

Determination of the Amine Value

Determination of the amine value by non-aqueous titration in glacial acetic acid with perchloric acid.

| | |
|-----------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Sample | MOCA (4,4'-Diamino-3,3'-dichlorodiphenylmethane) |
| Compound | Amine groups in polymers and polymer raw materials / building blocks. |
| Chemicals | 60 mL glacial acetic acid |
| Titrant | Perchloric acid (HClO ₄) in glacial acetic acid. C(HClO ₄) = 0.1 mol/L |
| Standard | TRIS / THAM (IUPAC: 2-Amino-2-hydroxymethyl-propane-1,3-diol) |
| Indication | DG113-SC |
| Chemistry | $\text{HClO}_4 + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COOH}_2^+ + \text{ClO}_4^- \text{ (titrant)}$ $\text{MOCA} + \text{CH}_3\text{COOH}_2^+ \rightleftharpoons \text{MOCA-H}^+ + \text{CH}_3\text{COOH} \text{ (sample titration)}$ |
| Calculation | <p>Amine value in mg KOH/g: $R = (Q - B[\text{Amine Value}]) \cdot C/m$ $C = M/z$</p> <p>B[Amine Value] = blank value solvent.</p> |
| Waste disposal | Organic solvent waste. MOCA is harmful for the environment. |
| Author, Version | Melanie Nijman, v2.0 |

Preparation and Procedures

1) The amount of sample used depends on the expected amine number.

2) The recommended volume used for the titration should be between 30% and 70% of the total burette volume.

Sensor cleaning:

1) Rinse the sensor after each titration with glacial acetic acid (or a stronger solvent like e.g. acetone, if necessary).

2) Condition the sensor in water for at least 2 minutes to rehydrate the pH membrane of the electrode.

3) Rinse the electrode with glacial acetic acid before going to the next sample to remove of all the water.

Water is a stronger base than glacial acetic acid and would interfere with the titration; therefore its presence should be avoided.

Remarks

A blank value for the solvent is usually not required, if it is, a blank value like e.g. B[Amine Value] as given in the calculation should be used. If no blank value is required, B[Amine Value] can be omitted from the calculation.

When used for amine value determination of polyurethane raw materials, this application can be used as a basis for compliance with ASTM D6979-03 or ISO 25761.

The CH₃COOH₂⁺ ions created in the titrant composed of perchloric acid in glacial acetic acid, are very strong proton donors to normally weak bases, therefore the titrant works as an extremely strong acid solution.

With a weak base like an amine this means that the solvent / titrant combination enhances the alkaline properties of the amine. This makes it possible to titrate the amine solution and get a sharp endpoint which would not be possible in aqueous solutions.

Instruments

Titration Excellence T70/T90
Rondo 20 Sample Changer
1 additional dosing unit (20 mL)

Accessories

DV1010 and DV1020 Burettes
1 SP250 peristaltic pump ME-51108016
Titration beakers ME-101974
LabX titration software

Results

All results

| | |
|------------------|--------------------|
| Method-ID | m242-08 |
| Sample | MOCA (1/6) |
| R1 (Amine value) | 410.07197 mg KOH/g |
| Sample | MOCA (2/6) |
| R1 (Amine value) | 413.07536 mg KOH/g |
| Sample | MOCA (3/6) |
| R1 (Amine value) | 412.40496 mg KOH/g |
| Sample | MOCA (4/6) |
| R1 (Amine value) | 413.25155 mg KOH/g |
| Sample | MOCA (5/6) |
| R1 (Amine value) | 413.93275 mg KOH/g |
| Sample | MOCA (6/6) |
| R1 (Amine value) | 411.56977 mg KOH/g |

Statistics

| | |
|-----------|------------------------|
| Method-ID | m242-08 |
| R1 | Amine value (mg KOH/g) |
| Samples | n=6 |
| Mean | 412.38439 |
| s | 1.388390 |
| srel | 0.337% |

Titration curve

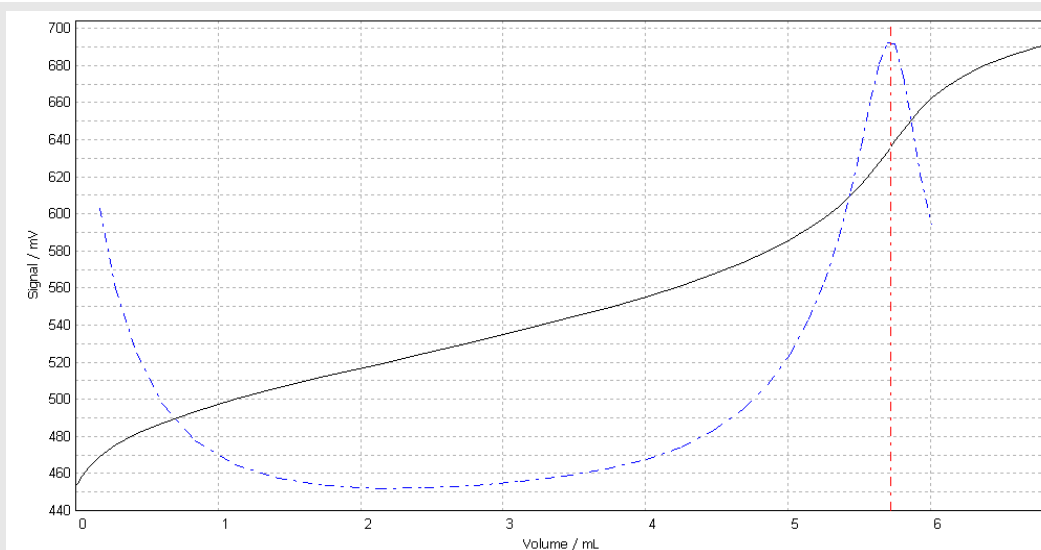


Table of measured values

| | Volume [mL] | Increment [mL] | Signal [mV] | Change [mV] | 1st deriv. [mV/mL] | Time [s] | Temperature [°C] |
|------|-------------|----------------|-------------|-------------|--------------------|----------|------------------|
| | 0 | NaN | 452.7 | NaN | NaN | 0 | 25 |
| | 0.010 | 0.010 | 453.8 | 1.1 | NaN | 5 | 25 |
| | 0.020 | 0.010 | 455.2 | 1.4 | NaN | 10 | 25 |
| | 0.045 | 0.025 | 458.3 | 3.1 | NaN | 15 | 25 |
| | 0.098 | 0.053 | 463.5 | 5.2 | NaN | 20 | 25 |
| | 0.173 | 0.075 | 469.1 | 5.6 | 72.19 | 25 | 25 |
| | 0.281 | 0.108 | 475.2 | 6.1 | 56.62 | 30 | 25 |
| | 0.424 | 0.143 | 481.3 | 6.1 | 44.01 | 36 | 25 |
| | 0.608 | 0.184 | 487.4 | 6.1 | 34.18 | 41 | 25 |
| | 0.839 | 0.231 | 493.5 | 6.1 | 26.94 | 46 | 25 |
| | 1.123 | 0.284 | 500.0 | 6.5 | 22.24 | 51 | 25 |
| | 1.424 | 0.301 | 506.2 | 6.2 | 19.64 | 56 | 25 |
| | 1.752 | 0.328 | 512.2 | 6.0 | 18.28 | 61 | 25 |
| | 2.118 | 0.366 | 518.9 | 6.7 | 17.72 | 66 | 25 |
| | 2.450 | 0.332 | 524.8 | 5.9 | 17.75 | 71 | 25 |
| | 2.796 | 0.346 | 531.0 | 6.2 | 18.20 | 76 | 25 |
| | 3.124 | 0.328 | 537.2 | 6.2 | 19.01 | 81 | 25 |
| | 3.432 | 0.308 | 543.2 | 6.0 | 20.02 | 86 | 25 |
| | 3.726 | 0.294 | 549.2 | 6.0 | 21.49 | 92 | 25 |
| | 4.004 | 0.278 | 555.4 | 6.2 | 23.42 | 96 | 25 |
| | 4.254 | 0.250 | 561.5 | 6.1 | 25.84 | 102 | 25 |
| | 4.481 | 0.227 | 567.5 | 6.0 | 29.07 | 107 | 25 |
| | 4.684 | 0.203 | 573.7 | 6.2 | 33.10 | 112 | 25 |
| | 4.858 | 0.174 | 579.6 | 5.9 | 37.84 | 117 | 25 |
| | 5.016 | 0.158 | 585.8 | 6.2 | 43.87 | 122 | 25 |
| | 5.148 | 0.132 | 592.0 | 6.2 | 50.69 | 127 | 25 |
| | 5.258 | 0.110 | 597.7 | 5.7 | 58.01 | 132 | 25 |
| | 5.360 | 0.102 | 603.8 | 6.1 | 66.82 | 137 | 25 |
| | 5.446 | 0.086 | 610.0 | 6.2 | 75.75 | 142 | 25 |
| | 5.517 | 0.071 | 615.7 | 5.7 | 84.34 | 147 | 25 |
| | 5.585 | 0.068 | 621.8 | 6.1 | 93.45 | 152 | 25 |
| | 5.643 | 0.058 | 627.6 | 5.8 | 100.40 | 158 | 25 |
| | 5.697 | 0.054 | 633.3 | 5.7 | 104.42 | 162 | 25 |
| EQP1 | 5.718689 | NaN | 635.6 | NaN | 104.71 | NaN | NaN |
| | 5.752 | 0.055 | 639.2 | 5.9 | 104.24 | 168 | 25 |
| | 5.808 | 0.056 | 645.0 | 5.8 | 97.97 | 173 | 25 |
| | 5.866 | 0.058 | 650.7 | 5.7 | 88.90 | 178 | 25 |
| | 5.932 | 0.066 | 656.4 | 5.7 | 78.89 | 183 | 25 |
| | 6.008 | 0.076 | 662.2 | 5.8 | 68.93 | 188 | 25 |
| | 6.102 | 0.094 | 667.8 | 5.6 | NaN | 193 | 25 |
| | 6.223 | 0.121 | 673.9 | 6.1 | NaN | 198 | 25 |
| | 6.370 | 0.147 | 679.6 | 5.7 | NaN | 203 | 25 |
| | 6.566 | 0.196 | 685.5 | 5.9 | NaN | 208 | 25 |
| | 6.827 | 0.261 | 691.7 | 6.2 | NaN | 213 | 25 |

Comments

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Method

001 Title

| | |
|-----------------|---------------------|
| Type | General titration |
| Compatible with | T70 / T90 |
| ID | m242-08 |
| Title | Amine value |
| Author | Administrator |
| Date/Time | 19.05.2008 08:27:11 |
| Modified at | 22.05.2008 08:06:27 |
| Modified by | Administrator |
| Protect | No |
| SOP | None |

002 Sample

| | |
|-------------------|--------|
| Number of IDs | 1 |
| ID 1 | MOCA |
| Entry type | Weight |
| Lower limit [g] | 0.0 |
| Upper limit [g] | 5.0 |
| Density [g/mL] | 1.0 |
| Correction factor | 1.0 |
| Temperature [°C] | 25.0 |
| Entry | Before |

003 Titration stand (Rondo/Tower A)

| | |
|-----------------|---------------|
| Type | Rondo/Tower A |
| Titration stand | Rondo60/1A |
| Lid handling | No |

004 Rinse

| | |
|---------------------|--------------|
| Auxiliary reagent | Acetic acid |
| Rinse cycles | 1 |
| Vol. per cycle [mL] | 15 |
| Position | Rinse beaker |
| Drain | Yes |
| Drain pump | SP250 |
| Condition | No |

005 Dispense (normal) [1]

| | |
|----------------------|-------------|
| Titrant | Acetic acid |
| Concentration | 100 |
| Volume [mL] | 60 |
| Dosing rate [mL/min] | 60.0 |
| Condition | No |

006 Stir

| | |
|--------------|-----|
| Speed [50%] | 50 |
| Duration [s] | 330 |
| Condition | No |

007 Titration (EQP) [1]

Titrant

| | |
|-----------------------|-------|
| Titrant | HClO4 |
| Concentration [mol/L] | 0.1 |

Sensor

| | |
|--------|----------|
| Type | pH |
| Sensor | DG113-SC |
| Unit | mV |

Temperatur acquisition

| | |
|-------------------------|----|
| Temperature measurement | No |
|-------------------------|----|

Stir

| | |
|-----------|----|
| Speed [%] | 50 |
|-----------|----|

Predispense

| | |
|------------------|------|
| Mode | None |
| Waiting time [s] | 0 |

Control

| | |
|---------------------|------------------------|
| Control | User |
| Titrant addition | Dynamic |
| dE (set value) [mV] | 6.0 |
| dV (min) [mL] | 0.01 |
| dV (max) [mL] | 0.5 |
| Mode | Equilibrium controlled |
| dE [mV] | 0.5 |
| dt [s] | 2 |
| t (min) [s] | 5 |
| t (max) [s] | 30 |

Evaluation and recognition

| | |
|-------------------|----------|
| Procedure | Standard |
| Threshold [mV/mL] | 30 |
| Tendency | None |
| Ranges | 0 |
| Add. EQP criteria | No |

Termination

| | |
|---------------------------------|------|
| At Vmax [mL] | 12.0 |
| At potential | No |
| At slope | No |
| After number of recognized EQPs | Yes |
| Number of EQPs | 1 |
| Combined termination criteria | No |

Accompanying stating

| | |
|----------------------|----|
| Accompanying stating | No |
|----------------------|----|

Condition

| | |
|-----------|----|
| Condition | No |
|-----------|----|

008 Rinse

| | |
|---------------------|-----------------|
| Auxiliary reagent | Acetic acid |
| Rinse cycles | 1 |
| Vol. per cycle [mL] | 15 |
| Position | Actual position |
| Drain | Yes |
| Drain pump | SP250 |
| Condition | No |

009 Calculation R1

| | |
|-------------------------|------------------------------------------------|
| Result | Amine value |
| Result unit | mg KOH/g |
| Formula | $R1 = (Q - B[\text{Amine Value}]) \cdot C / m$ |
| Constant | $C = M / z$ |
| M | M[Potassium hydroxide] |
| z | z[Potassium hydroxide] |
| Decimal places | 5 |
| Result limits | No |
| Record statistics | Yes |
| Extra statistical func. | No |
| Send to buffer | No |
| Condition | No |

010 Conditioning

| | |
|-----------|---------------------|
| Type | Fix |
| Interval | 1 |
| Position | Conditioning beaker |
| Time [s] | 120 |
| Speed [%] | 30 |
| Condition | No |

011 End of sample