



Standard Test Method for Polyurethane Raw Materials: Acidity by Argentometric Determination of Hydrolyzable Chlorine in Monomeric, Aromatic Isocyanates¹

This standard is issued under the fixed designation D5523; 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 the hydrolyzable chlorine content of monomeric, aromatic isocyanates used as polyurethane raw materials and expresses it as HCl acidity. The test method is applicable to toluene diisocyanate (TDI) and monomeric methylene di(phenylisocyanate), known as MDI. The main sources of hydrolyzable chlorine and, therefore, acidity in monomeric aromatic isocyanates are carbamyl chlorides, acid chlorides, and dissolved phosgene. All of these compounds react with alcohols and water to form hydrochloric acid.

1.2 This test method applies only to monomeric isocyanates in which all of the acidity is derived from species that generate HCl on solvolysis.

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *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](#)

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*:

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.

3.2.1 *acidity*—the acid strength of a sample expressed as parts per million hydrochloric acid (HCl) present.

3.2.2 *hydrolyzable chlorine*—the amount of chlorine released as chloride ion under the conditions of the test, expressed as parts per million chlorine.

4. Summary of Test Method

4.1 The sample reacts with 2-propanol to form urethanes and hydrochloric acid, which is liberated from the labile carbamyl chlorides, acid chlorides, and dissolved phosgene. The chlorides of the liberated acid are then determined potentiometrically using standard methanolic silver nitrate solution and calculated as parts per million HCl.

5. Significance and Use

5.1 This test method is suitable for research or for quality control to characterize TDI and MDI.

5.2 This test method was developed to overcome problems with low-level acidity determinations that use glass electrodes in the presence of reagent alcohol solvents. Reagent alcohols contain acidic and basic species, which complicate the glass electrode methods at low levels of acidity.

6. Interferences

6.1 Acidic species that do not generate chloride ions under the conditions of this test method will not be determined because acidity is determined indirectly from the chloride ion concentration.

6.2 Acidic species that do not produce chloride ions are expected to be negligible at low levels of acidity and for the monomeric isocyanates in this test method.

6.3 Care must be taken to avoid chloride contamination of glassware and sample containers.

7. Apparatus

7.1 *Potentiometric Titrator*.

7.2 *Combination Silver Billet Electrode* ([Note 2](#)).

7.3 *Oven, 70°C* ([Note 3](#)).

7.4 *Magnetic Stirrer*.

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

NOTE 2—The combination silver billet electrode is to be stored in 0.01 *N* methanolic silver nitrate solution in order to keep the electrode conditioned properly. The use of chloride containing solutions must be avoided during storage and maintenance of the apparatus.

NOTE 3—Monomeric MDI samples can be solid when received in the laboratory. An oven is to be used to melt the sample prior to beginning the test procedure.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used 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.³ Other grades can 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 *Methanol.*

8.3 *2-Propanol.*

8.4 *Nitric Acid*, concentrated, 70 %.

8.5 *Silver Nitrate.*

8.6 *Methanolic Silver Nitrate Solution* (0.01 *N*)—Prepare by dissolving 1.70 g AgNO₃/L of solution. Potentiometrically standardize with titration-grade sodium chloride frequently enough to detect changes of 0.00005 *N*.

8.7 *Methanolic Silver Nitrate Solution* (0.001 *N*)—Prepare by dissolving 0.170 g AgNO₃/L of solution. Potentiometrically standardize with titration-grade sodium chloride frequently enough to detect changes of 0.000005 *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 over-exposure 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 warning statement in 9.1.

³ *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.

11. Procedure

11.1 Weigh 10.0 g of the sample into a beaker and record the weight to the nearest 0.0001 g (Note 4).

11.2 Add 100 mL of 2-propanol to the beaker, cover, and stir the sample for 10 min.

11.3 Add 100 mL of methanol, cover, and continue stirring the sample solution for an additional 20 min (Note 5).

11.4 Add ten drops of concentrated nitric acid solution to the sample solution.

11.5 Cool the sample solution to room temperature in an ice bath if necessary.

11.6 Titrate the sample solution potentiometrically with the appropriate methanolic silver nitrate solution (Note 6).

11.7 Record the volume of titrant used to reach the end point to at least the nearest 0.001 mL.

11.8 If the chloride content of the reagents is in question, run a blank (steps 11.1 to 11.7 with no isocyanate sample added) to ensure that the reagents are free of chloride interferences. If chloride is detected, subtract the volume (mL) of AgNO₃ required to titrate the blank from the volume (mL) of AgNO₃ required to titrate the sample.

NOTE 4—The beaker must be of such size to accommodate approximately 300 mL of solution, and it must be of a shape to allow the proper coverage for the electrode. For monomeric MDI, it is acceptable to gently warm the beaker on a hot plate to keep the sample molten prior to the addition of 2-propanol. This will assist in dissolution of the sample. Once 2-propanol has been added, remove the beaker from the hot plate.

NOTE 5—The stirring times were chosen to ensure an adequate reaction time for material that has been adjusted with an acid chloride. In monomeric, unadjusted material, it is acceptable to reduce the stirring times to those required to obtain uniform solutions and stable electrode responses (approximately 2 min).

NOTE 6—For expected acidities or hydrolyzable chlorines below 20 ppm, use the 0.001 *N* methanolic silver nitrate solution as the titrant. For expected acidities or hydrolyzable chlorines above 20 ppm, use the 0.01 *N* methanolic silver nitrate solution as the titrant.

12. Calculation

12.1 Calculate the acidity, as ppm HCl, as follows:

$$\text{acidity} = \frac{S \times N \times 36.465 \times 10^6}{W \times 1000} \quad (1)$$

where:

- S* = AgNO₃ required for titration of the sample, mL (If a blank is run, subtract the volume in mL of AgNO₃ required to titrate the blank from the volume (mL) of AgNO₃ required to titrate the sample),
- N* = normality of AgNO₃ solution, meq/mL,
- W* = sample weight, g,
- 36.465 = equivalent weight of HCl, mg/meq,
- 1000 = factor for converting milligrams to grams, and
- 10⁶ = factor for converting to parts per million.

12.2 Because hydrolyzable chlorine is measured, the ppm hydrolyzable chlorine can be calculated as follows:

$$\text{hydrolyzable chlorine} = \frac{S \times N \times 35.465 \times 10^6}{W \times 1000} \quad (2)$$

where:

- S = AgNO_3 required for titration of the sample, mL (If a blank is run, subtract the volume in mL of AgNO_3 required to titrate the blank from the volume (mL) of AgNO_3 required to titrate the sample),
- N = normality of AgNO_3 solution, meq/mL,
- W = sample weight, g,
- 35.465 = equivalent weight of Cl, mg/meq,
- 1000 = factor for converting milligrams to grams, and
- 10^6 = factor for converting to parts per million.

13. Precision and Bias⁴

13.1 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. Contact the Chairman, Subcommittee D20.22 (Section D20.22.01), ASTM, 100 Barr Harbor Drive, PO Box C700, West

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D20-1181.

Conshohocken, PA 19428–2959, if you are interested in participating in the development of precision and bias data for this test method.

13.2 A limited round robin was conducted with nine laboratories.

13.2.1 It has been estimated that duplicate results for either acidity or hydrolyzable chlorine by the same analyst are to be considered suspect if they differ by ± 3.9 ppm for results greater than 10 ppm and ± 0.6 ppm for results less than 10 ppm.

13.2.2 It has been estimated that results reported by different laboratories for either acidity or hydrolyzable chlorine are to be considered suspect if they differ by ± 15.5 ppm for results greater than 10 ppm and ± 3.5 ppm for results less than 10 ppm.

14. Keywords

14.1 acidity; HC; hydrolyzable chlorine; isocyanates; isocyanates aromatic; MDI; methylene-4,4'-di(phenylisocyanate); methylene di(phenylisocyanate); polyurethane; raw materials; TDI; test method; titration; toluene diisocyanate

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D5523 – 10) that may impact the use of this standard. (April 1, 2015)

(1) 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.

(2) Section 10: Test Conditions—Removed redundant information.

(3) Section 12: Calculations—Added calculations to perform if a blank is used.

(4) Section 14: Keywords—Changed keyword for MDI to be consistent with that used in the other polyurethane raw material analysis methods.

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