	6	25.0
	0.010	0.005	200.2	-3.3	NaN	12	25.0
	0.020	0.010	194.0	-6.2	NaN	18	25.0
	0.030	0.010	189.3	-4.7	NaN	24	25.0
	0.044	0.014	183.9	-5.4	-404.38	29	25.0
	0.057	0.013	179.0	-4.9	-366.35	34	25.0
	0.073	0.016	173.3	-5.7	-323.18	39	25.0
	0.087	0.014	169.1	-4.2	-292.04	44	25.0
	0.107	0.020	163.5	-5.6	-257.76	49	25.0
	0.126	0.019	158.8	-4.7	-230.93	54	25.0
	0.150	0.024	154.2	-4.6	-204.74	58	25.0
	0.182	0.032	148.1	-6.1	-179.07	63	25.0
	0.209	0.027	143.3	-4.8	-161.98	68	25.0
	0.238	0.029	139.1	-4.2	-147.50	73	25.0
	0.282	0.044	132.8	-6.3	-130.41	79	25.0
	...	...	...	...	...	...	...
	4.212	0.031	-95.5	-4.9	-165.50	305	25.0
	4.240	0.028	-100.2	-4.7	-183.13	310	25.0
	4.268	0.028	-105.9	-5.7	-199.82	315	25.0
	4.288	0.020	-110.1	-4.2	-210.67	319	25.0
	4.312	0.024	-115.2	-5.1	-220.13	324	25.0
	4.334	0.022	-120.2	-5.0	-224.49	328	25.0
EQP1	4.349976	NaN	-123.7	NaN	-225.16	NaN	NaN
	4.355	0.021	-124.8	-4.6	-224.87	332	25.0
	4.379	0.024	-130.1	-5.3	-222.12	336	25.0
	4.401	0.022	-135.2	-5.1	-214.21	341	25.0
	4.422	0.021	-139.5	-4.3	-201.45	345	25.0
	4.450	0.028	-145.1	-5.6	-183.24	349	25.0
	4.476	0.026	-149.6	-4.5	-164.35	354	25.0
	4.510	0.034	-154.9	-5.3	NaN	358	25.0
	4.543	0.033	-159.3	-4.4	NaN	363	25.0
	4.588	0.045	-164.4	-5.1	NaN	368	25.0
	4.642	0.054	-169.3	-4.9	NaN	372	25.0

Comments

1) This titration was also carried out with titrant $c(\text{KOH}) = 0.01 \text{ mol/L}$ to determine lower acid values.

rapeseed oil:

6 samples (13 – 16 g) in 50 mL solvent mixture

mean: 0.158 mg KOH/g s: 0.001 mg KOH/g srel: 0.870%

synthetic resin paint (clear):

6 samples (0.4 – 0.6 g) in 50 mL solvent mixture

mean: 5.164 mg KOH/g s: 0.168 mg KOH/g srel: 3.267%

remark: very difficult to find the EQP because of the unsettled titration curve

A titration with titrant $c(\text{KOH}) = 0.002 \text{ mol/L}$ is extremely difficult: In the flat titration curve the EQP can hardly be determined. Alternatively an EP titration to -71 mV (pH 8.2) can be used.

2) Rinse the sensor with a solvent or solvent mixture that dissolves the sample. Between two samples the sensor should be conditioned with water. Use for instance position 6 at the program selection button of Rondolino and ethanol for rinsing with the PowerShower™.

3) The titration can also be indicated photometrically using a DP5 Phototrode™ and a color indicator. It can be affected by the amounts of the indicators, by the formation of precipitates, or by change in turbidity.

4) Use the same amount of solvent mixture for the blank as well as for the sample determination.

5) Substances which undergo side reactions with the alkaline titrant can not be titrated.

Method

001 Title		
Type	General titration	
Compatible with	T50 / T70 / T90	
ID	m084A	
Title	Acid Value DIN EN ISO 2114	
Author	widmer	
Date/Time	18.03.2008	07:46:34
Modified at	18.03.2008	11:07:03
Modified by	widmer	
Protect	No	
SOP	None	
002 Sample		
Number of IDs	1	
ID 1	resin glue	
Entry type	Weight	
Lower limit	0.0 g	
Upper limit	50.0 g	
Density	1.0 g/mL	
Correction factor	1.0	
Temperature	25.0°C	
Entry	Arbitrary	
003 Titration stand (Rondolino TTL)		
Type	Rondolino TTL	
Titration stand	Rondolino TTL 1	
004 Stir		
Speed	60%	
Duration	120 s	
Condition	No	
005 Titration (EQP) [1]		
Titrant		
Titrant	KOH in ethanol	
Concentration	0.1 mol/L	
Sensor		
Type	pH	
Sensor	DG113-SC	
Unit	mV	
Temperature acquisition		
Temperature acquis.	No	
Stir		
Speed	35%	
Predispense		
Mode	None	
Waiting time	0 s	
Control		
Control	User	
Titrant addition	Dynamic	
dE (set value)	5 mV	
dV (min)	0.005 mL	
dV (max)	0.5 mL	
Mode	Equilibrium controlled	
dE	0.5 mV	
dt	2 s	
t (min)	3 s	
t (max)	30 s	
Evaluation and recognition		
Procedure	Standard	
Threshold	100 mV	
Tendency	Negative	
Ranges	0	
Add. EQP criteria	No	
Termination		
At Vmax	10	
At potential	Yes	
Potential	-240	
Termination tendency	Negative	
At slope	No	
After number of recognized EQPs	Yes	
Number of EQPs	1	
Combined termination criteria	No	
006 Calculation R1		
Result	Acid Value	
Result unit	mg KOH/g	
Formula	R1=(QE-Q-B[Blank M084])*C/m	
Constant	C=M/z	
M	M[Potassium hydroxide]	
z	z[Potassium hydroxide]	
Decimal places	3	
Result limits	No	

007 Record		
Summary	Per Series	
Results	Per Series	
Raw results	Per Series	
Table of meas. values	Last titration function	
Sample data	Per Series	
Resource data	No	
E - V	Last titration function	
dE/dV - V	Last titration function	
log dE/dV - V	No	
d2E/dV2 - V	No	
BETA - V	No	
E - t	No	
V - t	No	
dV/dt - t	No	
T - t	No	
E - V & dE/dV - V	No	
V - t & dV/dt - t	No	
Method	No	
Series data	No	
Condition	No	
008 End of sample		
Blank determination		
001 Title		
Type	General titration	
Compatible with	T50 / T70 / T90	
ID	m084B	
Title	Blank Value	
Author	widmer	
Date/Time	14.03.2008	11:22:56
Modified at	14.03.2008	11:22:56
Modified by	widmer	
Protect	No	
SOP	None	
002 Sample		
Number of IDs	1	
ID 1	Solvent DIN ISO 2114	
Entry type	Fixed Volume	
Volume	50 mL	
Density	1.0 g/mL	
Correction factor	1.0	
Temperature	25.0°C	
003 Titration stand (Rondolino TTL)		
Type	Rondolino TTL	
Titration stand	Rondolino TTL 1	
004 Stir		
Speed	60%	
Duration	120 s	
Condition	No	
005 Titration (EQP) [1]		
Titrant		
Titrant	KOH in ethanol	
Concentration	0.1 mol/L	
Sensor		
Type	pH	
Sensor	DG113-SC	
Unit	mV	
Temperature acquisition		
Temperature acquis.	No	
Stir		
Speed	35%	
Predispense		
Mode	None	
Waiting time	0 s	
Control		
Control	User	
Titrant addition	Dynamic	
dE (set value)	5 mV	
dV (min)	0.001 mL	
dV (max)	0.005 mL	
Mode	Equilibrium controlled	
dE	0.5 mV	
dt	2 s	
t (min)	3 s	
t (max)	60 s	
Evaluation and recognition		
Procedure	Standard	
Threshold	100 mV	
Tendency	Negative	
Ranges	0	

Add. EQP criteria	No
Termination	
At Vmax	10
At potential	Yes
Potential	-240
Termination tendency	Negative
At slope	No
After number of recognized EQPs	Yes
Number of EQPs	1
Combined termination criteria	No
007 Record	
Summary	No
Results	Per Series
Raw results	Per Series
Table of meas. values	Last titration function
Sample data	Per Series
Resource data	No
E - V	Last titration function
dE/dV - V	No
log dE/dV - V	No
d ² E/dV ² - V	No
BETA - V	No
E - t	Last titration function
V - t	No
dV/dt - t	No
T - t	No
E - V & dE/dV - V	No
V - t & dV/dt - t	No
Method	No
Series data	No
008 End of sample	
009 Blank	
Name	Blank M084
Value	B=Mean[R1]
Unit	mmol
Limits	No
010 Calculation R2	
Result	Mean Consumption
Result unit	mmol
Formula	R2=Mean[R1]
Constant	C=1
M	M[None]
z	z[None]
Decimal places	5
Result limits	No
Record statistics	Yes
Extra statistical functions	No
Send to buffer	No
011 Record	
Summary	No
Results	Yes
Raw results	No
Resource data	No
Calibration curve	No
Method	No
Series data	No

