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Plastics — Epoxy resins — Determination of 1,2-glycol content

Plastiques — Résines époxydes — Détermination de la teneur en 1,2-glycol

Reference number
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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information.

The committee responsible for this document is ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

This second edition cancels and replaces the first edition (ISO 21048:2004), which has been technically revised.

Introduction

In producing epoxy resin based on epichlorohydrin, impurities containing 1,2-glycol may be formed. Owing to the hydrophilic characteristics of 1,2-glycol, it is necessary to control the level of these impurities, since they could affect final properties such as electrical insulation. Additionally, these impurities could affect the speed of the curing reaction when using curing agents such as amines and acid anhydrides. Therefore, it is important to determine the 1,2-glycol content in epoxy resins for both resin manufacture and customer use.

Plastics — Epoxy resins — Determination of 1,2-glycol content

SAFETY STATEMENT — Persons using this document should be familiar with normal laboratory practice, if applicable. This document does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any regulatory requirements.

1 Scope

This International Standard specifies a method for the determination of the 1,2-glycol content in epoxy resins.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
1,2-glycol
the 1,2-glycol group [-CH(OH)CH_2OH] in epoxy resins, the content of which is expressed in moles per kilogram of the epoxy resin

Note 1 to entry: This moiety is chemically equivalent to two OH groups.

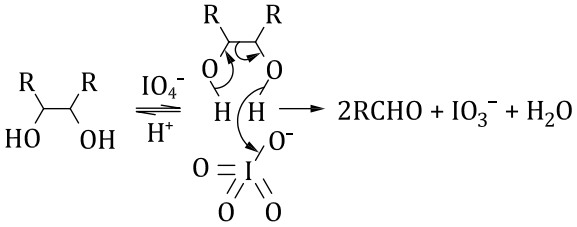
Note 2 to entry: Other possible nomenclatures are vicinal-OH group, 1,2-dihydroxyl group, α-glycol group.

4 Principle

1,2-glycol is determined on the basis of the following reactions.

1,2-glycol is oxidized to aldehyde compounds by an excess of orthoperiodic acid (reaction 1), then potassium iodide is added to the reaction mixture in the presence of sulfuric acid (reaction 2). The generated iodine is then titrated by standardized sodium thiosulfate solution (reaction 3). The 1,2-glycol content is calculated from the sodium thiosulfate consumption.

Reaction 1



Reaction 2 $HIO_4 + 4H_2SO_4 + 7KI \rightarrow 3K_2SO_4 + KHSO_4 + 4H_2O + 4I_2$

$HIO_3 + 3H_2SO_4 + 5KI \rightarrow 2K_2SO_4 + KHSO_4 + 3H_2O + 3I_2$

Reaction 3 $I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$

5 Reagents

Use reagents of recognized analytical grade, and water of grade 3 (as defined in ISO 3696) or better.

5.1 Chloroform.

WARNING — Chloroform is toxic. Avoid inhalation of its vapour. Prevent skin and eye contact. Work in a fume hood or in a well ventilated area. The threshold limit is 10 µg/g.

5.2 Methanol.

WARNING — Methanol is toxic. Avoid inhalation of its vapour. Prevent skin and eye contact. Work in a fume hood or in a well ventilated area. The threshold limit is 200 µg/g.

5.3 Benzyltrimethylammonium hydroxide, 40 % (by mass) solution in methanol.

5.4 Acetic acid.

5.5 Orthoperiodic acid.

5.6 Orthoperiodic acid, 0,2 mol/l solution.

5.6.1 Preparation

Weigh 2,70 g to 2,75 g of orthoperiodic acid into a 500 ml beaker (6.7) and dissolve in 450 ml of methanol (5.2), mixing with a magnetic stirrer (6.2). Place the pH electrode (6.3) into the solution. Neutralize the solution to pH 7,0 by adding benzyltrimethylammonium hydroxide solution (5.3) slowly with stirring. Add 15 ml of acetic acid (5.4) and 5 ml of water, using a 20 ml graduated glass cylinder (6.8), and, using a 500 ml volumetric flask (6.9), fill to the mark with methanol.

5.7 Sulfuric acid, 10 % (by mass) solution.

Add 10 g of sulfuric acid dropwise to 90 g of water with stirring.

5.8 Potassium iodide, 20 % (by mass) solution.

Dissolve 20 g of potassium iodide in 80 g of water.

5.9 Anhydrous sodium carbonate.

5.10 Potassium iodate.

5.11 Oxygen-free water.

5.11.1 Preparation

Put grade 3 water (as specified in ISO 3696) into the conical flask (6.5), boil it for about 5 min to expel dissolved oxygen and allow it to cool to room temperature by sealing with nitrogen gas. Alternatively, it is permissible to expel dissolved oxygen by sparging high purity nitrogen gas for about 15 min.

5.12 Sodium thiosulfate, 0,1 mol/l solution.

5.12.1 Preparation

Weigh out 26,0 g of sodium thiosulfate 5-hydrate and 0,20 g of anhydrous sodium carbonate (5.9). Add 1 l of oxygen-free water (5.11) and store in an airtight container. Allow to stand for two days before using.

5.12.2 Standardization

Heat the required amount of potassium iodate (reference material for volumetric analysis) (5.10) at 130 °C for about 2 h, and allow it to cool in a desiccator. Weigh 0,9 g to 1,1 g of the dried KIO_3 to the nearest 0,1 mg into a 250 ml volumetric flask (6.9), dissolve in water and fill to the mark with water. Using a pipette, place 25 ml of the solution in a 300 ml conical flask (6.5). Add 2 g of potassium iodide and 2 ml of sulfuric acid (1 + 1) to the conical flask, stopper immediately, shake gently, and allow to stand for 5 min in the dark. As an indicator, add 0,5 ml of starch solution (5.13), and titrate with 0,1 mol/l sodium thiosulfate solution (5.12). Add another 0,5 ml of the starch solution when nearing the end point. Continue to titrate until the blue colour of the solution just disappears.

Separately, measure 25 ml of water (using a pipette) and 2 g of potassium iodide into a 300 ml conical flask (6.5), then add 2 ml of sulfuric acid (1 + 1), stopper immediately, shake gently, and allow to stand for 5 min in the dark. Carry out a blank titration by the same procedure as described, and use the result to correct the volume needed for the standardization titration.

5.12.3 Calculation of concentration

Calculate the concentration from the following equation:

$$c = \frac{a \times p}{0{,}003\,566\,7 \times (V_2 - V_1) \times 10\,000} \quad (1)$$

where

c is the concentration of the sodium thiosulfate solution, expressed in moles per litre;

a is the mass of potassium iodate, expressed in grams;

p is the purity of the potassium iodate, expressed in percent;

0,003 566 7 is the mass of potassium iodate equivalent to 1 ml of 0,1 mol/l sodium thiosulfate solution;

V_1 is the volume of sodium thiosulfate solution used in the titration, expressed in millilitres;

V_2 is the volume of sodium thiosulfate solution used in the blank titration, expressed in millilitres.

Round the result to three significant figures.

5.13 Starch solution, 1 % (by mass).

Dissolve 1 g of water-soluble starch in 99 g of hot water.

6 Apparatus

Usual laboratory apparatus, plus the following.

6.1 Analytical balance, accurate to 0,1 mg.

6.2 Magnetic stirrer, equipped with a polytetrafluoroethylene-coated bar.

6.3 pH-meter, accurate to 0,1 pH-units, calibrated in advance, equipped with a glass combination electrode and electrode stand.

6.4 Burette, 50 ml.

6.5 Conical flask, 300 ml, with a ground-glass stopper.

6.6 Pipettes, 5 ml, 20 ml and 25 ml.

6.7 Beaker, 500 ml.

6.8 Graduated glass cylinders, 20 ml and 100 ml.

6.9 Volumetric flasks, 250 ml and 500 ml.

7 Procedure

7.1 Select the mass of the test portion in accordance with the expected 1,2-glycol content (see Table 1).

Table 1 — Mass of test portion

1,2-glycol content, w mol/kg	**Mass of test portion** g
$w < 0{,}01$	10
$0{,}01 \leq w < 0{,}05$	8
$0{,}05 \leq w < 0{,}1$	4
$0{,}1 \leq w < 0{,}2$	2
$0{,}2 \leq w$	1

7.2 Weigh the test portion to the nearest 0,1 mg into a 300 ml conical flask (6.5). Add 25 ml of chloroform (5.1) and warm the mixture to obtain a clear solution. Then cool to ambient temperature.

7.3 Using a pipette, add 25 ml of 0,2 mol/l orthoperiodic acid solution (5.6) to the conical flask. Wet a ground-glass stopper with water and stopper the conical flask tightly. Mix well and allow the reaction mixture to stand at room temperature for 2 h.

7.4 Add 100 ml of cold water to the conical flask and then stopper again. Mix vigorously, using a magnetic stirrer, for 30 s.

7.5 Wash the inside of the conical flask and the glass stopper with a small quantity of water. Using a pipette, add 5 ml of 10 % sulfuric acid solution (5.7).

7.6 Using a pipette, add 20 ml of 20 % potassium iodide solution (5.8).

7.7 Mix well for 30 s with a magnetic stirrer. Titrate with 0,1 mol/l sodium thiosulfate solution (5.12), with stirring. As an indicator, add about 1 ml of starch solution (5.13) when the colour of the solution becomes pale yellow which shows the end point is near.

7.8 Continue to titrate until the blue colour of the solution just disappears.

7.9 Carry out a blank test, following the same procedure and using the same reagents, but omitting the test portion.

8 Expression of results

Calculate the 1,2-glycol content of the sample from the following equation:

$$w = \frac{(V_2 - V_1) \times c}{2m_0} \tag{2}$$

where

w is the 1,2-glycol content of the sample, expressed in moles per kilogram;

m_0 is the mass of the test portion, expressed in grams;

V_1 is the volume of sodium thiosulfate solution used in the titration of the test portion, expressed in millilitres;

V_2 is the volume of sodium thiosulfate solution used in the blank titration, expressed in millilitres;

c is the concentration of the sodium thiosulfate solution, expressed in moles per litre.

9 Precision

Precision data were determined from a round-robin experiment organized in January 2000 involving eight laboratories in Japan. Three commercial epoxy resins with different levels of 1,2-glycol content were tested and the results were analysed in accordance with ISO 5725-2.

The repeatability and reproducibility calculated from the experiments are given in Table 2.