Designation: D4672 – 12

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

This standard is issued under the fixed designation D4672; 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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method measures 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—This test method is equivalent to ISO 14897.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D883 Terminology Relating to Plastics

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

3. Terminology

3.1 *Definitions:*

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 D883.)

4. Summary of Test Methods

4.1 This method is 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 is either 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 This test method is suitable for quality control, as a specification test, and for research. The water content of a polyol is important since isocyanates react with water.

6. Apparatus

6.1 Several commercial Karl Fischer autotitrators are available[4] that employ volumetric or coulometric titrations. 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.

[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and are the direct responsibility of Subcommittee D20.22 on Cellular Materials - Plastics and Elastomers.

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

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] 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).

***A Summary of Changes section appears at the end of this standard**

7. Reagents

7.1 Commercial reagents and reagent systems of various types are available[5] 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.

8. Sampling

8.1 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.

8.1.1 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 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.

10. Procedure

10.1 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 2—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 1 and Table 2.

11. Calculation

11.1 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.

[5] 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).

TABLE 1 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 2 Coulometric Titration

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

12. Precision and Bias[6, 7]

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

12.1.1 *Repeatability*—Duplicate results obtained by the same analyst are to be considered suspect if they differ by more than the percent relative listed in Table 3 for the water level which most closely matches the sample being analyzed.

12.1.2 *Reproducibility*—The average result of duplicates obtained in one laboratory are to be considered suspect if they differ from that of another laboratory by more than the relative percentage given in Table 4 for the water levels listed.

12.2 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 E180 was used to develop the precision estimates listed in Table 5. Values are listed in weight percent of water.

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

13. Keywords

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

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D20-1068.

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D20-1209.

TABLE 3 Repeatability Statistics

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

TABLE 4 Reproducibility Statistics

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

TABLE 5 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.

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue, D4672 - 00(06)$^{\varepsilon 1}$, that may impact the use of this standard. (August 1, 2012)

(1) Removed Test Method A—Determination of Water in Polyols by Manual Karl Fischer Titration since it is no longer used today.

(2) Various editorial changes as a result of the change referenced above.