Designation: D 1979 – 97

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM

Standard Test Method for Free Formaldehyde Content of Amino Resins[1]

This standard is issued under the fixed designation D 1979; 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 covers the determination of free formaldehyde in amino resins and their aqueous and non-aqueous solutions. Amino resin-free formaldehyde levels from about 0.02 to 5.0 % can be determined by this test method. The applicability of this test method to other matrices is unknown.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 1959 Test Method for Iodine Value of Drying Oils and Fatty Acids[3]

3. Summary of Test Method

3.1 Specimens are mixed with borate buffer solution and ice water, then kept cool in an ice bath. Excess sodium sulfite is added to consume free formaldehyde as follows:

$$CH_2O + Na_2SO_3 + H_2O \rightarrow HOCH_2SO_3Na + NaOH \quad (1)$$

3.2 The excess sodium sulfite is removed by titration with iodine using starch as the indicator as follows:

$$Na_2SO_3 + I_2 + H_2O \rightarrow Na_2SO_4 + 2\ HI \quad (2)$$

3.3 The sodium sulfite-formaldehyde complex is then decomposed with sodium carbonate to quantitatively regenerate sodium sulfite and formaldehyde as follows:

$$HOCH_2SO_3Na + Na_2CO_3 \rightarrow CH_2O + Na_2SO_3 + NaHCO_3 \quad (3)$$

3.4 The liberated sodium sulfite is titrated with iodine (Eq 2) and free formaldehyde is calculated from this second iodine titration.

4. Significance and Use

4.1 The amount of free formaldehyde in amino resins may be of concern to both producer and user, as its presence in air above threshold amounts may produce objectionable odors and irritant effects. This test method can be useful for evaluating suppliers' products and for quality control.

5. Apparatus

5.1 *Analytical Balance*, ±0.1 mg.

5.2 *Magnetic Stirrer and Stir Bar*—A "heavy duty" magnetic stirrer is necessary.

5.3 *Buret*, 50 mL manual or electronic. Manual burets should be of the type designed to minimize the exposure of reagent to air. Electronic burets are preferred.

5.4 *Beakers*, glass, 100 mL, 600 mL, and 1500 mL.

5.5 *Stopwatch or Timer*.

5.6 *Graduated Cylinders*, glass, 50 mL and 250 mL.

5.7 *Glass Pipet*, 2 mL.

5.8 *Thermometer*, subdivision 1°C.

6. Reagents

6.1 *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.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

6.3 *Acetic Acid Solution (1.0 M)*—Dissolve 60 mL of glacial acetic acid (CH_3CO_2H) in water and dilute to 1 L.

6.4 *Boric Acid Buffer Solution*—Prepare a sodium hydroxide solution (1.0 *M*) by dissolving 40 g of sodium hydroxide (NaOH) in water and diluting to 1 L. Dissolve 12.39 g of boric acid (H_3BO_3) in 100 mL of 1.0 *M* NaOH, then dilute to 1 L. Maintain temperature at 0°C in an ice bath. The pH at 0°C should be 9.4 (glass electrode).

6.5 *Ice*, finely crushed.

6.6 *Iodine Solution* (0.1 *N*)—Dissolve 40 g of iodate free potassium iodide in 25 mL of water in a 100-mL beaker. Weigh

---

[1] This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.33 on Polymers and Resins.

Current edition approved Nov. 10, 1997. Published June 1998.Originally published as D 1979 - 91. Last previous edition D 1979 - 91(l997).

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

[3] *Annual Book of ASTM Standards*, Vol 06.03.

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

out 12.6905 g of dry re-sublimed iodine and add to the beaker. Stir until the iodine is dissolved and dilute to 1 L with water. Store iodine titrant in the dark. This reagent can be purchased as a standardized solution or must be standardized against sodium thiosulfate.

6.7 *Methylene Chloride* (CH_2Cl_2)—Cool to 0°C in an ice bath.

6.8 *Sodium Carbonate Solution* (1.0 *M*)—Dissolve 106 g of sodium carbonate (Na_2CO_3) in water and dilute to 1 L.

6.9 *Sodium Sulfite Solution* (1.0 *M*)—Dissolve 126 g of sodium sulfite (Na_2SO_3) in water and dilute to 1 L. This reagent is unstable and must be prepared fresh daily.

6.10 *Starch*—0.2 % aqueous (weight/volume) or 1.0 % aqueous (weight/volume). This indicator can be purchased as a stabilized solution or prepared in accordance with Test Method D 1959. Store in a cool, dark place.

6.11 *Water* (H_2O)—Cool Type II water to 0°C in an ice bath.

7. Procedure

7.1 A blank determination is run following this procedure, omitting 7.2 (addition of sample).

7.2 Taking the appropriate specimen size from Table 1, weigh the specimen to the nearest mg into a 600-mL beaker.

7.3 Place the beaker into the ice bath that rests upon a heavy-duty magnetic stirrer.

7.4 Place a stirring bar in the beaker and immediately dissolve the specimen as described in 7.4.1 (for aqueous specimens) or 7.4.2 (for non-aqueous specimens). Maintain the temperature of the specimen solution at 0°C by adding ice. The temperature must not rise above 2°C during subsequent steps. Note that boric acid buffer (6.4), methylene chloride (6.7) and water (6.11) should be pre-cooled to 0°C.

7.4.1 *Aqueous Specimens*—Rapidly mix the specimen with 150 mL of ice water and 25 mL of boric acid buffer solution.

7.4.2 *Non-aqueous Specimens*—Rapidly mix the specimen with 50 mL of methylene chloride cooled to 0°C. Stir to dissolve specimen. Add 150 mL of ice water and 25 mL of boric acid buffer. Continue extraction for 5 min. Uninterrupted stirring must be maintained through 7.5-7.10.

7.5 While constantly stirring the specimen solution, pipet 2 mL of 1.0 *M* sodium sulfite solution into the beaker.

TABLE 1 Specimen Size According to Expected Formaldehyde Content

Free Formaldehyde, weight, %	Specimen Weight, g
0.2–0.5	3.0
0.5–1.0	1.5
1.0–2.0	1.0
2.0–3.0	0.5
3.0–5.0	0.25

7.6 Continue stirring for 15 min.

7.7 Add 10 mL of 1.0 *M* acetic acid solution and 10 mL of the starch solution.

7.8 Titrate the excess sodium sulfite with 0.1 *N* iodine solution to a green-blue color that persists for 10 s. Re-zero the buret.

7.9 Add 30 mL of 1.0 *M* sodium carbonate solution.

7.10 Titrate the liberated sodium sulfite with 0.1 *N* iodine solution to a constant blue color that persists for 1 min. The shade of blue varies with the sample under test and may appear slightly different in emulsions when compared to the blank. Record the volume of the iodine solution used in this step for use in the calculation, Section 8.

8. Calculation

8.1 Calculate the weight percent free formaldehyde in the sample as follows:

$$\text{Formaldehyde, \%} = \frac{(A - B) \times 3}{W \times 20} \tag{4}$$

where:

A = volume of iodine solution for specimen titration (7.10), mL,

B = volume of iodine solution for blank titration (7.10), mL, and

W = sample weight, g.

9. Precision and Bias

9.1 *Precision*—The precision statements are based upon an interlaboratory study in which one analyst in each of five different laboratories analyzed three samples of commercial melamine resins with free formaldehyde contents between 0.2 and 2.7 % in duplicate on two different days. The within-laboratory coefficient of variation was found to be 4.07 % at 12 df, and the between-laboratories coefficient of variation was found to be 13.69 % at 9 df. Based on these coefficients of variation, the following criteria should be used in judging the acceptability of results at the 95 % confidence level.

9.1.1 *Repeatability*—Two results, each the means of duplicates, obtained by the same operator on different days should be considered suspect if they differ by more than 12.5 % relative.

9.1.2 *Reproducibility*—Two results, each the means of duplicates, obtained by operators in different laboratories should be considered suspect if they differ by more than 43.8 % relative.

9.2 *Bias*—No bias can be determined for this test method since no standard resin exists.

10. Keywords

10.1 amino resins; formaldehyde; sodium sulfite