



**International
Standard**

ISO 4764

**Plastics — Polyols for use in the
production of polyurethanes
— Determination of degree of
unsaturation by using iodine method**

*Plastiques — Polyols pour la production des polyuréthanes —
Détermination du degré de non-saturation par la méthode à l'iode*

**First edition
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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 document 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 of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Conventionally, a titration method using mercuric acetate (see ISO 17710) has been used as a method for measuring a polyether polyol for polyurethanes. However, in recent years, the treatment of mercury waste liquid associated with analysis has become a global problem.

This document formulates a measurement method to replace the mercuric acetate method.

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Plastics — Polyols for use in the production of polyurethanes — Determination of degree of unsaturation by using iodine method

1 Scope

This document specifies a method for quantifying the total unsaturation using an addition reaction of the interhalogen compound iodine monochloride (ICl), using glacial acetic acid as a solvent as a method for measuring the total unsaturation of a polyether polyol for polyurethanes. It is not applicable to unsaturated compounds that are conjugated with a carbonyl group, a carboxyl group, or a nitrile group.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385, *Laboratory glassware — Burettes*

ISO 472, *Plastics — Vocabulary*

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 4797, *Laboratory glassware — Boiling flasks with conical ground joints*

ISO 6353-2, *Reagents for chemical analysis — Part 2: Specifications — First series*

ISO 6353-3, *Reagents for chemical analysis — Part 3: Specifications — Second series*

ISO 8655-2, *Piston-operated volumetric apparatus — Part 2: Pipettes*

ISO 8655-3, *Piston-operated volumetric apparatus — Part 3: Burettes*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472 apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

4 Principle

After dissolving the sample in a solvent, the carbon-carbon unsaturated compound in the sample is added with glacial acetic acid solution of iodine monochloride (Wijs reagent) and left in a dark place to add iodine. After completion of the addition reaction, add aqueous solution of potassium iodide, liberate iodine and titrate with a sodium thiosulfate solution. When the colour of the solution turns pale yellow, add a starch solution and titrate until the blue disappears. The degree of unsaturation is calculated from the difference from the blank measured at the same time.

5 Solvents and reagents

5.1 Solvents

Use analytical-grade solvents, such as

5.1.1 methanol, as specified in ISO 6353-2,

5.1.2 ethanol, as specified in ISO 6353-2,

5.1.3 normal propanol,

5.1.4 2-propanol, as specified in ISO 6353-3,

5.1.5 1-butanol, as specified in ISO 6353-3,

5.1.6 cyclohexane, as specified in ISO 6353-2, and

5.1.7 chloroform, as specified in ISO 6353.

NOTE The above solvents are only examples and are not limited thereto (shown in [Annex C](#)).

5.2 Reagents

5.2.1 Wijs reagent

Iodine monochloride solution (Wijs reagent) shall be prepared as follows.

Dissolve 9,0 g of Iodine, to the nearest 1 mg, in 900 ml of warm glacial acetic acid.

Dissolve 8,0 g of iodine trichloride (ICl₃), to the nearest 1 mg, in 60 ml of warm glacial acetic acid.

Then, get together them, and dilute it with acetic acid to make 1 l.

This Wijs reagent should be sealed and stored in a cool and dark place.

5.2.2 0,1 N sodium thiosulfate solution

Dissolve 26 g of sodium thiosulfate pentahydrate (Na₂S₂O₃·5H₂O) (specified in ISO 6353-2), to the nearest 1 mg, in water to make 1 l, and add 0,1 g of sodium carbonate (Na₂CO₃) (specified in ISO 6353-2), to the nearest 1 mg.

This solution is standardized with potassium iodate (KIO₃) as follows.

Put 40 mg of KIO₃, to the nearest 1 mg, into a 300 ml flask with a stopcock and dissolve it in 30 ml of water.

Add 2 g of potassium iodide (KI), to the nearest 1 mg, and dissolve.

Add 5 ml of 2 mol/l hydrochloric acid solution.

The free iodine is quickly titrated with a Na₂S₂O₃ solution using starch as an indicator.

The normality of the Na₂S₂O₃ solution is calculated by [Formula \(1\)](#).

$$F = W / (35,67 \times V) \quad (1)$$

where

F is the normality of $\text{Na}_2\text{S}_2\text{O}_3$ solution;

W is the mass of the KIO_3 , in mg;

V is the volume of the $\text{Na}_2\text{S}_2\text{O}_3$ solution required for the titration of KIO_3 , in ml.

5.2.3 KI solution

Dissolve 2 g of KI in 100 ml of water.

5.2.4 Starch indicator

Make 10 g of soluble starch into a paste, dissolve it in 200 ml of hot water, and stir rapidly and cool.

Add about 10 g of thymol as a stabilizer.

6 Apparatus

Usual laboratory apparatus and, in particular, the following.

6.1 Weighing scoops, suitable for the test portion and for insertion into the flasks.

6.2 Conical flasks, with a capacity of 500 ml and 300 ml, with a stopcock in accordance with ISO 4797.

6.3 Analytical balance, with a readability of 0,000 1 g and weighing accuracy of 0,001 g.

6.4 Volumetric flask, with a capacity of 1 000 ml (1 l), in accordance with ISO 1042, class A.

6.5 Pipette, with a capacity of 2 ml and 25 ml ISO 648, class A, fitted with an aspiration bulb, or automatic one, specified in ISO 8655-2.

CAUTION — Do not use a mouth pipette for the Wijs reagent.

6.6 Burette, with capacity of 25 ml and 50 ml, graduated in 0,1 ml divisions, ISO 385, class A, or automatic one specified in ISO 8655-3.

7 Procedure

Procedure, using methanol as a solvent for one thing, shall be carried out as follows.

Weigh 10 g of the sample, to the nearest 1 mg, into a 500 ml flask with a stopcock and dissolve in methanol.

If the degree of unsaturation is 0,07 or less, 10 g of sample and 30 ml of methanol are recommended.

Add 20 ml of Wijs reagent, stopper and keep in the dark for 1 h.

Add 100 ml of KI solution to the flask, stopper and shake to release iodine.

Titrate free iodine from a 50 ml burette with $\text{Na}_2\text{S}_2\text{O}_3$ solution (under stirring, starch is an indicator).

The end point of titration shall be the point where it becomes colourless.

Titrate a blank using the same procedure, but without adding the sample.

Calculate the degree of unsaturation using [Formula \(2\)](#):

$$U_T = (B - V) \times F / 2S \quad (2)$$

where

U_T is the total degree of unsaturation, in meq/g;

B is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution required for blank titration, in ml;

V is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution required for sample titration, in ml;

F is the normality of $\text{Na}_2\text{S}_2\text{O}_3$ solution;

S is the mass of the sample, in g.

The numerator is divided by 2 in [Formula \(2\)](#) for the following reasons.

In the Wijs method, since one carbon-to-carbon double bond reacts with the iodine chloride molecule, it becomes a 2-equivalent reaction.

8 Correction

If additive having unsaturated bond (both of aromatic and aliphatic), like antioxidant, is added to the sample, it can cause an incorrect result (see [Annex A](#)).

It should be measured the additive alone and corrected. Weigh the appropriate amount of the additive, such as 10 mg for BHT, to the nearest 1 mg. The appropriate amount of additive is the value in mg, which is about twice the expected degree of unsaturation of the additive. Add additive into a 500 ml stopcock flask and dissolve in 30 ml methanol. Add 20 ml of Wijs reagent, stopcock and leave in the dark for 1 h. Add 100 ml of KI solution to the flask, close the stopcock and shake to release iodine. Titrate free iodine from a 50 ml burette with $\text{Na}_2\text{S}_2\text{O}_3$ solution (under stirring, starch is an indicator).

The end point of titration is the point where the colour changes from purple to colourless.

Titrate a blank using the same procedure, but without adding an additive. Calculate the degree of unsaturation of the additive using [Formula \(3\)](#):

$$U_A = (B' - V') \times F' / 2 b' \quad (3)$$

where

U_A is the degree of unsaturation of the additive, in meq/g;

B' is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution required for the blank, in ml;

V' is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution required for the additive, in ml;

F' is the normality of $\text{Na}_2\text{S}_2\text{O}_3$ solution;

b' is the mass of the additive, in g.

9 Degree of unsaturation after correction

The degree of unsaturation after correcting the influence of the additive, the true degree of unsaturation of the polyol (U_P) can be expressed as shown in [Formula \(4\)](#).

$$U_T = a \times U_P + c \times U_A \quad (4)$$

where

U_T is the total degree of unsaturation, in meq/g;

U_P is the true degree of unsaturation, in meq/g;

U_A is the degree of unsaturation of the additive, in meq/g;

a is the mass of the polyol component in 1 g of the measurement sample, which can be expressed as $1-c$, in g;

c is the mass of the additive in 1 g of the measurement sample, in g.

Therefore,

$$U_T = (1-c) \times U_P + c \times U_A \quad (5)$$

$$U_P = (U_T - c \times U_A) / (1-c) \quad (6)$$

If " c ", the mass of additive, is too small, U_P can be expressed following [Formula \(7\)](#)

$$U_P = U_T - c \times U_A \quad (7)$$

NOTE In routine analysis, it is available to determine " $c \times U_A$ " of each product in advance.

10 Precision and bias

The precision and bias of this test are not available at the time of publication.

The measurement results of same samples from several testing laboratories, and results of using ISO17710 are shown [Annex B](#).

11 Test report

The test report shall include the following particulars:

- a reference to this document, i.e. ISO 4764:2024;
- details of the sample (a type of polyol and all details necessary for complete identification of the sample);
- test conditions (room temperature, information of each reagent and solvent);
- test result(s) (degree of unsaturation, mass of sample, titrated volume, and remarks if any);
- the date of analysis;
- the name of measurer(s).

Annex A

(informative)

Correction of effect by additives

Iodine monochloride can react with compound having unsaturated bond, aromatic and/or aliphatic.

It is necessary to gain information or research about additive (product name, content, etc.) in measuring sample, in advance.

If the additive contained in the measurement sample is a compound with aromatic and/or aliphatic unsaturated bonds, this additive should be measured alone to correct.

One of the typical examples is Dibutylhydroxytoluene, BHT, as an antioxidant.

[Table A.1](#) shows the degree of unsaturation of BHT by this document.

Table A.1 — Degree of unsaturation of BHT

Product name	Mass of measuring (mg)	Degree of unsaturation U_A (meq/g)
Dibutylhydroxytoluene (BHT)	10	4,8

In case there are two or more unsaturated compounds, each compound should be measured and corrected.

On the other hand, ISO 17710 does not consider effect of aromatic additives like BHT, because it used mercuric acetate which does not react with aromatic unsaturated bond on usual condition.