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Plastics — Amine epoxide hardeners — Determination of primary, secondary and tertiary amine group nitrogen content

Plastiques — Durcisseurs pour résines époxy — Détermination de la teneur en azote des groupes amine primaire, secondaire, tertiaire

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Foreword

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Plastics — Amine epoxide hardeners — Determination of primary, secondary and tertiary amine group nitrogen content

1 Scope

This International Standard specifies a method for the determination of the primary, secondary and tertiary amine group nitrogen content of aliphatic or aromatic amine hardeners for epoxy resins.

2 Principle

2.1 Aliphatic amines

2.1.1 Determination of total amine group nitrogen content (X_T)

The total alkalinity is determined by potentiometric titration against hydrobromic or perchloric acid in glacial acetic acid, as described by the following reactions:

$$RNH_2 + H^+ \rightarrow RNH_3^+$$

$$(RR'NH + H^+ \rightarrow (RR')NH_2^+$$

$$(RR'R'')N + H^+ \rightarrow (RR'R'')NH^+$$

The results are expressed as percentage nitrogen.

NOTE 1 Perchloric acid is not suitable for use with amine hardeners such as *N*-aminoethylpiperazine.

2.1.2 Determination of tertiary amine group nitrogen content (X_3)

The primary and secondary amine groups are converted into amide groups with acetic anhydride, as described by the following reactions:

$$RNH_2 + (CH_3CO)_2O \rightarrow RNHCOCH_3 + CH_3COOH$$

$$(RR')NH + (CH_3CO)_2O \rightarrow (RR')NCOCH_3 + CH_3COOH$$

The tertiary amine group alkalinity is determined by potentiometric titration against hydrobromic or perchloric acid in glacial acetic acid/acetic anhydride, as described by the following reaction:

$$(RR'R'')NH + H^+ \rightarrow (RR'R'')NH^+$$

The results are expressed as percentage nitrogen.

2.1.3 Determination of primary amine group nitrogen content (X_{L1})

The primary amine groups are reacted with a measured excess of 2,4-pentanedione (acetylacetone) in *N,N*-di-methylformamide to form imines, as described by the following reaction:

$$RNH_2 + CH_3COCH_2COCH_3 \rightarrow CH_3CNRCH_2COCH_3 + H_2O$$

The excess acetylacetone is determined by potentiometric titration against potassium hydroxide (the reaction products of acetylacetone and primary amine groups are neutral under these conditions).

The results are expressed as percentage nitrogen.

2.1.4 Determination of secondary amine group nitrogen content (X_{L2})

The secondary amine group nitrogen content is determined by calculating the difference between the total amine group nitrogen content and the sum of the primary and tertiary amine group nitrogen contents.

2.2 Aromatic amines

2.2.1 Determination of total amine group nitrogen content (X_T)

The total alkalinity is determined by potentiometric titration against hydrobromic or perchloric acid in glacial acetic acid, as described by the following reactions:

$$ArNH_2 + H^+ \rightarrow ArNH_3^+$$

$$(ArAr')NH + H^+ \rightarrow (ArAr')NH_2^+$$

$$(ArAr'Ar'')N + H^+ \rightarrow (ArAr'Ar'')NH^+$$

The results are expressed as percentage nitrogen.

2.2.2 Determination of tertiary amine group nitrogen content (X_3)

The primary and secondary amine groups are converted into amide groups with acetic anhydride as described by the following reactions:

$$ArNH_2 + (CH_3CO)_2O \rightarrow ArNHCOCH_3 + CH_3COOH$$

$$(ArAr')NH + (CH_3CO)_2O \rightarrow (ArAr')NCOCH_3 + CH_3COOH$$

The tertiary amine group alkalinity is determined by potentiometric titration against hydrobromic or perchloric acid in glacial acetic acid/acetic anhydride, as described by the following reaction.

$$(ArAr'Ar'')N + H^+ \rightarrow (ArAr'Ar'')NH^+$$

The results are expressed as percentage nitrogen.

2.2.3 Determination of the sum of the secondary and tertiary amine group nitrogen contents (X_{R2+3})

The primary amine groups are converted into Schiff bases by salicylaldehyde in glacial acetic acid, as described by the following reaction:

$$ArNH_2 + C_6H_4(OH)CHO \rightarrow ArN{=}CHC_6H_4(OH) + H_2O$$

With strongly basic amines, the secondary and tertiary amine group alkalinity is determined by potentiometric titration against hydrochloric acid in glacial acetic acid, as described by the following reactions:

$$(ArAr')NH + H^+ \rightarrow (ArAr')NH_2^+$$

$$(ArAr'Ar'')N + H^+ \rightarrow (ArAr'Ar'')NH^+$$

The results are expressed as percentage nitrogen.

NOTE 2 Weakly basic amines, such as 4,4′-diaminodiphenylsulfone, are titrated with hydrobromic or perchloric acid in glacial acetic acid.

2.2.4 Determination of primary amine group nitrogen content (X_{R1})

The primary amine group nitrogen content is determined by calculating the difference between the total amine group nitrogen content and the sum of the secondary and tertiary amine group nitrogen contents.

2.2.5 Determination of secondary amine group nitrogen content (X_{R2})

The secondary amine group nitrogen content is determined by calculating the difference between the sum of the secondary and tertiary amine group nitrogen contents and the tertiary amine group nitrogen content.

3 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

3.1 Acetic acid, glacial.

3.2 Acetic anhydride.

3.3 2,4-Pentanedione (acetylacetone).

3.4 *N,N*-diamethylformamide.

3.5 Acetylacetone, 1,5 mol/l solution in *N,N*-dimethylformamide.

Dissolve 15 ml of acetylacetone (3.3) in 90 ml of *N,N*-dimethylformamide (3.4).

3.6 Salicylaldehyde.

3.7 Ethan-1,2-diol (ethylene glycol).

3.8 Propan-2-ol.

3.9 Ethylene glycol/propan-2-ol mixed solvent.

Mix 500 ml of ethylene glycol (3.7) and 500 ml of propan-2-ol (3.8).

3.10 Potassium hydrogen phthalate.

3.11 Hydrobromic acid, 250 g/l solution in acetic acid.

3.12 Perchloric acid, 70 % or 60 % solution in water.

3.13 Potassium hydroxide.

3.14 Hydrochloric acid, concentrated.

3.15 Sodium carbonate.

3.16 Hydrobromic acid, 0,1 mol/l standard volumetric solution in glacial acetic acid.

3.16.1 Preparation

Add 25 ml of hydrobromic acid (3.11) slowly to 100 ml of glacial acetic acid (3.1) in a 1 000 ml brown-glass volumetric flask (4.9) and stir carefully. Dilute to the mark with glacial acetic acid.

3.16.2 Standardization

Weigh out, to the nearest 0,1 mg, 0,1 g to 0,2 g of potassium hydrogen phthalate (3.10) and dissolve in 50 ml of glacial acetic acid (3.1).

Titrate this solution potentiometrically against the solution of hydrobromic acid prepared in 3.16.1 (V_1).

Perform a blank test by titrating 50 ml of glacial acetic acid against the solution of hydrobromic acid prepared in 3.16.1 (V_2).

Calculate the concentration c_1 of the hydrobromic acid solution, expressed in moles of HBr per litre to the nearest 0,001 mol HBr/l, using the equation

$$c_1 = \frac{1\ 000 \times m_0}{204{,}23\,(V_1 - V_2)}$$

where

m_0 is the mass, in grams, of potassium hydrogen phthalate used;

V_1 is the volume, in millilitres, of the solution of hydrobromic acid prepared in 3.16.1 required to reach the end point in the titration;

V_2 is the volume, in millilitres of the above solution (3.16.1) required in the blank test.

3.17 Perchloric acid, 0,1 mol/l standard volumetric solution in glacial acetic acid.

3.17.1 Preparation

Mix 8,5 ml of 70 % perchloric acid (or 9,9 ml of 60 % perchloric acid) (3.12) with 500 ml of glacial acetic acid (3.1) in a 1 000 ml brown-glass volumetric flask (4.9). Add 30 ml (or 35 ml if 60 % perchloric acid was used) of acetic anhydride (3.2) and mix well. Dilute to the mark with glacial acetic acid.

3.17.2 Standardization

Use the same procedure as that in 3.16.2, calculating the concentration using the same equation. In this case, c_1 is the concentration of the perchloric acid solution prepared in 3.17.1.

3.18 Potassium hydroxide, 0,5 mol/l standard volumetric solution in propan-2-ol.

3.18.1 Preparation

Take 1 000 ml of propan-2-ol (3.8) in a round-bottomed flask and add 30 g of potassium hydroxide (3.13). Reflux for several hours to dissolve completely. Leave the solution in a carbon-dioxide-free atmosphere for a few days, then transfer the clear upper solution to a polyethylene bottle and keep it in the bottle equipped with a guard tube filled with soda lime. Take care that the solution does not touch a cork or rubber stopper or stopper grease, which may be saponified.

3.18.2 Standardization

Weigh, to the nearest 0,1 mg, 0,5 g to 1,0 g of potassium hydrogen phthalate (3.10) and dissolve in 100 ml of water.

Titrate this solution potentiometrically against the potassium hydroxide solution prepared in 3.18.1 (V_3).

Perform a blank test separately (V_4).

Calculate the concentration c_2 of the potassium hydroxide solution, expressed in moles of KOH per litre to the nearest 0,001 mol KOH/l, using the equation

$$c_2 = \frac{1\ 000 \times m_1}{204{,}23\,(V_3 - V_4)}$$

where

m_1 is the mass, in grams, of potassium hydrogen phthalate used;

V_3 is the volume, in millilitres, of the solution of potassium hydroxide prepared in 3.18.1 required to reach the end point in the titration;

V_4 is the volume, in millilitres, of the above solution (3.18.1) required in the blank test.

3.19 Hydrochloric acid, 0,1 mol/l standard volumetric solution in mixed solvent.

3.19.1 Preparation

Add 1 000 ml of the ethylene glycol/propan-2-ol mixed solvent (3.9) to 9 ml of concentrated hydrochloric acid (3.14).

3.19.2 Standardization

Weigh out, to the nearest 0,1 mg, 0,13 g to 0,16 g of sodium carbonate (3.15) and dissolve in 100 ml of water.

Titrate this solution potentiometrically against the solution of hydrochloric acid prepared in 3.19.1 (V_5).

Perform a blank test separately (V_6).

Calculate the concentration c_3 of the hydrochloric acid solution, expressed in moles of HCl per litre to the nearest 0,001 mol HCl/l, using the equation

$$c_3 = \frac{1\ 000 \times m_2}{52{,}99\,(V_5 - V_6)}$$

where

m_2 is the mass, in grams, of sodium carbonate used;

V_5 is the volume, in millilitres, of the hydrochloric acid solution prepared in 3.19.1 required to reach the end point in the titration;

V_6 is the volume, in millilitres, of the above solution (3.19.1) required in the blank test.

4 Apparatus

4.1 Analytical balance, accurate to 0,1 mg.

4.2 Beakers, of capacity 100 ml.

4.3 Graduated glass cylinder, of capacity 50 ml.

4.4 Conical flask with ground-glass stopper, of capacity 20 ml.

4.5 Pipette, of capacity 5 ml.

4.6 Graduated pipette, of capacity 1 ml.

4.7 Water bath, capable of being maintained at 40 °C.

4.8 Flasks, of capacities 100 ml, 1 000 ml and 2 000 ml.

4.9 Graduated flasks, capacity 1 000 ml, made of brown glass.

4.10 Potentiometric-titration apparatus, equipped with a glass-calomel electrode.

5 Procedure

5.1 Aliphatic amines

5.1.1 Determination of total amine group nitrogen content (X_T)

Weigh, to the nearest 0,1 mg, an amount of amine hardener containing approximately 0,001 mol of amine group (m_T) into a 100 ml beaker (4.2). Dissolve in 50 ml of glacial acetic acid (3.1). Then titrate potentiometrically against 0,1 mol/l hydrobromic acid (3.16) or perchloric acid (3.17) (V_1).

Because one nitrogen in *N*-aminoethylpiperazine reacts only slowly with perchloric acid, it is difficult to detect the end point. In the determination of *N*-aminoethylpiperazine or its derivatives, therefore, use 0,1 mol/l hydrobromic acid.

Perform a blank test separately (V_2) by titrating 50 ml of glacial acetic acid (3.1).

5.1.2 Determination of tertiary amine group nitrogen content (X_3)

Weigh, to the nearest 0,1 mg, an amount of amine hardener containing approximately 0,001 mol of amine group (m_3) into a 100 ml beaker (4.2). Dissolve in 10 ml of glacial acetic acid (3.1).

Add 10 ml of acetic anhydride (3.2) and mix thoroughly. Leave at room temperature for 30 min. Add 40 ml of glacial acetic acid (3.1) and titrate potentiometrically against 0,1 mol/l hydrobromic acid (3.16) or perchloric acid (3.17) (V_1).

Perform a blank test separately (V_2).

5.1.3 Determination of primary amine group nitrogen content (X_{L1})

Weigh, to the nearest 0,1 mg, an amount of amine hardener containing approximately 0,002 mol of amine group (m_1) into a 20 ml conical flask with a ground-glass stopper (4.4).

Using a pipette (4.5), add 5 ml of 1,5 mol/l solution of acetylacetone in *N,N*-dimethylformamide (3.5), tightly stopper the flask, and mix thoroughly. Keep at 40 °C in the water bath (4.7) for 30 min.

After cooling down to room temperature, wash the mixture into a 100 ml beaker (4.2), using 50 ml of *N,N*-dimethylformamide (3.4).

Titrate potentiometrically against 0,5 mol/l potassium hydroxide solution (3.18) (V_3).

Perform a blank test separately (V_4).

5.1.4 Determination of secondary amine group nitrogen content (X_{L2})

Determine the secondary amine group nitrogen content by calculating the difference between the total amine group nitrogen content and the sum of the primary and tertiary amine group nitrogen contents.

5.2 Aromatic amines

5.2.1 Determination of total amine group nitrogen content (X_T)

Determine in the same way as for aliphatic amines (see 5.1.1).

5.2.2 Determination of tertiary amine group nitrogen content (X_3)

Determine in the same way as for aliphatic amines (see 5.1.2).

5.2.3 Determination of the sum of the secondary and tertiary amine group nitrogen contents (X_{R2+3})

5.2.3.1 With strongly basic amines, weigh, to the nearest 0,1 mg, an amount of amine hardener containing 0,001 mol of amine group (m_{2+3}) into a 100 ml beaker (4.2). Dissolve in 10 ml of glacial acetic acid (3.1).

Add 1 ml of salicylaldehyde (3.6) and mix thoroughly. Leave at room temperature for 30 min.

Add 50 ml of ethylene glycol/propan-2-ol mixed solvent. Then titrate potentiometrically against 0,1 mol/l hydrochloric acid (3.19) (V_5).

Perform a blank test separately (V_6).

5.2.3.2 With weakly basic amines, such as 4,4′-diaminodiphenylsulfone, use the following procedure:

Weigh, to the nearest 0,1 mg, an amount of amine hardener containing approximately 0,001 mol of amine group (m_{2+3}) into a 100 ml beaker (4.2). Dissolve in 10 ml of glacial acetic acid (3.1).

Add 1 ml of salicylaldehyde (3.6) and mix thoroughly. Leave at room temperature for 30 min.

Add 40 ml of glacial acetic acid (3.1). Then titrate potentiometrically against 0,1 mol/l hydrobromic acid (3.16) or perchloric acid (3.17) (V_1).

Perform a blank test separately (V_2).

5.2.4 Determination of primary amine group nitrogen content (X_{R1})

Determine the primary amine group nitrogen content by calculating the difference between the total amine group nitrogen content and the sum of the secondary and tertiary amine group nitrogen contents.

5.2.5 Determination of secondary amine group nitrogen content (X_{R2})

Determine the secondary amine group nitrogen content by calculating the difference between the sum of the secondary and tertiary amine group nitrogen contents and the tertiary amine group nitrogen content.

6 Expression of results

Calculate each amine group nitrogen content from the equations given in 6.1 to 6.7, reporting the results to one place of decimals.

6.1 Total amine group nitrogen content (X_T), in mass percent (see 5.1.1 and 5.2.1)

$$X_T = \frac{0{,}014 \times c_1 \times (V_1 - V_2) \times 100}{m_T}$$

where

c_1 is the concentration, in moles per litre, of the hydrobromic acid (3.16) or perchloric acid (3.17) used;

V_1 is the volume, in millilitres, of the above solution (3.16 or 3.17) required to reach the end point in the titration;

V_2 is the volume, in millilitres, of the above solution (3.16 or 3.17) required in the blank test;

m_T is the mass, in grams, of amine hardener taken.

6.2 Tertiary amine group nitrogen content (X_3), in mass percent (see 5.1.2 and 5.2.2)

$$X_3 = \frac{0{,}014 \times c_1 \times (V_1 - V_2) \times 100}{m_3}$$

where

c_1 is the concentration, in moles per litre, of the hydrobromic acid (3.16) or perchloric acid (3.17) used;

V_1 is the volume, in millilitres, of the above solution (3.16 or 3.17) required to reach the end point in the titration;

V_2 is the volume, in millilitres, of the solution (3.16 or 3.17) required in the blank test;

m_3 is the mass, in grams, of amine hardener taken.

6.3 Aliphatic primary amine group nitrogen content (X_{L1}), in mass percent (see 5.1.3)

$$X_{L1} = \frac{0{,}014 \times c_2 \times (V_3 - V_4) \times 100}{m_1}$$

where

c_2 is the concentration, in moles per litre, of the potassium hydroxide solution (3.18) used;

V_3 is the volume, in millilitres, of the above solution (3.18) required to reach the end point in the titration;

V_4 is the volume, in millilitres, of the above solution (3.18) required in the blank test;

m_1 is the mass, in grams, of amine hardener taken.

6.4 Aliphatic secondary amine group nitrogen content (X_{L2}), in mass percent (see 5.1.4)

$$X_{L2} = X_T - (X_{L1} + X_3)$$

where

X_T is the total amine group nitrogen content, in mass percent, of the amine hardener;

X_{L1} is the aliphatic primary amine group nitrogen content, in mass percent, of the amine hardener;

X_3 is the tertiary amine group nitrogen content, in mass percent, of the amine hardener.

6.5 Sum of aromatic secondary and tertiary amine group nitrogen contents (X_{R2+3}), in mass percent (see 5.2.3)

$$X_{R2+3} = \frac{0{,}014 \times c_3 \times (V_5 - V_6) \times 100}{m_{2+3}}$$

or

$$\frac{0{,}014 \times c_1 \times (V_1 - V_2) \times 100}{m_{2+3}}$$

where

c_3 is the concentration, in moles per litre, of the hydrochloric acid (3.19) used;

V_5 is the volume, in millilitres, of the above solution (3.19) required to reach the end point in the titration;

V_6 is the volume, in millilitres, of the above solution (3.19) required in the blank test;

m_{2+3} is the mass, in grams, of amine hardener taken.

c_1 is the concentration of the hydrobromic acid (3.16) or perchloric acid (3.17) used;

V_1 is the volume, in millilitres, of the above solution (3.16 or 3.17) required to reach the end point in the titration;

V_2 is the volume, in millilitres, of the above solution (3.16 or 3.17) required in the blank test.

6.6 Aromatic primary amine group nitrogen content (X_{R1}), in mass percent (see 5.2.4)

$$X_{R1} = X_T - X_{R2+3}$$

where

X_T is the total amine group nitrogen content, in mass percent, of the amine hardener;

X_{R2+3} is the sum of the secondary and tertiary amine group nitrogen contents, in mass percent, of the amine hardener.

6.7 Aromatic secondary amine group nitrogen content (X_{R2}), in mass percent (see 5.2.5)

$$X_{R2} = X_{R2+3} - X_3$$

where

X_3 is the tertiary amine group nitrogen content, in mass percent, of the amine hardener;

X_{R2+3} is the sum of the secondary and tertiary amine group nitrogen contents, in mass percent, of the amine hardener.

7 Precision

Following round-robin testing organized in Japan in 1994, the precision of this test method is as follows:

Aliphatic amine group nitrogen content

The values of m, s_r, s_R, r and R are given in mass percent.

Type of amine group nitrogen	Mean	Repeatability		Reproducibility	
	m	s_r	r	s_R	R
Primary amine group nitrogen	8,49	0,59	1,64	1,37	3,83
Secondary amine group nitrogen	6,90	0,49	1,38	1,46	4,08
Tertiary amine group nitrogen	10,23	0,12	0,34	0,54	1,51

Aromatic amine group nitrogen content

The values of m, s_r, s_R, r and R are given in mass percent.

Type of amine group nitrogen	Mean	Repeatability		Reproducibility	
	m	s_r	r	s_R	R
Primary amine group nitrogen	3,38	0,34	0,94	0,74	2,08
Secondary amine group nitrogen	4,27	0,32	0,89	0,75	2,11
Tertiary amine group nitrogen	4,44	0,04	0,10	0,14	0,39

m = mean of all the laboratories

s_r = standard deviation within a laboratory

s_R = standard deviation for the total deviation between the laboratories

r = repeatability (in units of measurement) = 2,8 s_r

R = reproducibility (in units of measurement) = 2,8 s_R

8 Test report

The test report shall include the following particulars:

a) a reference to this International Standard;

b) all details necessary for the identification of the material tested (type, source, manufacturer's designation, form in which supplied, etc.);

c) the test conditions;

d) the individual results and their average value;

e) the date of the test;

f) notes in relation to the determination;

g) details of any operation not specified in this International Standard and of any incident which may have influenced the results.

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