Designation: D 4672 – 00

Standard Test Methods for Polyurethane Raw Materials: Determination of Water Content of Polyols [1]

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:*

D 1193 Specification for Reagent Water[2]

D 883 Terminology Relating to Plastics[3]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals[4]

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.)

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_5H_5N) or a similar amine (R′N) are present to react with the sulfur trioxide (SO_3) and hydriodic acid (HI) produced according to the following reactions:

$$ROH + SO_2 + R'N \rightarrow [R'NH]SO_3R$$

$$H_2O + I_2 + [R'NH]SO_3R + 2R'N \rightarrow [R'NH]SO_4R + 2[R'NH]I$$

4.2 To determine water, Karl Fischer reagent (a solution of iodine, sulfur dioxide, 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.

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[1] 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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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 08.01.

[4] *Annual Book of ASTM Standards*, Vol 15.05.

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 Ω 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 µA 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.[5] 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. A100-mL portion of the treated solvent should require 1 to 10 mL of dilute Karl Fischer reagent.

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 ±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:

$$\text{equivalency factor, } F = A/B \tag{1}$$

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 µV that persists for at least 30 s.

11. Calculation

11.1 Calculate the water content of the sample as follows:

$$\text{water, \%} = VF/10W \tag{2}$$

TABLE 1 Recommended Sample Size

Water Content, %	Sample Size, g
Below 0.5	weight containing approximately 25 mg of water[A]
Over 0.5	5

[A] This weight should not exceed 30 g.

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[5] *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.

where:

V = Karl Fischer reagent required by the sample, mL

F = equivalency factor for Karl Fischer reagent, mg water/mL reagent, and

W = sample used, g.

12. Precision and Bias

12.1 Attempts to develop a precision and bias statement for this test method have not been successful. For this reason, data on precision and bias cannot be given. Anyone wishing to participate in the development of precision and bias data should contact the Chairman, Subcommittee D20.22 (Section 20.22.01), ASTM, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428–2959.

TEST METHOD B: AUTOMATED PROCEDURE

13. Apparatus

13.1 Several commercial autotitrators are available[6] that employ volumetric or coulometric titrations and provide results superior to those of the manual procedure, described above. These instruments consist of an automated buret assembly, a sealed titration vessel with appropriate electrodes and sensing circuitry, and a vacuum system for removal of solution after analysis. These automated systems provide several advantages and conveniences. 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. Autotitrators automatically calculate and display or print the water concentration.

14. Reagents

14.1 Commercial reagents and reagent systems of various types are available[7] for use with autotitrators for water determination. Pyridine-free reagents have improved stability and less objectionable odor 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 the components required for a Karl Fischer titration in a single solution. *Split* implies separate solutions of the solvent and titrant.

15. Sampling

15.1 Sampling is conveniently accomplished by use of a tared syringe. The material is drawn into the syringe, weighed, and delivered through the sample port of the autotitrator vessel. The syringe is then reweighed to obtain the sample weight by difference.

15.1.1 Take note of the sample handling warnings in 8.1.

16. Standardization of Reagent

16.1 Since different autotitrators may vary in standardization procedures, consult the operating manual for the autotitrator in use. Water is an excellent primary standard. In addition, stable, prepackaged, primary standards are also available for establishing the standardization factor.

17. Procedure

17.1 Refer to the operating manual for the autotitrator in use. Basically, after preneutralization of the reagent in the titrator vessel, the sample is introduced, and the volumetric titration (or coulometric generation of titrant) proceeds automatically to the end point.

NOTE 5—In choosing the appropriate sample size for use with specific autotitrators, use the manufacturer's recommendations. If no instructions are available, use the guidelines listed in Table 2 and Table 3.

TABLE 2 Volumetric Titration[A]

% Water Expected	Suggested Sample Size, g
Below 0.5	5–10
0.5–1.0	1
Above 1.0	0.5

[A] For titrant concentration equivalent to 5 mg H_2O per mL.

TABLE 3 Coulometric Titration

% Water Expected	Suggested Sample Size, g
Below 0.1	5
0.1–0.5	1
0.5–1.0	0.1

18. Calculation

18.1 Following each titration, autotitrator automatically calculates and displays the water content, based on the stored values of sample weight, standardization factor, and titrant volume consumed. (See 11.1 for the manual calculation.)

19. Precision and Bias [8]

19.1 *Precision*—The following data should be used for judging the acceptability of results (95 % confidence limits):

19.1.1 *Repeatability*—Duplicate results obtained by the same analyst should be considered suspect if they differ by more than the percent relative listed in Table 4 for the water level which most closely matches the sample being analyzed.

TABLE 4 Repeatability Statistics

Water Level	Volumetric	Coulometric
0.03	8.2	2.8
0.42	1.6	3.1
1.6	1.1	3.1

19.1.2 *Reproducibility*—The average result of duplicates obtained in one laboratory should not differ from that of another laboratory by more than the relative percentage given in Table 5 for the water levels listed.

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[6] Instruments similar to and including the following types have been found suitable for determining water content of polyols, based on round-robin studies: Metrohm models 633, 652, 658, 665, 684, 701, 720, 737, and 758 (available from Brinkmann Instruments, Inc. at www.brinkmann.com) and Mettler Toledo models DL 18, 31, 37, and 38 (www.mt.com).

[7] Reagents for Karl Fischer titrations include Hydranal products from Riedel-deHaën (www.rdhlab.de), which are available through Sigma-Aldrich (www.sigma-aldrich.com) and AquaStar products which are sold by EMScience (www.em-science.com).

[8] Supporting data are available at ASTM Headquarters. Request RR:D20-1068.

TABLE 5 Reproducibility Statistics

Water Level	Volumetric	Coulometric
0.03	16.0	15.9
0.42	4.4	3.2
1.6	5.0	5.2

19.2 The precision statements above are based on a 2000 interlaboratory study of three polyol samples with water contents of approximately 0.03, 0.42, and 1.6 %. One analyst in each of nine to twelve laboratories performed duplicate determinations and repeated them on a second day. The samples were analyzed by both volumetric and coulometric methodologies. Practice E 180 was used to develop the precision estimates listed in Table 6. Values are listed in weight percent of water.

TABLE 6 Round Robin Results (Weight Percent of Water)

Volumetric	Average	S_r[A]	S_R[B]	r[C]	R[D]	n[E]
Low water level	0.0281	0.0008	0.0016	0.0023	0.0045	10
Medium water level	0.4257	0.0025	0.0067	0.0069	0.0188	9
High water level	1.6451	0.0063	0.0295	0.0177	0.0827	10
Coulometric						
Low water level	0.0252	0.0003	0.0014	0.0007	0.0040	6
Medium water level	0.4178	0.0046	0.0048	0.0130	0.0135	7
High water level	1.6228	0.0178	0.0303	0.0499	0.0848	8

[A] S_r = within-laboratory standard deviation of the replicates.
[B] S_R = between-laboratory standard deviation of the averages.
[C] r = within-laboratory repeatability limit = 2.8 × S_r.
[D] R = between laboratory reproducibility limit = 2.8 × S_R.
[E] n = number of laboratories contributing valid data for this material.

19.3 *Bias*—The bias of these test methods have not been determined.

20. Keywords

20.1 Karl Fischer; polyols; polyurethane; raw materials; water content