Designation: D4661 – 23

Standard Test Methods for Polyurethane Raw Materials: Determination of Total Chlorine in Isocyanates[1]

This standard is issued under the fixed designation D4661; 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 These test methods determine the total chlorine content of aromatic isocyanates used as polyurethane raw materials. The difference between the total chlorine content and the hydrolyzable chlorine content (see Test Method D4663) is a measure of the amount of chlorobenzene, *o*-dichlorobenzene, and other ring-substituted chlorinated products that are present. Both procedures are applicable to a variety of organic compounds but the amount of sample used is varied. (See Note 1.)

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—This standard is identical to ISO 26603.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

D1193 Specification for Reagent Water

D4663 Test Method for Polyurethane Raw Materials: Determination of Hydrolyzable Chlorine of Isocyanates

2.2 *ISO Standard:*[3]

ISO 26603 Plastics—Aromatic isocyanates for use in the production of polyurethanes—Determination of total chlorine

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods see Terminology D883.

4. Summary of Test Method

4.1 In each test method, the organic matter in the sample is destroyed by combustion with oxygen, the organically combined chlorine being converted to ionic chloride. The chloride is determined potentiometrically by titration with silver nitrate ($AgNO_3$) solution.

4.1.1 *Test Method A*—The sample is combusted in a pressurized ignition vessel.

4.1.2 *Test Method B*—The sample is combusted at atmospheric pressure in a Schöniger oxygen flask.[4]

5. Significance and Use

5.1 These test methods are suitable for use for research or for quality control to determine the total chlorine content of aromatic isocyanates. In some instances total chlorine content may correlate with performance in polyurethane systems.

6. Interferences

6.1 Bromine and iodine, if present, will react with the silver nitrate ($AgNO_3$) solution leading to an erroneously high total chlorine value.

7. Reagents and Materials

7.1 *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] These test methods are 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] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[4] For information on the Schöniger flask, refer to *Microchemie,* Springer Publishers, Vienna, Austria, Vol 42, 1955, p. 123, or Vol 43, 1956, p. 869.

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

specifications are available.[5] Other grades are acceptable, 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 D1193.

8. Sampling

8.1 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.)

9. Test Conditions

9.1 It is essential that moisture be excluded from the sample by all means possible to ensure the accuracy of measurements in this standard. See Section 8 of this standard for guidance on how to keep moisture out of the sample.

TEST METHOD A—TOTAL CHLORINE BY OXYGEN IGNITION VESSEL

10. Apparatus

10.1 *Weighing Bottle and Balance,* suitable for weighing a liquid sample by difference to the nearest 0.5 milligram.

10.2 *Oxygen Ignition Vessel Apparatus.*[6]

10.3 *Fuse Wire,* iron-nickel-chromium, No. 34 B & S gauge.

10.4 *Potentiometric Titrator.*

10.5 *Silver-Silver Chloride Electrode.*

10.6 *Silver Electrode.*

10.7 *Bubble Counter,* a 100-mL graduate and delivery tube or a bent "L" glass tube connected to a piece of rubber tubing. The graduate is filled to the 50-mL mark with water to which 3 mL of 0.1 *N* $AgNO_3$ solution and 1 drop of concentrated nitric acid (HNO_3, sp gr 1.42) have been added. Any turbidity that develops indicates the HCl gas is being lost when venting the ignition vessel.

10.8 *Microburet,* 10-mL capacity, 0.05-mL graduations.

11. Reagents

11.1 *Ethyl Alcohol,* conforming to Formula No. 2 B of the U.S. Treasury Department Bureau of Alcohol, Tobacco, and Firearms.

11.2 *Nitric Acid*—To 100 mL of water cooled in an ice bath, add 100 mL of nitric acid (HNO_3, sp gr 1.42) while stirring vigorously.

11.3 *Oxygen*—Free of combustible materials and halogen compounds.[7]

11.4 *Silver Nitrate, Standard Solution* (0.01 *N*)—Prepare a 0.01 *N* silver nitrate ($AgNO_3$) solution, and standardize frequently enough to detect changes of 0.0005 *N,* either gravimetrically or potentiometrically, using standard hydrochloric acid (HCl).

11.5 *Sodium Carbonate Solution* (50 g/L)—Dissolve 135 g of sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$) in water and dilute to 1 liter.

12. Procedure

12.1 Make certain that the ignition vessel (Note 2), oxygen lines, and fittings are free of oil and grease. (**Warning—**Small quantities of either have been known to cause a violent explosion.)

NOTE 2—When the ignition vessel is used repeatedly, a film may form on its inner surface. Remove this film periodically by rotating the ignition vessel on a lathe at about 300 rpm and polishing the inside surface with Grit No. 2/0 or equivalent paper coated with a light machine oil to prevent cutting and then with a paste made from grit-free chromic oxide and water. This procedure will remove all but very deep pits while polishing the surface well. Before using the ignition vessel, wash it with soap and water to remove residual cutting oil or paste. Ignition vessels with pitted surfaces are not to be used because they will retain chlorine from sample to sample.

12.2 Weigh a 0.9-g sample by difference to ±0.0005 g into the combustion capsule. (**Warning—**A severe safety hazard exists if more than 1 g of sample is used.)

12.3 Fit a 100-mm, iron-nickel fuse wire onto the two electrodes. Place the combustion capsule on the loop electrode and adjust the fuse wire in the capsule so that it is under the surface of the sample but does not touch the capsule. Place about 5 mL of Na_2CO_3 solution in the ignition vessel and, with a rubber policeman, wet the interior surface of the ignition vessel, including the head, as thoroughly as possible. Put the ignition vessel head in the vessel cylinder and the contact ring on top of the ignition vessel head, screwing the cap down finger-tight. Close the outlet valve securely with the special wrench provided and open the main oxygen cylinder slightly. Place the ignition vessel in its bench-mounted holder and tighten the holder bolt with an Allen wrench. Attach the union

[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[6] These test methods as written are based on the use of Parr Bomb No. 1108 which has been found to be satisfactory for this purpose. The Parr Bomb No. 1108 is available from the Fisher Scientific Co., 585 Alpha Dr., Pittsburgh, PA. Equivalent apparatus may be substituted with appropriate changes in the procedure.

[7] Zero grade oxygen is suitable for this analysis. Any grade of oxygen that gives a suitable blank is to be used.

on the oxygen-filling connection to the inlet valve of the ignition vessel. Admit oxygen slowly (to prevent blowing the sample from the cup) to 20 to 25 atmospheres (2.03 to 2.53 MPa). Close the operating valve of the oxygen cylinder and observe the pressure on the ignition vessel gauge. If a leak is indicated by a gradual pressure drop, check and tighten all connections. Do not continue with the test until the leak is stopped and the ignition vessel holds pressure. Release the pressure from the oxygen tank and disconnect the ignition vessel. Place the valve thumb nut on the oxygen inlet valve and tighten finger tight. (**Warning—**Exercise extreme caution from this point on until the ignition vessel has been fired, cooled, and bled free of oxygen.)

12.4 Pull the plug to the ignition vessel ignition unit. Fill the ignition receptacle ¾-full with water. Submerge the ignition vessel in the center of the ignition receptacle and visually inspect it for oxygen leaks. If the needle valve is not gas tight, tighten the packing gland slightly. Do not fire the ignition vessel until all leaks are repaired. Allow cooling water to circulate around the ignition vessel the entire time it is in the receptacle. (**Warning—**A serious shock hazard exists around the ignition vessel ignition receptacle in the event the ignition unit is shorted. Always pull the electrical plug before touching this receptacle.)

12.5 Connect the terminal at the top of the ignition receptacle to the terminal on the top of the ignition vessel. Connect the plugs to the cooling receptacle, insert the plug to the ignition unit, and fire the ignition vessel. The red indicator light will flash on, then off, indicating the ignition vessel fired properly. Pull the electrical plug. If the ignition vessel does not fire as indicated, carefully feel the ignition vessel. If it is cold, this indicates that the test was incomplete, and that 12.1 through 12.5 must be repeated.

12.6 Allow the ignition vessel to cool at least 10 min, then remove it from the receptacle and connect the bubble counter to the outlet valve. Release the pressure slowly and uniformly, taking at least two min. When all of the gas has bled, open the ignition vessel and examine its contents. Traces of unburned sample or soot indicate incomplete combustion, and that the test must be repeated.

12.7 Carefully wash the ignition vessel head, the electrodes, the capsule, and the cylinder walls with water as follows: Rinse the walls of the cylinder with about 25 mL of distilled water and fill the capsule. Scrub both the interior of the ignition vessel and the inner surface of the ignition vessel cover with a rubber policeman and wash the policeman into the ignition vessel. Rinse the ignition vessel washings into a 250-mL beaker (Note 3). Evaporate the washings in the beaker to about 20 mL. Cool below 10°C and acidify the solution to methyl red indicator by the dropwise addition of HNO_3. Insert silver-silver chloride electrodes and add 60 to 100 mL of ethyl alcohol to cover the electrode tips. Cool the solution to 10°C, and titrate potentiometrically with 0.01 N $AgNO_3$, adding the $AgNO_3$ solution in 0.1-mL increments near the end point.

12.8 Titrate a blank exactly as described in 12.1 through 12.7, but without adding the sample.

NOTE 3—Because it is difficult to rinse the last traces of chloride from the walls of the ignition vessel, residual chloride tends to carry over from sample to sample. Therefore, avoid alternating samples with high and low chlorine contents.

13. Calculation

13.1 Calculate the total chlorine as follows:

$$\text{Total chlorine, \%} = 3.55(A - B)N/W$$

where:

- A = $AgNO_3$ solution required for titration of the sample, mL,
- B = $AgNO_3$ solution required for titration of the blank, mL,
- N = normality of the $AgNO_3$ solution,
- W = sample used, g, and
- *3.55* = constant combining the milligram atomic weight of chlorine (35.5), conversion from milligrams to grams (1000), and conversion to percent (100).

14. Precision and Bias

14.1 *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 are to contact the Chairman, Subcommittee D20.22 (Section D20.22.01), ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

14.2 A limited round-robin was conducted.

14.2.1 It has been estimated that duplicate results by the same analyst are to be considered suspect if they differ by more than 0.015 % total chlorine.

14.2.2 It has been estimated that results reported by different laboratories are to be considered suspect if they differ by more than 0.03 % total chlorine.

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

TEST METHOD B—TOTAL CHLORINE BY SCHÖNIGER OXYGEN FLASK

15. Apparatus

15.1 *Schöniger Combustion Flask*,[8] a chemically resistant, 1000-mL narrow-mouth (24/40 standard-taper joint) Erlenmeyer flask with a 101.60-mm (4-in.) No. 18 platinum wire sealed into the glass stopper. Using tweezers to avoid contamination from fingerprints (Note 4), make a basket from 45-mesh 0.20 mm (0.0078-in.) platinum gauze as follows: Fold over the edges of a 12.7 by 25.4-mm (0.50 by 1-in.) or 13 by 25-mm (0.50 by 1-in.) piece of gauze about 1.6 mm (0.06-in.) and crimp them to prevent the gauze from unraveling. Bend the last 25.4-mm (1-in.) of the No. 18 wire at a right angle and place the gauze on the 25.4-mm (1-in.) section. Bend the last one-half of the wire back over the gauze and crimp strongly to hold the gauze firmly in place. Bend the sides of the gauze to form an open basket.

[8] Arthur H. Thomas Co., Catalog No. 6513C30.