INTERNATIONAL STANDARD

ISO 3001

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Plastics — Epoxy compounds — Determination of epoxy equivalent

Plastiques — Compositions époxydiques — Détermination de l'équivalent époxy

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 3001 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

This fourth edition cancels and replaces the third edition (ISO 3001:1997), which has been technically revised.

Annex A forms an integral part of this International Standard.

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Plastics — Epoxy compounds — Determination of epoxy equivalent

1 Scope

This International Standard specifies a method for the determination of the epoxy equivalent and is applicable to all epoxy compounds. In the case of epoxyamines, it is necessary to apply the modification specified in annex A.

2 Definitions

For the purposes of this International Standard, the following definitions apply.

2.1
epoxy equivalent
the mass of resin, in grams, which contains one mole of epoxy groups

2.2
epoxy index
the number of moles of epoxy groups contained in 1 kg of resin

3 Principle

The epoxy groups in a test portion are reacted with nascent hydrogen bromide produced by the action of 0,1 mol/l standard volumetric perchloric acid solution on tetraethylammonium bromide. The end-point is determined either using crystal violet as indicator or by a potentiometric method.

4 Reagents

During the analysis, use only reagents of recognized analytical grade.

4.1 Glacial acetic acid.

4.2 Acetic anhydride, purity > 96 %.

4.3 Chloroform.

4.4 Potassium hydrogen phthalate.

4.5 Crystal violet, indicator solution.

Dissolve 100 mg of crystal violet in 100 ml of glacial acetic acid (4.1).

4.6 Perchloric acid, 0,1 mol/l standard volumetric solution.

4.6.1 Preparation

Add 8,5 ml of a 70 % (*m*/*m*) aqueous solution of perchloric acid to a solution consisting of a mixture of 500 ml of glacial acetic acid (4.1) and 30 ml of acetic anhydride (4.2). Make up to 1 000 ml with glacial acetic acid and mix thoroughly.

4.6.2 Standardization

WARNING — The use of safety goggles and a safety screen is recommended.

Standardize this solution by titrating it against 200 mg of potassium hydrogen phthalate (4.4) — previously dried, if necessary, for 2 h at 120 °C — dissolved in 20 ml of glacial acetic acid (4.1) and 10 ml of chloroform (4.3), using crystal violet indicator solution (4.5) or a potentiometric titration apparatus (5.1).

Carry out the end-point determination using 4 to 6 drops of crystal violet solution, titrating until a stable green colour is obtained, or carry out this procedure using a potentiometric titration apparatus. If a potentiometric method is used to determine the epoxy equivalent, it is necessary to use the same method for the standardization of the perchloric acid. Note the temperature t_s of the standard volumetric solution.

4.6.3 Calculation of the concentration

Calculate the concentration c of the perchloric acid solution (4.6.1), in moles per litre, by the following equation, rounding to four places of decimals:

$$c = \frac{m}{(V_1 - V_0) \times 0{,}204\,22}$$

where

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

V_0 is the volume, in millilitres, of perchloric acid solution (4.6.1) used in the blank test;

V_1 is the volume, in millilitres, of perchloric acid solution (4.6.1) used in the determination.

4.7 Tetraethylammonium bromide, reagent solution.

Dissolve 100 g of tetraethylammonium bromide in 400 ml of glacial acetic acid (4.1). Add a few drops of crystal violet solution (4.5). If it changes colour, bring it back to the original (blue-green) colour with standard volumetric perchloric acid solution (4.6).

For some epoxy compounds of low reactivity, the use of tetrabutylammonium iodide is advised, either as the solid or as a 10 % solution in chloroform. In this case, light shall be excluded as much as possible. Solutions of tetrabutylammonium iodide in chloroform are unstable and shall be freshly prepared for each titration.

5 Apparatus

5.1 Potentiometric titration apparatus, equipped with a silver electrode and a silver chloride or mercury sulfate electrode.

5.2 Balance, accurate to within 0,1 mg.

5.3 Conical flask, capacity 100 ml or 200 ml, with ground-glass neck and ground-glass stopper.

5.4 Microburette, with closed reservoir, or **calibrated burette**, capacity 10 ml.

5.5 Glass apparatus, with ground joints, vents being protected from moisture by calcium chloride tubes.

5.6 Magnetic stirrer, with polytetrafluoroethylene-coated bar.

5.7 Thermometer, calibrated to permit temperature measurements to within ± 0,1 °C.

5.8 Pipette, capacity 10 ml.

5.9 Volumetric flask, capacity 1 000 ml.

5.10 Measuring cylinders, capacity 50 ml and 500 ml.

6 Procedure

6.1 Weigh into the flask, to the nearest 0,1 mg, a test portion containing 0,6 mmol to 0,9 mmol of epoxy groups (this corresponds to a mass of between 0,6 × EE mg and 0,9 × EE mg, where EE is the estimated epoxy equivalent).

6.2 Add 10 ml of chloroform (4.3), then dissolve the test portion using the magnetic stirrer (5.6) and, if necessary, by heating slightly.

Cool to room temperature, add 20 ml of glacial acetic acid (4.1) and then, with the pipette (5.8), 10 ml of tetraethylammonium bromide solution (4.7).

In the case of high-molecular-mass epoxy resins, increase the chloroform volume to 30 ml.

6.3 If using the indicator method, add 4 to 6 drops of crystal violet solution (4.5) and titrate the solution on the magnetic stirrer with perchloric acid solution (4.6).

Carry out the titration until a stable green colour is obtained.

6.4 If using the potentiometric method, place the electrodes in the test solution. Adjust the speed of the magnetic stirrer to give vigourous stirring without splattering. Titrate the solution with perchloric acid solution (4.6).

6.5 Note the temperature t of the perchloric acid solution in order to be able to allow for expansion of the solution with increasing temperature.

6.6 Carry out a blank test at the same time as the determination, following the same procedure and using the same reagents but omitting the test portion.

7 Expression of results

Calculate the epoxy equivalent EE, in grams per mole, by the following equation, rounding to three places of decimals:

$$\mathrm{EE} = \frac{1\,000\, m}{(V_1 - V_0)\left(1 - \frac{t - t_s}{1\,000}\right) c}$$

where

m is the mass, in grams, of the test portion;

V_0 is the volume, in millilitres, of perchloric acid solution (4.6) used in the blank test;

V_1 is the volume, in millilitres, of perchloric acid solution (4.6) used in the determination;

t is the temperature, in degrees Celsius, of the perchloric acid solution (4.6) at the time of the determination and blank test;

t_S is the temperature, in degrees Celsius, of the perchloric acid solution (4.6) at the time of standardization;

c is the concentration, in moles per litre, of the perchloric acid solution (4.6) (usually 0,1 mol/l) at the time of standardization.

NOTE The use of the correction factor is necessary because of the significant coefficient of expansion of the perchloric acid solution ($1{,}07 \times 10^{-3}\ °C^{-1}$), which corresponds to a volume variation of 0,1 % per degree Celsius. Use of this factor can be avoided by working in a temperature-controlled room.

The result is sometimes expressed as the epoxy index, expressed in moles of epoxy groups per kilogram, calculated as follows:

$$\text{Epoxy index EI} = \frac{1000}{\text{EE}}$$

8 Precision

The precision of this method was determined in accordance with ISO 5725, *Accuracy (trueness and precision) of test methods and results*, following round-robin testing organized in Japan in 1996.

The repeatability and reproducibility values for liquid and solid bisphenol A type epoxy resins are as follows:

Liquid bisphenol A type epoxy resins

Titration method	Repeatability		Reproducibility		Average value of EE
	s_r	r	s_R	R	
Potentiometric	0,61	1,72	1,22	3,41	187,0
Indicator	0,68	1,91	1,04	2,91	188,2

Solid bisphenol A type epoxy resins

Titration method	Repeatability		Reproducibility		Average value of EE
	s_r	r	s_R	R	
Potentiometric	0,87	2,43	6,68	18,71	916,3
Indicator	2,94	8,24	8,01	22,44	919,2

where

s_r is the within-laboratory standard deviation;

r is the repeatability (absolute value);

s_R is the between-laboratory standard deviation;

R is the reproducibility (absolute value).

9 Test report

The test report shall include the following particulars:

a) a reference to this International Standard;

b) all details necessary for complete identification of the sample;

c) the reagent used, if not tetraethylammonium bromide;

d) the result of the test and the way in which it is expressed;

e) details of any operation not included in this International Standard as well as details of any incident likely to have affected the result;

f) the date of the test.

Annex A
(normative)

Modification applicable to epoxyamines

A.1 Scope

When determinations are carried out on nitrogen-containing epoxy resins (i.e. epoxyamines) using the method described in the body of this International Standard, the values determined for the epoxy equivalent are too low. This is due to a reaction between the perchloric acid and the amino nitrogen, leading to the formation of a salt.

If account is taken of the perchloric acid involved in the formation of the salt, then the method can also be used to determine the epoxy equivalent of epoxyamines.

A.2 Principle

The amino nitrogen in a test portion of the epoxyamine is titrated with a 0,1 mol/l standard volumetric perchloric acid solution. The second blank value thus obtained is used as a correction factor in the calculation of the epoxy equivalent, as shown in clause A.4.

A.3 Procedure

Determine the second blank value in accordance with clause 6 of this International Standard, but without addition of tetraethylammonium bromide solution (4.7).

A.4 Expression of results

Calculate the epoxy equivalent EE of the epoxyamine, in grams per mole, by the following equation:

$$\mathrm{EE} = \frac{1\,000\,m}{\left(V_1 - V_0 - V_2 \dfrac{m}{m_1}\right)\left(1 - \dfrac{t - t_s}{1\,000}\right)c}$$

where

m_1 is the mass, in grams, of the test portion used in the second blank test;

V_2 is the volume, in millilitres, of perchloric acid solution (4.6) used in the second blank test;

the other symbols are as defined in clause 7 of this International Standard.