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Standard Test Methods for Carboxyl Content of Cellulose[1]

This standard is issued under the fixed designation D1926; 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 cover the determination of the carboxyl content, or ion-exchange capacity, of cellulose from any source. Two test methods are described, the sodium chloride-sodium bicarbonate method (**1**)[2] and the methylene blue method (**2**). The test methods must be used within their limitations, and it must be recognized that there is no way of determining the accuracy of any method for the determination of carboxyl. The precision of the sodium chloride-sodium bicarbonate method is low in the lower range of carboxyl values. The methylene blue method can be used over the whole range of carboxyl values; it is especially useful in the low range. It is not applicable to the determination of carboxyl in soluble carbohydrate material. Although these test methods may be used to determine the ion-exchange capacity of unbleached pulps, the residual lignin will cause an undetermined error, especially the sulfonic acid groups in unbleached sulfite pulps (**3**).

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]
D1193 Specification for Reagent Water

3. Significance and Use

3.1 These test methods measure the amount of carboxyl groups present in wood or cotton linter pulp. Carboxyl groups are indicative of the surface charge of the pulp which is a very important quantity for use in the papermaking industry.

4. Purity of Reagents

4.1 Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall 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.

4.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193.

SODIUM CHLORIDE-SODIUM BICARBONATE METHOD

5. Summary of Test Method

5.1 In the sodium chloride-sodium bicarbonate method the specimen is de-ashed with hydrochloric acid, washed, soaked in sodium chloride-sodium bicarbonate solution, filtered, and an aliquot of the filtrate titrated with 0.01 *N* hydrochloric acid to a methyl red end point. The difference between the concentration of the filtrate and of the sodium chloride-sodium bicarbonate solution is a measure of the ion-exchange capacity of the cellulose.

6. Reagents

6.1 *Hydrochloric Acid, Standard (0.01 N)*—Prepare and standardize a 0.01 *N* solution of hydrochloric acid (HCl).

6.2 *Hydrochloric Acid (1 + 99)*—Dilute 1 volume of concentrated HCl (sp gr 1.19) with 99 volumes of water.

[1] These test methods are under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.36 on Cellulose and Cellulose Derivatives.

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[2] The boldface numbers in parentheses refer to the list of references at the end of these test methods.

[3] 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.

[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.

6.3 *Methyl Red Indicator Solution.*

6.4 *Sodium Chloride-Sodium Bicarbonate Solution*—Dissolve 5.85 g of sodium chloride (NaCl) and 0.84 g of sodium bicarbonate ($NaHCO_3$) in water and dilute to 1 L.

6.5 *Sodium Hydroxide Solution (0.4 g/L)*—Dissolve 0.4 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

7. Procedure

7.1 Condition the specimen in the atmosphere near the balance for at least 20 min before weighing duplicate portions of 2.5 ± 0.01 g. At the same time, weigh specimens for the determination of moisture. Disintegrate the specimen in water, filter through fritted glass, and disperse to about 1 % consistency in HCl (1 + 99) at room temperature. After 2 h collect the specimen on a fritted-glass filter funnel and wash with water saturated with carbon dioxide (CO_2). Continue the washing until the filtrate, after boiling, does not require more than 1 or 2 drops of NaOH solution to give an alkaline color with methyl red.

7.2 Weigh the wet pulp pad, transfer it immediately to a 250-mL glass-stoppered Erlenmeyer flask, add 50 mL of the NaCl-$NaHCO_3$ solution with a pipet, and shake to obtain a homogeneous slurry (Note 1). Allow the mixture to stand for 1 h at room temperature. Filter through a clean, dry, fritted glass funnel, pipet a 25-mL aliquot of the filtrate into an Erlenmeyer flask, and titrate with 0.01 *N* HCl, using methyl red solution as an indicator. When the first change in color occurs, boil the solution for about 1 min to expel the carbon dioxide and continue the titration to a sharp end point.

NOTE 1—If the cation-exchange capacity is very low, use a solution containing about 5.85 g of NaCl and 0.42 g of $NaHCO_3$ per litre. It is important that the excess of $NaHCO_3$ be large enough that the pH does not fall below 7.0.

7.3 Pipet 25 mL of the NaCl-$NaHCO_3$ solution into an Erlenmeyer flask and titrate as described in 7.2.

8. Calculation

8.1 Calculate the cation-exchange capacity, *c*, of the specimen in milliequivalents per 100 g as follows:

$$c = \left(b - a - \frac{av}{50} \right) \frac{2}{G} \quad (1)$$

where:

G = weight of oven-dry specimen, g,
v = weight of water in the wet pulp pad, g,
a = millilitres of 0.01 N HCl consumed by 25 mL of filtrate, and
b = millilitres of 0.01 N HCl consumed by 25 mL of the NaCl-$NaHCO_3$ solution.

9. Report

9.1 Until more data are obtained on the precision of this test method, it is suggested that the ion-exchange capacity be reported to 0.01 milliequivalent/100 g of pulp.

10. Precision and Bias

10.1 Work sponsored by ASTM, TAPPI, ACS, and ICCA (see Ref **4**) found that precision decreased with decreasing carboxyl content. For pulps varying in carboxyl content from 5.75 to 0.40 mmol/100 g pulp, the repeatability (intralaboratory) expressed as a percent coefficient of variance was 2.2 to 8.1 %, respectively. Interlaboratory results based on different materials and various test methods gave percent coefficient of variance of 9.0 to 33 % for these same materials.

10.2 No statement on bias can be made as no suitable reference material exists for determining bias.

METHYLENE BLUE METHOD

11. Summary of Test Method

11.1 In the methylene blue method the specimen is treated with 0.0002 *M* methylene blue solution buffered to a pH of 8 with diethylbarbituric acid (barbital). The decrease in methylene blue concentration, measured photometrically, is a function of the ion-exchange capacity of the cellulose.

12. Apparatus

12.1 *Spectrophotometer or Filter Photometer,* capable of measuring absorbance near 620 mm.

12.2 *Shaker or Mixer* for agitating the specimens in the methylene blue solution. A wheel or rod, to which the specimen vials can be attached, that rotates at about 15 r/min, has proven satisfactory.

12.3 *Centrifuge,* capable of settling the cellulose from the methylene blue solution.

13. Reagents

13.1 *Buffer, Stock Solution*—Dissolve 1.151 g of diethylbarbituric acid (barbital) in water, add the equivalent of 0.16 g of sodium hydroxide using a standard solution and buret, and dilute with water to 1 L in a volumetric flask.

13.2 *Hydrochloric Acid (1 + 99)*—Dilute 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 99 volumes of water.

13.3 *Methylene Blue, Stock Solution (0.002 M)*—Dissolve 0.640 g of methylene blue in water, making allowance for moisture, and dilute to 1 L in a volumetric flask.

NOTE 2—Information on the determination of the purity of methylene blue is given in the literature (**5**).

13.4 *Methylene Blue—Buffer Solution (0.0002 M)*—Mix 1 volume of methylene blue stock solution with 1 volume of buffer stock solution and dilute to a total of 10 volumes in a volumetric flask. The volume of solution to be prepared will vary with the requirements. For example, pipet 10 mL of each solution into a 100-mL volumetric flask, dilute to the mark with water, and mix thoroughly. Prepare a fresh solution for each determination.

14. Preparation of Calibration Curve for Ordinary Size Specimens

14.1 In order to prepare a calibration curve, make up a series of methylene blue buffer solutions containing the same amount of buffer but different amounts of methylene blue, to cover the desired range. Add 50 mL of the stock solution of buffer to

each of nine 500-mL volumetric flasks. Add to these flasks 10, 15, 20, 25, 30, 35, 40, 45, and 50 mL, respectively, of the 0.002 *M* stock solution of methylene blue. Dilute each solution to the mark with water and mix thoroughly.

NOTE 3—The concentrations suggested for preparing calibration curves need not be followed exactly as long as enough points are obtained to allow construction of an acceptable calibration curve.

14.2 Pipet 10 mL of each solution into 100-mL volumetric flasks, add 10 mL of HCl (1 + 99), dilute to the mark with water, and mix (Note 4). Measure the absorbance of the solutions and prepare a plot of absorbance at 620 nm against concentration (Note 5).

NOTE 4—The procedure described for the colorimetric determination of methylene blue is based on the use of the Beckman DU spectrophotometer with 1-cm absorption cells. The dilution procedure may have to be modified for use with filter photometers or for cells with a longer light path.

NOTE 5—It has been reported (5) that Beer's law is obeyed at 620 nm, and it is recommended that measurements be made at this wavelength. Measurements may also be made at 675 nm, which is close to the absorption peak, but Beer's law is not obeyed at this wavelength.

15. Preparation of Calibration Curve for Small Specimens

15.1 In order to prepare a calibration curve, pipet 1 mL of each of the nine solutions mentioned in Section 14 into 10-mL volumetric flasks, add 1 mL of HCl (1 + 99), dilute to the mark, mix, and measure the absorbance at 620 nm. If the volumetric apparatus is sufficiently precise, this calibration curve should be identical with the one described in Section 14. Obviously, any specific procedure that gives solutions in the right concentration range for the colorimetric measurements should be satisfactory.

16. Procedure for Ordinary Size Specimens

16.1 Determine the approximate carboxyl content in a preliminary experiment. Weigh out three specimens, one estimated to give 50 % exhaustion of the dye solution, one 10 to 15 % smaller, and one 10 to 15 % larger, making allowance for the moisture content. Weigh the specimens into 125-mL glass-stoppered flasks (any other convenient size flask may be used), and add 50 mL of 0.0002 *M* methylene blue-buffer solution from a pipet. Lubricate the stoppers with a little petroleum jelly and secure them with rubber bands. Place the flasks on a device that will turn them end over end or otherwise agitate the solutions.

16.2 After overnight agitation, centrifuge the solutions and pipet a 10-mL aliquot of the supernatant liquid into a 100-mL volumetric flask. Add 10 mL of HCl (1 + 99), and fill the flask to the mark with water. Measure the absorbance of the solutions at 620 nm.

16.3 Using the observed absorbances, refer to the calibration curve and read the concentration of methylene blue present for each of the three portions of specimen.

16.4 Plot the specimen size against the concentration of methylene blue in the supernatant liquid, and read from the plot the specimen size that gives 50 % exhaustion of the dye solution.

NOTE 6—It is not absolutely necessary to plot the specimen size against methylene blue concentration in order to calculate dye absorption. The dye absorption may be calculated from two slightly different weights of cellulose that will give approximately 50 % exhaustion, and the mean of the two results taken.

17. Procedure for Small Specimens

17.1 The general procedure is the same as for ordinary size specimens (Section 16). Weigh the specimens into glass-stoppered weighing bottles of about 10-mL capacity and add 5 mL of 0.0002 *M* methylene blue-buffer solution. After overnight agitation, centrifuge the solutions, remove a 1-mL aliquot with an automatic pipet, and transfer to a 10-mL volumetric flask. Add about 1 mL of HCl (1 + 99), dilute to the mark, and measure the absorbance at 620 nm. Determine the specimen size that gives 50 % exhaustion of the methylene blue solution as described in 16.4.

18. Calculations

18.1 *Ordinary Size Specimens*—The size specimen that gives 50 % exhaustion of 50 mL of 0.0002 *M* methylene blue solution has used 0.005 millimole of methylene blue in ion exchange with carboxyl groups. Therefore the millimoles of carboxyl per 100 g of cellulose, M_1, is calculated as follows:

$$M_1 = (0.005/W) \times 100 \quad (2)$$

where W = specimen to give 50 % exhaustion of 50 mL of 0.0002 *M* methylene blue solution, g.

18.2 *Small Specimens*—The size specimen that gives 50 % exhaustion of 5 mL of 0.0002 *M* methylene blue solution has used 0.0005 millimole of methylene blue in ion exchange with carboxyl groups. Therefore the millimoles of carboxyl per 100 g of cellulose, M_2, is calculated as follows:

$$M_2 = (0.0005/W) \times 100 \quad (3)$$

where W = specimen to give 50 % exhaustion of 5 mL of 0.0002 *M* methylene blue solution, g.

19. Report

19.1 Until more data are obtained on the precision of this test method, it is suggested that the ion-exchange capacity be reported to 0.01 meq/100 g of pulp.

20. Precision and Bias

20.1 Work sponsored by ASTM, TAPPI, ACS, and ICCA (see Ref **4**) found that precision decreased with decreasing carboxyl content. For pulps varying in carboxyl content from 5.75 to 0.40 mmol/100 g pulp, the repeatability (intralaboratory) expressed as a percent coefficient of variance was 2.2 to 8.1 %, respectively. Interlaboratory results based on different materials and various test methods gave percent coefficient of variance of 9.0 to 33 % for these same materials.

20.2 No statement of bias can be made as no suitable reference material exists for determining bias.

21. Keywords

21.1 carboxyl content; cellulose; ion exchange capacity; methylene blue method; sodium chloride/sodium bicarbonate method

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