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Plastics — Polyols for use in the production of polyurethane — Determination of water content

Plastiques — Polyols pour la production du polyuréthanne — Dosage de l'eau

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 14897 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

This second edition cancels and replaces the first edition (ISO 14897:2000), which has been technically revised. The principal technical change is the incorporation of significantly improved precision data.

The standard is based on ASTM D 4672, *Standard Test Methods for Polyurethane Raw Materials — Determination of Water Content of Polyols*.

Plastics — Polyols for use in the production of polyurethane — Determination of water content

CAUTION — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions prior to use.

1 Scope

This International Standard specifies methods used to measure the water content of polyols employed as polyurethane raw materials. Method A is a manual amperometric method which has been included to better define the principles of the Karl Fischer measurement. Amperometric methods are applicable to a wide range of polyols, including those which have enough colour to obscure a visual end-point. Method B includes an automated amperometric procedure and an automated coulometric procedure. The coulometric procedure is an absolute method that does not require calibration and gives improved sensitivity compared with amperometric methods.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 6353-1:1982, *Reagents for chemical analysis — Part 1: General test methods*

ISO 6353-2:1983, *Reagents for chemical analysis — Part 2: Specifications — First series*

ISO 6353-3:1987, *Reagents for chemical analysis — Part 3: Specifications — Second series*

3 Terms and definitions

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

3.1
polyol
an organic compound containing two or more hydroxyl groups suitable for reaction with isocyanates

3.2
polyurethane
a polymer prepared by the reaction of an organic di- or polyisocyanate with compounds containing two or more hydroxyl groups

NOTE Polyurethanes may be thermosetting, thermoplastic, rigid or soft and flexible, cellular or non-cellular.

4 Principle

4.1 Methods A and B are based on amperometric or coulometric titrations with Karl Fischer reagent. The sulfur dioxide in the reagent first reacts with the alcohol to form an ester which is neutralized by the base present in the reagent. The anion of the alkyl sulfurous acid is the reactive component. The titration of water present constitutes the oxidation of the alkyl sulfite to alkyl sulfate by the iodine, which consumes the water. The reaction can be formulated as follows:[1]

$$ROH + SO_2 + R'N \rightarrow (R'NH)SO_3R$$

$$H_2O + I_2 + (R'NH)SO_3R + 2R'N \rightarrow (R'NH)SO_4R + 2(R'NH)I$$

4.2 To determine water, Karl Fischer reagent [a solution of iodine, sulfur dioxide, ethylene glycol monomethyl ether ($HOCH_2CH_2OCH_3$) and pyridine or a pyridine substitute] is added to a solution of the test portion in methanol or another alcohol until all of the water present has been consumed. In an amperometric titration, this is evidenced by a current-measuring device that indicates the depolarization of a pair of platinum electrodes. In coulometric titrations, the iodine reagent is generated electrically, thus eliminating the need for standardization of the reagent.

5 Application

These test methods are suitable for quality control, as a specification test for products, and for research. The water content of a polyol is important because water reacts with isocyanates to form carbon dioxide and an amine which consumes additional isocyanate.

NOTE The description of the manual system presented below is principally for reference purposes and has been included in order to better define the principles of the Karl Fischer measurement. Commercially available automated Karl Fischer titrators of the type described in Method B are used extensively. Additional details and diagrams are available in ISO 760:1978, *Determination of water — Karl Fischer method (General method)*.

6 Interferences

6.1 Oxides, hydroxides and strongly basic compounds react with Karl Fischer reagent, producing an equivalent amount of water, thus giving falsely high results. Therefore, this method shall not be used for crude polyols containing KOH or other highly basic products unless corrections are made for the excess water produced.

6.2 Amine-based polyols may shift the pH of the Karl Fischer system into the alkaline range, causing incorrect results. This problem may be circumvented by adding salicylic or benzoic acid in greater than stoichiometric amounts before carrying out the titration. Tests should be run to determine the suitability of the procedure for a particular polyol type.

7 Reagents

7.1 Purity of reagents

Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of ISO 6353-1, ISO 6353-2 and ISO 6353-3. Other grades may be used, provided that it is first determined that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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[1] Scholz, Eugen: *Karl Fischer Titration*, Springer-Verlag, Berlin, Heidelberg, New York, 1984.

7.2 Purity of water

Unless otherwise indicated, references to water shall be understood to mean grade 3 water as defined in ISO 3696.

7.3 Reagents for Method A (manual titration)

7.3.1 Karl Fischer reagent, equivalent to 2,5 mg to 3,5 mg of water/ml. Dilute commercially available stabilized Karl Fischer reagent (6 mg of water/ml) with an equal volume of anhydrous ethylene glycol monomethyl ether (containing less than 0,1 % of water).

NOTE Improved, pyridine-free Karl Fischer reagents have been made available and are highly recommended as a replacement for the previous reagents.

7.3.2 Titration solvent (anhydrous methanol): Unless the methanol is extremely dry, it will require a large amount of dilute Karl Fischer reagent to react with its residual water. For this reason, dry the solvent further by adding undiluted Karl Fischer reagent (6 mg of water/ml) to a bottle of methanol until a light red-brown colour persists. Then add methanol until the solution is a pale yellow. A 100 ml portion of the treated solvent should require 1 ml to 10 ml of dilute Karl Fischer reagent.

7.4 Reagent for Method B

7.4.1 Karl Fischer reagent: Commercial reagents and reagent systems of various types are available for use with autotitrators for water determination. These pyridine-free reagents have improved stability and a less objectionable odour than the conventional Karl Fischer reagent. Reagents can be purchased in split or composite forms in different concentrations to fit various ranges of water content. A composite reagent contains all of the components required for a Karl Fischer titration in a single solution. A split reagent implies separate solutions of the solvent and titrant.

8 Apparatus

8.1 Apparatus for Method A (manual titration)

8.1.1 Titration vessel: A vessel of approximately 300 ml capacity, such as a tall-form, lipless beaker provided with a tight-fitting closure to protect the reaction mixture from atmospheric moisture. The vessel shall also be fitted with a nitrogen inlet tube, a 10 ml burette, a stirrer (preferably magnetic) and a port that may be opened momentarily for sample and solvent addition, or removal of electrodes. It is convenient to provide a vacuum line leading to a 1 litre trap bottle for drawing off the titrated solution. Pass the nitrogen through a drying tube containing anhydrous calcium sulfate before it enters the titration vessel.

8.1.2 Instrument electrodes, platinum, with a surface equivalent of two No. 26 wires, 4,76 mm long. The wires shall be 3 mm to 8 mm apart and inserted in the vessel so that 75 ml of solution will cover them.

8.1.3 Instrument depolarization indicator, having an internal resistance of less than 5 000 Ω, consisting of a means of applying and indicating a voltage of 20 mV to 50 mV across the electrodes, and capable of indicating a current flow of 10 µA to 20 µA by means of a galvanometer or ratio tuning circuit.

8.1.4 Burette assembly, for Karl Fischer reagent, consisting of a 10 ml burette with 0,05 ml subdivisions and connected by means of glass or polyethylene (not rubber) connectors to a source of reagent. Various types of automatic dispensing burette may be used. Since the reagent loses strength when exposed to moist air, all vents shall be protected against atmospheric moisture by adequate drying tubes containing anhydrous calcium sulfate. All stopcocks and joints shall be lubricated with an inert lubricant.

8.1.5 Weighing pipette, approximately 1 ml.

8.1.6 Syringes, 1 ml and 10 ml, suitable for weighing and delivering viscous liquid samples.

8.1.7 **Analytical balance,** capable of weighing to 0,1 mg.

8.2 Apparatus for Method B (automated titration)

8.2.1 **Autotitrator:** Several commercial autotitrators are available for amperometric or coulometric titrations and provide results equivalent to or better than those of the manual procedure described in Method A. These instruments consist of an automated burette assembly, a sealed titration vessel with appropriate electrodes and associated circuitry, and a means for removal of solution after analysis. These automated systems provide several advantages. Atmospheric-moisture contamination can be more closely controlled, calibration is simplified and the preneutralization step is automatic. Titrations are rapid and reagent consumption is low. The newer autotitrators automatically calculate and display or print out the water concentration.

8.2.2 **Syringes,** 1 ml and 10 ml, suitable for weighing and delivering viscous liquid samples.

8.2.3 **Analytical balance,** capable of weighing to 0,1 mg.

9 Sampling

9.1 It is essential to avoid changes in the water content of the material during sampling operations. Many polyols are quite hygroscopic, and errors from this source are particularly significant in the determination of the small amount of water usually present. It has been demonstrated that increases in the water content of hygroscopic liquids will occur, even when the analyses are carried out in an air-conditioned laboratory, without using special precautions to exclude atmospheric moisture. Therefore, use almost-filled, tightly capped containers and limit as much as possible contact of the sample with air when transferring the sample to the titration vessel. Notable improvements in accuracy can be expected from placing the entire titration equipment in a nitrogen (or dry air) purged enclosure. Avoid intermediate sample containers, if possible. If several different analyses are to be performed on the same sample, determine the water content first and do not open the sample prior to the actual analysis. If possible, keep the laboratory humidity low, preferably under 50 % relative humidity.

9.2 Sampling is conveniently accomplished by use of a tared syringe (8.2.2). The material is drawn into a syringe, weighed, and delivered through the sample port of the titrator vessel. The syringe is then reweighed to obtain the mass of the test portion by difference.

Table 1 — Recommended size of test portion for manual titration (Method A)

Water content %	Size of test portion
Below 0,5	Mass containing approximately 25 mg of water[a]
Over 0,5	5 g

[a] This mass shall not exceed 30 g.

Table 2 — Recommended size of test portion for amperometric titration[a] (Method B)

Water expected %	Suggested size of test portion g
Below 0,5	5 to 10
0,5 to 1,0	1
above 1,0	0,5

[a] For a titrant concentration equivalent to 5 mg of H_2O per ml.

Table 3 — Recommended size of test portion for coulometric titration (Method B)

Water expected %	Suggested size of test portion g
Below 0,1	5
0,1 to 0,5	1
0,5 to 1,0	0,1

NOTE The values shown in Tables 2 and 3 are given only as general guidelines. The design of a specific instrument may require a different test portion size. Consult the manufacturer's manual for recommended test portion sizes.

10 Standardization of reagent

10.1 Standardization of reagent for Method A (manual titration)

Standardize the Karl Fischer reagent (7.3.1) daily, using the same procedure as used for titrating the test portion, as follows:

Add 100 ml of titration solvent (7.3.2) to the titration vessel (8.1.1) and titrate the residual moisture as described in clause 11. To this titrated solvent, immediately add 1 drop of water from a weighing pipette (8.1.5). Weigh the pipette to ± 0,1 mg. Complete the titration with Karl Fischer reagent as described in clause 11.

10.2 Standardization of reagent for Method B (automatic amperometric or coulometric titration)

Since different autotitrators may vary in their standardization procedures, consult the operating manual for the autotitrator being used. Water is an excellent primary standard. In addition, stable prepackaged primary standards are available for establishing the equivalency factor F (see 10.3).

10.3 Calculation

Calculate the equivalency factor F, in terms of milligrams of water per millilitre of reagent, as follows:

$$F = A/B$$

where

A is the mass of water added, in mg;

B is the volume of Karl Fischer reagent required, in ml.

11 Procedure

11.1 Procedure for Method A (manual titration)

11.1.1 Adjust the nitrogen valve so that dry nitrogen flows into the titration vessel at a slow rate (20 ml/min to 50 ml/min). Introduce approximately 100 ml of titration solvent into the titration vessel, making sure that the electrodes are covered with solvent. Adjust the stirrer to give adequate mixing without splashing. Titrate the mixture with Karl Fischer reagent to the end-point.

11.1.2 To the prepared titration mixture, add a test portion as indicated in Table 1. Exercise care when the test portion is transferred so that water is not absorbed from the air, particularly under conditions of high humidity. Allow the solution to stir for 1 or 2 minutes until dissolution is complete.

11.1.3 Titrate the solution obtained in 11.1.2 with Karl Fischer reagent to the same end-point previously employed. Record the amount of reagent used to titrate the water in the test portion.

NOTE The end-point is that point in the titration when two small platinum electrodes upon which a potential of 20 mV to 50 mV has been impressed are depolarized by the addition of 0,05 ml of Karl Fischer reagent (equivalent to 2,5 mg to 3,0 mg of water/ml), causing a change in current flow of 10 µA to 30 µA that persists for at least 30 s.

11.2 Procedure for Method B (amperometric or coulometric titration)

Refer to the operating manual for the autotitrator being used. Basically, after preneutralization of the reagent in the titrator vessel, the test portion is introduced, the instrument is switched to the titrator mode, and the amperometric or coulometric titration proceeds automatically to the end-point.

In choosing an appropriate size of test portion for use with specific autotitrators, follow the manufacturer's recommendations. If no instructions are available, use the guidelines listed in Tables 2 and 3.

12 Expression of results

Calculate the water content $w(\mathrm{H_2O})$ of the sample, as a percentage by mass, as follows:

$$w(\mathrm{H_2O}) = \frac{V \times F}{10\,m}$$

where

V is the volume of Karl Fischer reagent required, in ml;

F is the equivalency factor for the Karl Fischer reagent, in mg of water/ml of reagent;

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

10 is a constant combining conversion from g to mg, and conversion to percent.

13 Precision and bias

13.1 General

Attempts to develop a precision and bias statement for the manual amperometric method have not been satisfactory. Therefore, data on the precision and bias of Method A (manual titration) are not given.

13.2 Precision and bias for Method B

13.2.1 Precision

Use the following criteria to judge the acceptability of results (95 % confidence limits):

Repeatability (single analyst): Duplicate results obtained by the same analyst on the same equipment on the same day shall only be considered suspect if they differ by more than the relative percent value listed in Table 4 for the water level which most closely matches the sample being analysed.

Table 4 — Repeatability data for Method B

Water level mass %	**Amperometric procedure** relative %	**Coulometric procedure** relative %
0,03	8,2	2,8
0,42	1,6	3,1
1,6	1,1	3,1

Reproducibility (multilaboratory): Results, each the mean of duplicates run on identical test material in separate laboratories, shall only be considered different if they differ by more than the relative percent value listed in Table 5 for the water level which most closely matches the sample being analysed.

Table 5 — Reproducibility data for Method B

Water level mass %	**Amperometric procedure** relative %	**Coulometric procedure** relative %
0,03	16,0	15,9
0,42	4,4	3,2
1,6	5,0	5,2

13.2.2 Bias

Bias is the difference between the expectation of the test results and an accepted reference value. The bias of this method has not yet been determined.

14 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary for complete identification of the product tested;

c) the method of titration used (automated coulometric, automated amperometric or manual amperometric);

d) the results obtained, including the units in which they are expressed;

e) any incident or detail not stipulated in this International Standard which may have influenced the results;

f) the date of the analysis.