Designation: D4661 – 13

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 *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 may have to be 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 and health practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—There is no known ISO equivalent to this standard.

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

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 oxygen bomb.

4.1.2 *Test Method B*—The sample is combusted at atmospheric pressure in a Schöniger oxygen flask.[3]

5. Significance and Use

5.1 These test methods can be used 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 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.

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

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

[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.

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

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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—**Many diisocyanates are known or suspected sensitizers. Overexposure to diisocyanates can lead to adverse health effects, which include the development of occupational asthma and other respiratory, skin and eye effects. Engineering controls and/or personal protective equipment, including respiratory, skin and eye protection, are to be used when there is a potential for over-exposure to diisocyanates. The product suppliers' Safety Data Sheet (SDS) provides more detailed information about potential adverse health effects and other important safety and handling information. Always follow the specific instructions provided on the SDS.)

9. Test Conditions

9.1 Since isocyanates react with moisture, it is highly recommended that moisture be excluded from the sample.

TEST METHOD A—TOTAL CHLORINE BY OXYGEN BOMB

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 Bomb Apparatus.*[5]

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 bomb.

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.[6]

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 litre.

12. Procedure

12.1 Make certain that the bomb (Note 2), oxygen lines, and fittings are free of oil and grease. (**Warning—**Small quantities of either may cause a violent explosion.)

NOTE 2—When the bomb is used repeatedly, a film may form on its inner surface. Remove this film periodically by rotating the bomb 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 bomb, wash it with soap and water to remove residual cutting oil or paste. Bombs 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 bomb and, with a rubber policeman, wet the interior surface of the bomb, including the head, as thoroughly as possible. Put the bomb head in the bomb cylinder and the contact ring on top of the bomb 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 bomb in its bench-mounted holder and tighten the holder bolt with an Allen wrench. Attach the union on the oxygen-filling connection to the inlet valve of the bomb. 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 bomb 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 bomb holds pressure. Release the pressure from the oxygen tank and disconnect the bomb. Place the valve thumb nut on the oxygen inlet valve and tighten finger tight. (**Warning—**Exercise extreme caution from this point on until the bomb has been fired, cooled, and bled free of oxygen.)

12.4 Pull the plug to the bomb ignition unit. Fill the bomb ignition receptacle ¾-full with water. Submerge the bomb 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 bomb until all leaks are repaired. Allow cooling water to circulate around the bomb the entire time the bomb is in the receptacle. (**Warning—**A serious shock hazard exists around the bomb ignition receptacle should the ignition unit be shorted. Always pull the electrical plug before touching this receptacle.)

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[5] 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.

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

12.5 Connect the terminal at the top of the ignition receptacle to the terminal on the top of the bomb. Connect the plugs to the cooling receptacle, insert the plug to the ignition unit, and fire the bomb. The red indicator light should flash on, then off, indicating the bomb fired properly. Pull the electrical plug. If the bomb does not fire as indicated, carefully feel the bomb. 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 bomb 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 bomb 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 bomb 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 bomb and the inner surface of the bomb cover with a rubber policeman and wash the policeman into the bomb. Rinse the bomb 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 bomb, 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 should 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,*[7] 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.

NOTE 4—Because small amounts of chloride are involved, contamination from fingerprints can be significant.

15.2 *Absorbent Cotton,* cut into squares weighing approximately 50 milligrams.

15.3 *Filter Paper,* cut into 6.4 by 25.4 mm (0.25 by 1-in.) pieces.

15.4 *Weighing Buret or Dropping Bottle.*

15.5 *Tweezers,* for handling the cotton squares.

15.6 *Potentiometric Titrator,* or pH meter with calomel and silver-silver chloride electrodes.

15.7 *Microburet,* 5-mL capacity, 0.01-mL graduations.

15.8 *Magnetic Stirrer.*

16. Reagents

16.1 *Nitric Acid*—To 100 mL of water cooled in an ice bath, add 100 mL of concentrated nitric acid (HNO_3, sp gr 1.41) while stirring vigorously.

16.2 *Oxygen.*

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

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

16.4 *Sodium Carbonate Solution* (10 g/L)—Dissolve 27 g of sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$) in water and dilute to 1 litre.

17. Procedure

17.1 Place 25 mL of Na_2CO_3 absorbing solution in an empty combustion flask. Sweep the flask with a moderate stream of oxygen for about 30 s to displace air.

17.2 While the flask is swept with oxygen, use tweezers to place an absorbent cotton square and filter paper strip (fuse) in the platinum basket. Add about 200 mg of sample to the absorbent cotton from a weighing buret containing a known amount of sample weighed to the nearest 0.0005 g. A little practice will enable one to judge by eye the number of TDI drops equivalent to 200 milligrams.

NOTE 5—Throughout this procedure, handle cotton squares and filter paper strips with tweezers to avoid contamination from fingerprints.

17.3 While holding the flask nearly horizontal in one hand and the stopper in the other, light the filter-paper fuse with a Bunsen flame and quickly and smoothly insert the stopper. In the same motion and after the stopper is firmly seated, tilt the flask beyond the horizontal so that the liquid will run down and form a seal around the stopper. Hold the stopper firmly in place. (**Warning—**Ignition may cause a sudden buildup of pressure within the flask. While the sample is being combusted, handle the flask with leather or heavy vinyl gloves behind a safety shield. Alternatively, the risk of explosion can be minimized using a Thomas-Lisk combustion flask with a rubber balloon attached to a side arm for the safe expansion of gas. The combustion is to be carried out in a safety cabinet such as the Schöniger Combustion Ignitor.[8] This apparatus uses an infrared lamp to ignite black filter paper in the combustion flask.))

17.4 After the combustion is complete, rotate the flask to wet the flask wall being careful not to wet the platinum basket. Allow the flask to stand 5 to 10 minutes.

17.5 Remove the stopper, sweep the flask with oxygen, and burn two more 200-mg portions of the same sample in the same flask in accordance with 17.2 through 17.4. To the nearest 0.0005 g, reweigh the weighing buret to determine accurately the total amount of sample burned. Transfer the solution into a 100-mL beaker. Rinse the flask with small portions of Na_2CO_3 solution, adding the rinses to the 100-mL beaker. Acidify the solution to methyl red by adding HNO_3 dropwise, then add 0.1 mL excess. Add a magnetic stirring bar and, using a 5-mL buret, titrate potentiometrically with standard 0.01 N $AgNO_3$ solution, using a silver-silver chloride electrode system.

17.6 Titrate a blank exactly as described in 17.1 through 17.5, but without adding the sample.

18. Calculation

18.1 Calculate the total chlorine as follows:

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

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).

19. Precision and Bias

19.1 *Precision*—Attempts to develop a full precision and bias statement for this test 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.

19.2 A limited round-robin was conducted.

19.2.1 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.

19.2.2 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.

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

20. Keywords

20.1 aromatic isocyanates; chlorine; isocyanates; oxygen bomb; polyurethane raw materials; Schöniger ignition; titration

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[8] Arthur H. Thomas Co., Catalog No. 6513C05.

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D4661 - 09) that may impact the use of this standard. (November 1, 2013)

(1) Replaced *Sampling* section with wording consistent with the other polyurethane raw material methods.
(2) Removed recommendation for lab humidity.
(3) Removed nonstandard concentration usage "1+1" throughout methods.
(4) Removed duplicate calculation equations.
(5) Renumbered footnotes.

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