



Designation: D 4672 – 00

## Standard Test Methods for Polyurethane Raw Materials: Determination of Water Content of Polyols<sup>1</sup>

This standard is issued under the fixed designation D 4672; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 These test methods measure water content of polyols and many other organic compounds.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—ISO Standard 14897 is equivalent to these test methods.

### 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

D 1193 Specification for Reagent Water

D 883 Terminology Relating to Plastics

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals

### 3. Terminology

3.1 *Definition:*

3.1.1 *polyurethane, n*—a polymer prepared by the reaction of an organic diisocyanate with compounds containing hydroxyl groups.

3.1.1.1 *Discussion*—Polyurethanes, or urethanes, as they are sometimes called, may be thermosetting, thermoplastic, rigid or soft and flexible, cellular or solid. (See Terminology D 883.)

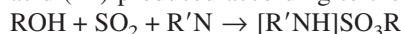
<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D20 on Plastics and are the direct responsibility of Subcommittee D20.22 on Cellular Plastics. It was recommended to ASTM by the American Plastics Council.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

### 4. Summary of Test Methods

4.1 Test Methods A and B are based essentially on volumetric or coulometric titrations that follow the reduction of iodine by sulfur dioxide in the presence of water. This reaction proceeds quantitatively when methanol or another alcohol (ROH) and pyridine (C<sub>5</sub>H<sub>5</sub>N) or a similar amine (R'N) are present to react with the sulfur trioxide (SO<sub>3</sub>) and hydriodic acid (HI) produced according to the following reactions:



4.2 To determine water, Karl Fischer reagent (a solution of iodine, sulfur dioxide, imidazole, and pyridine or a pyridine substitute) is added to a solution of the sample in methanol or other alcohol until all the water present has been consumed. The titrant can either be added by buret (volumetry) or generated electrochemically in the titration cell (coulometry). Coulometric titrations eliminate the need for standardizing the reagent.

### 5. Significance and Use

5.1 These test methods are suitable for quality control, as a specification test, and for research. The water content of a polyol is important since isocyanates react with water.

#### TEST METHOD A: MANUAL PROCEDURE

NOTE 2—Commercially available automated Karl Fischer titrators are used extensively.

5.2 The description of the manual systems presented below is for reference purposes and has been included in order to better define the principles of the Karl Fischer measurement.

### 6. Apparatus

6.1 *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 buret, 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-L 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.

6.2 *Instrument Electrodes*—Platinum with a surface equivalent of two No. 26 wires, 4.762 mm (0.19 in.) long. The wires should be 3 to 8 mm apart and inserted in the vessel so that 75 mL of solution will cover them.

6.3 *Instrument Depolarization Indicator*—Having an internal resistance of less than 5000  $\Omega$  and consisting of a means of impressing and showing a voltage of 20 to 50 mV across the electrodes and capable of indicating a current flow of 10 to 20  $\mu$ A by means of a galvanometer or ratio tuning circuit.

6.4 *Buret Assembly*—For Karl Fischer reagent, consisting of a 10-mL buret with 0.05-mL subdivisions connected by means of glass or polyethylene (not rubber) connectors to a source of reagent. Several types of automatic dispensing burets may be used. Since the reagent loses strength when exposed to moist air, all vents must be protected against atmospheric moisture by adequate drying tubes containing anhydrous calcium sulfate. All stopcocks and joints should be lubricated with an inert lubricant.

## 7. Reagents

7.1 *Purity of Reagents*—Use reagent-grade chemicals in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>3</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification D 1193.

7.3 *Karl Fischer Reagent*—Equivalent to 2.5 to 3.0 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 % water). (See Note 3.)

NOTE 3—Improved, pyridine-free Karl Fischer reagents have been made available and are now highly recommended as a replacement for the previous reagents. See Section 14, under Test Method B, Automated Procedure.

7.4 *Titration Solvent, Anhydrous Methanol*—Unless the methanol is extremely dry it will require a large amount of dilute Karl Fischer solution to react with its residual water. For this reason the solvent shall be further dried by adding undiluted Karl Fischer reagent (6 mg of water/mL) to a bottle of methanol until a light red-brown color persists. Add methanol until the solution is a pale yellow. A 100-mL portion of the treated solvent should require 1 to 10 mL of dilute Karl Fischer reagent.

<sup>3</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

## 8. Sampling

8.1 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. 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. Avoid intermediate sample containers, if possible. If several different analyses are to be performed on the same sample, determine the water first and do not open the sample prior to the actual analysis.

## 9. Standardization of Reagent

9.1 Standardize the Karl Fischer reagent daily using the same procedures as used for titrating the sample.

9.1.1 Add 100 mL of titration solvent to the flask and titrate the residual moisture as described in Section 10. To this titrated solvent, immediately add 1 drop of water from a weighing pipet. Weigh the pipet to  $\pm 0.1$  mg. Complete the titration with Karl Fischer reagent as described in Section 10. It may be necessary to refill the buret during the titration.

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

$$\text{equivalency factor, } F = A/B \quad (1)$$

where:

$A$  = water added, mg, and

$B$  = Karl Fischer reagent required, mL.

## 10. Procedure

10.1 Adjust the nitrogen valve so that dry nitrogen flows into the titration vessel at a slow rate (20 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. (See Note 4.)

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

10.3 Titrate the mixture again with Karl Fischer reagent to the same end point previously employed. Record the amount of reagent used to titrate the water in the sample.

NOTE 4—The end point is that point in the titration when two small platinum electrodes upon which a potential of 20 to 50 mV has been impressed are depolarized by the addition of 0.05 mL of Karl Fischer reagent (equivalent to 2.5 to 3.0 mg water/mL) causing a change of current flow of 10 to 30  $\mu$ V that persists for at least 30 s.

TABLE 1 Recommended Sample Size

Water Content, %	Sample Size, g
Below 0.5	weight containing approximately 25 mg of water <sup>A</sup>
Over 0.5	5

<sup>A</sup> This weight should not exceed 30 g.