

## Determination of Epoxide Values in Resins

Determination of the epoxide values in resins according to ASTM D1652-04.

|                    |                                                                                                                                                                                                                                                                                                 |
|--------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Sample             | Araldit® epoxy resin stick,<br>3-4 g<br>Araldit® epoxy resin liquid,<br>0.2-0.5 g                                                                                                                                                                                                               |
| Compound           | Epoxide groups                                                                                                                                                                                                                                                                                  |
| Chemicals          | - 40 mL dichloromethane<br>- 20 mL TEAB/acetic acid sol.<br>(see Preparation and Procedures)<br>TEAB:<br>Tetraethylammonium bromide                                                                                                                                                             |
| Titrant            | Perchloric acid in acetic acid,<br>HClO <sub>4</sub><br>c(HClO <sub>4</sub> ) = 0.1 mol/L                                                                                                                                                                                                       |
| Standard           | Tris(hydroxymethyl)aminomethane,<br>TRIS,<br>0.05-0.07 g                                                                                                                                                                                                                                        |
| Indication         | DGi113-SC                                                                                                                                                                                                                                                                                       |
| Chemistry          | Opening of the oxirane ring,<br>-CHOCH-, by hydrogen bromide<br>(HBr) generated by HClO <sub>4</sub> addition:<br><br>-CHOCH- + HBr =<br>-CH(OH)-CH(Br)-                                                                                                                                        |
| Calculation        | <b>Blank (method 086b):</b> R1=Q; mmol<br>R1 is stored as B[Epoxy value]<br><b>Epoxide value (method 086a):</b><br>R1= (Q-B[Epoxy value])/(10*m)<br>mol/100g (Epoxy value)<br>R2= (m*1000)/(Q-B[Epoxy value])<br>g/mol (Epoxy equiv. mass)<br>R3= (Q-B[Epoxy value])*C/m,<br>C=1.6, % (Oxirane) |
| Waste disposal     | Halogenated, organic solvent<br>waste                                                                                                                                                                                                                                                           |
| Author,<br>Version | Cosimo De Caro<br>MSG Anachem, May 2008                                                                                                                                                                                                                                                         |

## Preparation and Procedures

1) TEAB/glacial acetic acid solution:  
Dissolve under stirring at room temperature 100 g tetraethylammonium bromide in 400 mL glacial acetic acid.

2) Epoxide resins are dissolved in a solvent mixture solution consisting of dichloromethane:TEAB/acetic acid (2:1 v/v). In this application, dichloromethane and TEAB solution are dispensed automatically using two additional dosing units.

3) Liquid resin is added using a syringe, whereas the resin stick is cut in slices. To compare results external dissolution was applied and aliquots were titrated.

Note:

Water in the solvent can affect the results.

Anhydrous reagents should be used.

Thus, choose reagents where only traces of water are present.

If necessary, dry the solvents with e.g. molecular sieve. Perchloric acid can be dried using acetic acid anhydride (see ASTM D165-04).

## Remarks

1) Epoxide resins are resins containing epoxide groups.

2) This application cannot be used for epoxide resins containing alkaline groups since they are neutralized by HClO<sub>4</sub> leading to higher results.

3) The epoxide value (EV) indicates the amount-of-substance of epoxide groups in 100 g of sample:  

$$EV = Q / (10 \cdot m) \quad \text{mol/100 g sample}$$

4) The epoxide equivalent weight (EEW) is the amount of resin in g which contains 16 g of oxygen (i.e. 1 mol) bound as epoxide:

$$EEW = m \cdot 1000 / Q \quad \text{g/mol}$$

$$EV = 100 / EEW \quad \text{mol/100 g sample}$$

5) Weight percent epoxide (oxirane oxygen):

$$R3 = 1.6 \cdot Q / m \quad \%$$

Literature:

- ASTM D1652-04
- DIN 53188-75 was withdrawn and was replaced by ISO DIN EN 7142:2007 (05).

**Instruments**

- T50/T70/T90 Titration Excellence
- Two additional dosing units
- Rondo 20 Sample Changer (fixed conditioning beaker with acetic acid)

**Accessories**

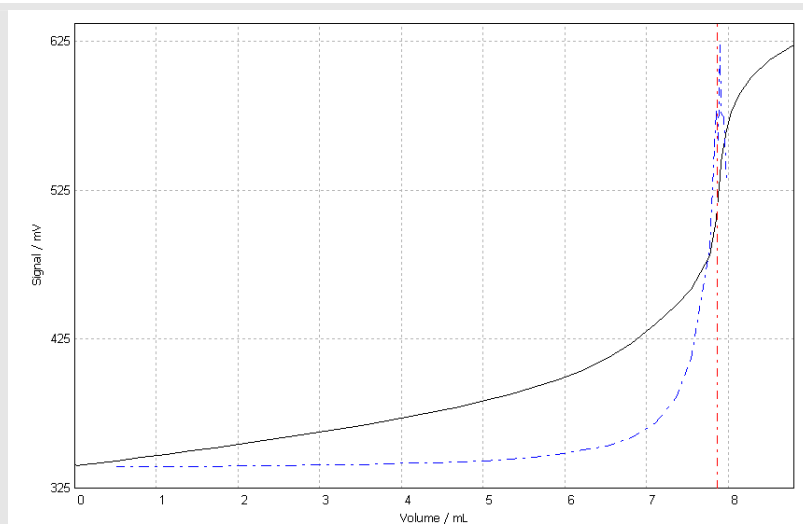
- 100 mL glass titration beaker ME-101446
- 3 DV1020 glass burettes
- XP205 Balance
- LabX Titration Software

**Results****Liquid resin**

| Rx                                           | Name                | n                  | Mean value | Unit     | s      | srel[%] |
|----------------------------------------------|---------------------|--------------------|------------|----------|--------|---------|
| <b>Direct weighing into titration beaker</b> |                     |                    |            |          |        |         |
| R1                                           | Epoxy value         | 8                  | 0.289      | mol/100g | 0.014  | 4.747   |
| R2                                           | Epoxide equiv. mass | 8                  | 346.519    | g/mol    | 16.029 | 4.626   |
| R3                                           | Oxirane             | 8                  | 4.626      | %        | 0.218  | 4.706   |
| R1                                           | Epoxy value         | 8                  | 0.283      | mol/100g | 0.011  | 3.824   |
| R2                                           | Epoxide equiv. mass | 8                  | 353.878    | g/mol    | 13.018 | 3.679   |
| R3                                           | Oxirane             | 8                  | 4.527      | %        | 0.170  | 3.765   |
| <b>External dissolution/aliquot</b>          |                     |                    |            |          |        |         |
| R1                                           | Epoxy value         | 7                  | 0.266      | mol/100g | 0.007  | 2.751   |
| R2                                           | Epoxide equiv. mass | 7                  | 376.317    | g/mol    | 10.212 | 2.714   |
| R3                                           | Oxirane             | 7                  | 4.254      | %        | 0.116  | 2.726   |
| R1                                           | Epoxy value         | 6 (1 outlier of 7) | 0.271      | mol/100g | 0.006  | 2.292   |
| R2                                           | Epoxide equiv. mass | 6 (1 outlier of 7) | 368.624    | g/mol    | 8.499  | 2.306   |
| R3                                           | Oxirane             | 6 (1 outlier of 7) | 4.343      | %        | 0.101  | 2.325   |
| R1                                           | Epoxy value         | 5 (1 outlier of 6) | 0.268      | mol/100g | 0.005  | 1.911   |
| R2                                           | Epoxide equiv. mass | 5 (1 outlier of 6) | 373.396    | g/mol    | 7.062  | 1.891   |
| R3                                           | Oxirane             | 5 (1 outlier of 6) | 4.286      | %        | 0.082  | 1.918   |

**Resin stick**

| Rx                                           | Name                | n                  | Mean value | Unit     | s      | srel[%] |
|----------------------------------------------|---------------------|--------------------|------------|----------|--------|---------|
| <b>Direct weighing into titration beaker</b> |                     |                    |            |          |        |         |
| R1                                           | Epoxy value         | 4                  | 0.063      | mol/100g | 0.003  | 4.541   |
| R2                                           | Epoxide equiv. mass | 4                  | 1581.624   | g/mol    | 62.680 | 3.963   |
| R3                                           | Oxirane             | 4                  | 1.012      | %        | 0.041  | 4.050   |
| <b>External dissolution/aliquot</b>          |                     |                    |            |          |        |         |
| R1                                           | Epoxy value         | 6 (1 outlier of 7) | 0.057      | mol/100g | 0.001  | 1.424   |
| R2                                           | Epoxide equiv. mass | 6 (1 outlier of 7) | 1741.848   | g/mol    | 28.762 | 1.651   |
| R3                                           | Oxirane             | 6 (1 outlier of 7) | 0.919      | %        | 0.015  | 1.634   |
| R1                                           | Epoxy value         | 5 (1 outlier of 6) | 0.059      | mol/100g | 0.001  | 1.695   |
| R2                                           | Epoxide equiv. mass | 5 (1 outlier of 6) | 1659.265   | g/mol    | 16.987 | 1.002   |
| R3                                           | Oxirane             | 5 (1 outlier of 6) | 0.944      | %        | 0.009  | 0.991   |

**Titration curve**

Liquid resin / direct weighing, 27.5.2008 10:53 (sample 8/8)

## Table of measured values

|      | Volume<br>mL | Increment<br>mL | Signal<br>mV | Change<br>mV | 1st deriv.<br>mV/mL | Time<br>s | Temperature<br>°C |
|------|--------------|-----------------|--------------|--------------|---------------------|-----------|-------------------|
|      | 0.000        | NaN             | 340.4        | NaN          | NaN                 | 0         | 25.0              |
|      | 0.020        | 0.020           | 340.3        | -0.1         | NaN                 | 5         | 25.0              |
|      | 0.040        | 0.020           | 340.3        | 0.0          | NaN                 | 10        | 25.0              |
|      | 0.090        | 0.050           | 340.4        | 0.1          | NaN                 | 15        | 25.0              |
|      | 0.215        | 0.125           | 341.1        | 0.7          | NaN                 | 20        | 25.0              |
|      | 0.515        | 0.300           | 343.3        | 2.2          | 6.73                | 25        | 25.0              |
|      | 0.815        | 0.300           | 345.5        | 2.2          | 7.18                | 30        | 25.0              |
|      | 1.115        | 0.300           | 347.6        | 2.1          | 7.32                | 36        | 25.0              |
|      | ...          | ...             | ...          | ...          | ...                 | ...       | ...               |
|      | ...          | ...             | ...          | ...          | ...                 | ...       | ...               |
|      | 6.515        | 0.300           | 411.8        | 7.7          | 28.59               | 127       | 25.0              |
|      | 6.815        | 0.300           | 421.8        | 10.0         | 36.49               | 132       | 25.0              |
|      | 7.115        | 0.300           | 435.1        | 13.3         | 52.57               | 138       | 25.0              |
|      | 7.359        | 0.244           | 448.0        | 12.9         | 77.80               | 154       | 25.0              |
|      | 7.550        | 0.191           | 458.2        | 10.2         | 118.60              | 180       | 25.0              |
|      | 7.771        | 0.221           | 481.2        | 23.0         | 232.20              | 209       | 25.0              |
|      | 7.830        | 0.059           | 498.4        | 17.2         | 336.92              | 221       | 25.0              |
|      | 7.850        | 0.020           | 505.7        | 7.3          | 373.35              | 231       | 25.0              |
| EQP1 | 7.869667     | NaN             | 517.3        | NaN          | 450.00              | NaN       | 25.0              |
|      | 7.876        | 0.026           | 521.1        | 15.4         | 343.12              | 237       | 25.0              |
|      | 7.896        | 0.020           | 533.5        | 12.4         | 441.98              | 242       | 25.0              |
|      | 7.916        | 0.020           | 544.1        | 10.6         | 371.48              | 247       | 25.0              |
|      | 7.942        | 0.026           | 554.9        | 10.8         | 367.45              | 252       | 25.0              |
|      | 7.978        | 0.036           | 565.3        | 10.4         | 298.24              | 257       | 25.0              |
|      | 8.039        | 0.061           | 577.2        | 11.9         | NaN                 | 262       | 25.0              |
|      | 8.128        | 0.089           | 588.5        | 11.3         | NaN                 | 267       | 25.0              |
|      | 8.275        | 0.147           | 600.5        | 12.0         | NaN                 | 272       | 25.0              |
|      | 8.504        | 0.229           | 612.3        | 11.8         | NaN                 | 277       | 25.0              |
|      | 8.804        | 0.300           | 622.7        | 10.4         | NaN                 | 282       | 25.0              |

Liquid resin / direct weighing, 27.5.2008 10:53 (sample 8/8)

## Comments

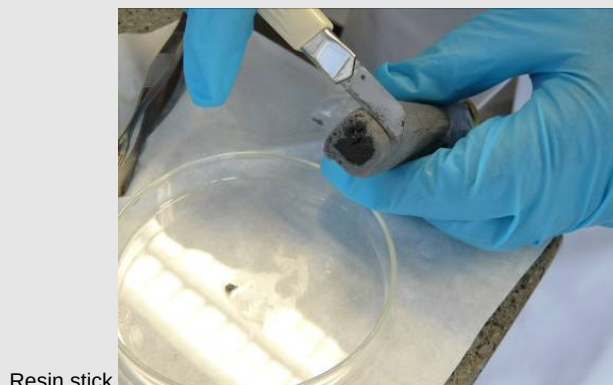
- The sample size used depends on the expected epoxide equivalent weight (EEW) as follows:

| EEW / g/mol | Approx. sample size / g |
|-------------|-------------------------|
| 170 – 375   | 0.4                     |
| 375 – 600   | 0.6                     |
| 600 – 1000  | 0.8                     |
| 1000 – 1500 | 1.3                     |
| 1500 – 2000 | 1.8                     |
| 2000 – 2500 | 2.3                     |
| 2500 – 5000 | 2.8                     |

- Sample handling:



Liquid resin



Resin stick

## Method

|                                            |                                 |
|--------------------------------------------|---------------------------------|
| <b>001 Title</b>                           |                                 |
| Type                                       | General titration               |
| Compatible with                            | T50 / T70 / T90                 |
| ID                                         | m086a                           |
| Title                                      | Epoxide value                   |
| Author                                     | Administrator                   |
| Date/Time                                  | 26.05.2008 16:00:55             |
| Modified at                                | 27.05.2008 10:56:25             |
| Modified by                                | Administrator                   |
| Protect                                    | No                              |
| SOP                                        | None                            |
| <b>002 Sample</b>                          |                                 |
| Number of IDs                              | 1                               |
| ID 1                                       | Liquid resin                    |
| Entry type                                 | Weight                          |
| Lower limit                                | 0.3 g                           |
| Upper limit                                | 0.5 g                           |
| Density                                    | 1.0 g/mL                        |
| Correction factor                          | 1.0                             |
| Temperature                                | 25.0°C                          |
| Entry                                      | Arbitrary                       |
| <b>003 Titration stand (Rondo/Tower A)</b> |                                 |
| Type                                       | Rondo/Tower A                   |
| Titration stand                            | Rondo60/1A                      |
| Lid handling                               | No                              |
| <b>004 Dispense (normal) [1]</b>           |                                 |
| Titrant                                    | TEAB/CH <sub>3</sub> COOH       |
| Concentration                              | 0.25 mol/L                      |
| Volume                                     | 20 mL                           |
| Dosing rate                                | 60.0 mL/min                     |
| Condition                                  | No                              |
| <b>005 Dispense (normal) [2]</b>           |                                 |
| Titrant                                    | CH <sub>2</sub> Cl <sub>2</sub> |
| Concentration                              | 1 mol/L                         |
| Volume                                     | 40 mL                           |
| Dosing rate                                | 60.0 mL/min                     |
| Condition                                  | No                              |
| <b>006 Stir</b>                            |                                 |
| Speed                                      | 40 %                            |
| Duration                                   | 600 s                           |
| Condition                                  | No                              |
| <b>007 Titration (EQP) [1]</b>             |                                 |
| <b>Titrant</b>                             |                                 |
| Titrant                                    | HClO <sub>4</sub>               |
| Concentration                              | 0.1 mol/L                       |
| <b>Sensor</b>                              |                                 |
| Type                                       | pH                              |
| Sensor                                     | DG1113-SC                       |
| Unit                                       | mV                              |
| <b>Temperature acquisition</b>             |                                 |
| Temperature acquisition                    | No                              |
| <b>Stir</b>                                |                                 |
| Speed                                      | 30 %                            |
| <b>Predispense</b>                         |                                 |
| Mode                                       | None                            |
| Waiting time                               | 0 s                             |
| <b>Control</b>                             |                                 |
| Control                                    | User                            |
| Titrant addition                           | Dynamic                         |
| dE (set value)                             | 12 mV                           |
| dV (min)                                   | 0.02 mL                         |
| dV (max)                                   | 0.3 mL                          |
| Mode                                       | Equilibrium controlled          |
| dE                                         | 0.5 mV                          |
| dt                                         | 2 s                             |
| t (min)                                    | 5 s                             |
| t (max)                                    | 30 s                            |
| <b>Evaluation and recognition</b>          |                                 |
| Procedure                                  | Standard                        |
| Threshold                                  | 50                              |
| Tendency                                   | Positive                        |
| Ranges                                     | 0                               |
| Add. EQP criteria                          | No                              |
| <b>Termination</b>                         |                                 |
| At Vmax                                    | 60 mL                           |
| At potential                               | No                              |
| At slope                                   | No                              |
| After number of recognized EQPs            | Yes                             |
| Number of EQP's                            | 1                               |
| Combined termination criteria              | No                              |

|                                   |                                                       |
|-----------------------------------|-------------------------------------------------------|
| Condition                         | No                                                    |
| <b>008 Calculation R1</b>         |                                                       |
| Result                            | User result                                           |
| Result unit                       | Epoxide value                                         |
| Formula                           | $R1 = (Q - B[\text{Epoxide value}]) / (10 \cdot m)$   |
| Constant                          | C=1                                                   |
| M                                 | M[None]                                               |
| z                                 | z[None]                                               |
| Decimal places                    | 3                                                     |
| Result limits                     | No                                                    |
| Record statistics                 | Yes                                                   |
| Extra statistical func.           | No                                                    |
| Send to buffer                    | No                                                    |
| Condition                         | No                                                    |
| <b>009 Calculation R2</b>         |                                                       |
| Result                            | User result                                           |
| Result unit                       | Epoxide equivalent mass                               |
| Formula                           | $R2 = (m \cdot 1000) / (Q - B[\text{Epoxide value}])$ |
| Constant                          | C=1                                                   |
| M                                 | M[None]                                               |
| z                                 | z[None]                                               |
| Decimal places                    | 3                                                     |
| Result limits                     | No                                                    |
| Record statistics                 | Yes                                                   |
| Extra statistical func.           | No                                                    |
| Send to buffer                    | No                                                    |
| Condition                         | No                                                    |
| <b>010 Calculation R3</b>         |                                                       |
| Result                            | User result                                           |
| Result unit                       | Oxirane                                               |
| Formula                           | $R3 = (Q - B[\text{Epoxide value}]) \cdot C / m$      |
| Constant                          | C=1.6                                                 |
| M                                 | M[None]                                               |
| z                                 | z[None]                                               |
| Decimal places                    | 3                                                     |
| Result limits                     | No                                                    |
| Record statistics                 | Yes                                                   |
| Extra statistical func.           | No                                                    |
| Send to buffer                    | No                                                    |
| Condition                         | No                                                    |
| <b>011 Conditioning</b>           |                                                       |
| Type                              | Fix                                                   |
| Interval                          | 1                                                     |
| Position                          | Conditioning beaker                                   |
| Time                              | 60 s                                                  |
| Speed                             | 30%                                                   |
| Condition                         | No                                                    |
| <b>012 End of sample</b>          |                                                       |
| -----                             |                                                       |
| <b>Blank value determination:</b> |                                                       |
| ...                               |                                                       |
| <b>Control</b>                    |                                                       |
| Control                           | User                                                  |
| Titrant addition                  | Dynamic                                               |
| dE (set value)                    | 12 mV                                                 |
| dV (min)                          | 0.002 mL                                              |
| dV (max)                          | 0.05 mL                                               |
| Mode                              | Equilibrium controlled                                |
| dE                                | 0.5 mV                                                |
| dt                                | 2 s                                                   |
| t (min)                           | 5 s                                                   |
| t (max)                           | 30 s                                                  |
| <b>Evaluation and recognition</b> |                                                       |
| Procedure                         | Standard                                              |
| Threshold                         | 25                                                    |
| Tendency                          | Positive                                              |
| Ranges                            | 0                                                     |
| Add. EQP criteria                 | No                                                    |
| <b>Termination</b>                |                                                       |
| At Vmax                           | 1 mL                                                  |
| At potential                      | No                                                    |
| At slope                          | No                                                    |
| After number of recognized EQPs   | Yes                                                   |
| Number of EQP's                   | 1                                                     |
| Combined termination criteria     | No                                                    |
| Condition                         | No                                                    |
| . . . .                           |                                                       |