Designation: D 4663 – 98

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

This standard is issued under the fixed designation D 4663; 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. This test method may also be applied 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.* For specific hazards statements see Note 3.

NOTE 1—This test method may be applicable with crude polymeric isocyanates. However, the precision with crude polymeric isocyanates has not been established.

NOTE 2—There is no equivalent ISO standard.

2. Referenced Document

2.1 *ASTM Standards:*

D 883 Terminology Relating to Plastics[2]

D 1193 Specification for Reagent Water[3]

3. Terminology

3.1 Definitions—For definitions of terms used in this test method see Terminology D 883.

3.2 *Description of Term 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 ion, as well as substances capable of reducing silver ion 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 *Silver-Silver Chloride Electrode.*

7.5 *Silver or Glass Electrode.*

7.6 *Calomel 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

[1] [1] This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.22 on Cellular Plastics.

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

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

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 D 1193.

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 (**Warning: Precaution**—Note 3). Usual sampling methods (for example, sampling an open drum with a thief), even when carried out rapidly, can cause contamination of the sample with insoluble urea. Therefore, blanket the sample with dry air or nitrogen at all times.

NOTE 3—**Warning:** Organic isocyanates are toxic when they are absorbed through the skin, or when the vapors are breathed. **Precaution**—Provide adequate ventilation and wear protective gloves and eyeglasses.

10. Test Conditions

10.1 Since isocyanates react with moisture, keep laboratory humidity low, preferably around 50 % relative humidity.

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 4). Add 50 mL of methanol and stir. Stir continually while the reaction starts at which point the beaker will become warm and crystals may form on the sides of the beaker (Note 5). Fill the beaker half-full with water (Note 6) and boil gently for 30 min.

NOTE 4—If the hydrolyzable chlorine content is expected to be less than 0.01 %, use 18 to 22 g of sample.

NOTE 5—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 6—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 silver-silver chloride electrode pair. 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:

$$\text{Hydrolyzable chlorine, \%} = 3.55AN/W$$

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
3.55	=	constant combining the atomic weight of chlorine (35.5), mg, the conversion from milligrams to grams (1000), and conversion to percent (100).

$$\text{Hydrolyzable chlorine, \%} = 35.5AN(100)/1000W = 3.55AN/W$$

13. Precision and Bias

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 should be considered suspect if they differ by more than 0.001 % hydrolyzable cholorine at the 0.001 to 0.2 % level.

13.2.2 It has been estimated that results reported by different laboratories should 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

[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.