Designation: D4663 – 15

Standard Test Method for
Polyurethane Raw Materials: Determination of Hydrolyzable Chlorine of Isocyanates [1]

This standard is issued under the fixed designation D4663; 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 determines the hydrolyzable chlorine content of toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, or mixtures of the two. It is acceptable to apply this test method to other isocyanates of suitable solubility. (See Note 1.) The main sources of hydrolyzable chlorine in the isocyanates are carbamoyl chloride and dissolved phosgene. Both of these compounds react with alcohols and water, forming ureas, carbamates, carbon dioxide, and hydrochloric acid. (See Note 2.)

1.2 *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—It is possible that this test method is applicable to crude polymeric isocyanates. However, the precision with crude polymeric isocyanates has not been established.

NOTE 2—This standard is identical to ISO 15028.

2. Referenced Document

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

D1193 Specification for Reagent Water

2.2 *ISO Standards:*

ISO 15028 Plastics—Aromatic Isocyanates for Use in the Production of Polyurethanes—Determination of Hydrolysable Chlorine[3]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method see Terminology D883.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *hydrolyzable chloride*—the low level chlorine-containing components of the isocyanate, such as carbamoyl chlorides, which react with water or alcohol to form HCl.

4. Summary of Test Method

4.1 The hydrolyzable chlorine reacts with methanol, liberating hydrochloric acid. The titratable chlorides are then determined potentiometrically using a standard silver nitrate solution.

5. Significance and Use

5.1 This test method can be used for research or for quality control to characterize toluene diisocyanates. Hydrolyzable chlorine correlates with performance in some polyurethane systems.

6. Interferences

6.1 Thiocyanate, cyanide, sulfide, bromide, iodide, or other substances capable of reacting with silver ions, as well as substances capable of reducing silver ions in acid solution, will interfere with the determination.

7. Apparatus

7.1 *Weighing Bottle,* or any device capable of weighing a liquid by difference to the nearest 0.1 g.

7.2 *Hot Plate,* with magnetic stirrer.

7.3 *Potentiometric Titrator,* or pH meter.

7.4 *Combination Silver Billet Electrode.*

8. Reagents and Materials

8.1 *Purity of Reagents*—Use reagent grade chemicals in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such

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[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is 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] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

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

specifications are available.[4] 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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification D1193.

8.3 *Concentrated Nitric Acid* (HNO_3 sp gr 1.42).

8.4 *Methanol.*

8.5 *Silver Nitrate Standard Solution* (0.01 *N*)—Standardize with standard hydrochloric acid, either gravimetrically or potentiometrically, frequently enough to detect changes of 0.0005 *N*.

9. Sampling

9.1 Since organic isocyanates react with atmospheric moisture, take special precautions in sampling. Usual sampling methods, even when conducted rapidly, can cause contamination of the sample with insoluble urea. Therefore, blanket the sample with dry air or nitrogen at all times. (**Warning—** Diisocyanates are eye, skin and respiratory irritants at concentrations above the occupational exposure limit (TLV or PEL). Diisocyanates can cause skin and respiratory sensitization (asthma) in some people. Once sensitized, it is essential to limit further exposure to diisocyanates. Use a combination of engineering controls and personal protective equipment, including respiratory, skin and eye protection, to prevent overexposure to diisocyanates. Consult the product suppliers' Safety Data Sheet (SDS) for more detailed information about potential health effects and other specific safety and handling instructions for the product.)

10. Test Conditions

10.1 Since isocyanates react with moisture, keep laboratory humidity low, preferably around 50 % relative humidity. See Section 9 of this standard for guidance on how to keep moisture out of the sample.

11. Procedure

11.1 Weigh (by difference to the nearest 0.1 g) 9 to 11 g of sample from a sampling weighing bottle into a clean, dry 400-mL beaker (Note 3). Add 50 mL of methanol and stir. Stir continuously while the reaction starts at which point the beaker will become warm and crystals may form on the sides of the beaker (Note 4). Fill the beaker half-full with water (Note 5) and boil gently for 30 min.

NOTE 3—If the hydrolyzable chlorine content is expected to be less than 0.01 %, use 18 to 22 g of sample.

NOTE 4—Some isocyanates will not react readily and slight warming may be necessary to initiate reaction. Other isocyanates may react, as indicated by warming of reactants, but may not form crystals.

NOTE 5—Add the water quickly to keep the reactants from solidifying and to minimize the loss of HCl.

11.2 Wash the sides of the beaker with water and remove and wash the stirring bar. Cool the beaker in an ice bath to about 10°C and add 10 drops of HNO_3. Titrate potentiometrically with 0.01 *N* $AgNO_3$ solution using a combination silver billet electrode. If the chloride content is greater than 0.2 %, use 0.1 *N* instead of 0.01 *N* $AgNO_3$ solution.

12. Calculation

12.1 Calculate the hydrolyzable chlorine as weight percent as follows:

$$\begin{aligned}\text{Hydrolyzable chlorine, \%} &= 35.45 \times A \times N \times 100/(1000 \times W) \\ &= 3.545 \times A \times N/W\end{aligned}$$

where:

A = $AgNO_3$ solution required for titration of the sample, mL,
N = normality of the $AgNO_3$ solution, meq/mL,
W = sample used, g, and
3.545 = constant combining the atomic weight of chlorine (35.45 mg/meq), the conversion from milligrams to grams (1000), and conversion to percent (100).

13. Precision and Bias

NOTE 6—Estimate of precision below was determined using a silver-silver chloride electrode which is no longer commercially available.

13.1 *Precision*—Attempts to develop a precision and bias statement for this test method have not been successful due to the limited number of laboratories participating in round-robin tests. Data on precision and bias cannot be given for this reason. Anyone wishing to participate in the development of precision and bias data should contact the Chairman, Subcommittee D20.22 (Section D20.22.01), ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

13.2 A limited round-robin was conducted.

13.2.1 It has been estimated that duplicate results by the same analyst shall be considered suspect if they differ by more than 0.001 % hydrolyzable chlorine at the 0.001 to 0.2 % level.

13.2.2 It has been estimated that results reported by different laboratories shall be considered suspect if they differ by more than 0.003 % hydrolyzable chlorine.

13.3 *Bias*—There are no recognized standards by which to estimate the bias of this test method.

14. Keywords

14.1 aromatic isocyanates; hydrolyzable chlorine; isocyanates; polyurethane raw materials; titration; toluene diisocyanate

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[4] *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D4663 - 10) that may impact the use of this standard. (May 1, 2015)

(1) Various editorial changes throughout the standard.
(2) Section 1: Scope—Verified that ISO 15028 is identical to this standard.
(3) Section 2: Referenced Documents—Added ISO 15028 as a reference.
(4) Subsection 9.1: Sampling—The previous warning statement was edited to remove non-mandatory language and updated with input from the Center for the Polyurethanes Industry's (CPI) Product Stewardship Committee.
(5) Section 10: Test Conditions—Removed redundant information.
(6) Subsection 11.2: Procedure—Changed electrode to the one specified in 7.4.
(7) Section 12: Calculations—Replaced picture of equation in 12.1 with text version.
(8) Subsection 13.2: Precision and Bias—Removed non-mandatory language.

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