Designation: D2363 – 79 (Reapproved 2011)

Standard Test Methods for Hydroxypropyl Methylcellulose[1]

This standard is issued under the fixed designation D2363; 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 testing of hydroxypropyl methylcellulose.

1.2 The test procedures appear in the following order:

	Sections
Moisture	4 to 6
Ash (as Sulfate)	7 to 10
Chlorides (as NaCl)	11 to 14
Alkalinity (as Na_2CO_3)	15 to 18
Iron	19 to 24
Heavy Metals	25 to 29
Methoxyl Content	30 to 35
Hydroxypropoxyl Content	36 to 41
Viscosity	42 to 46
pH	47
Solids	48 to 51
Density	52 to 56

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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.* For a specific hazard statement, see 33.5.1.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D96 Test Method for Water and Sediment in Crude Oil by Centrifuge Method (Field Procedure) (Withdrawn 2000)[3]

E70 Test Method for pH of Aqueous Solutions With the Glass Electrode

3. Purity of Reagents

3.1 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.

3.2 Unless otherwise indicated, references to water shall be understood to mean distilled water.

MOISTURE

4. Scope

4.1 This test method covers the determination of the volatile content of hydroxypropyl methylcellulose and, by common usage, designated moisture.

5. Procedure

5.1 Transfer 2 to 5 g of the sample weighed to the nearest 0.01 g to a tared dish (fitted with a lid) and dry for 2 h in an oven at 100 to 105°C with lid removed. Remove the dish from the oven, cover with a lid, cool in a desiccator, and weigh.

6. Calculation

6.1 Calculate the percent of moisture as follows:

$$\text{Moisture, \%} = (A/B) \times 100 \tag{1}$$

where:

A = mass loss on heating, and
B = sample used, g.

ASH—AS SULFATE

7. Scope

7.1 This test method covers the determination of the amount of residue left from igniting a sample of hydroxypropyl methylcellulose after being moistened with sulfuric acid.

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[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] 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] The last approved version of this historical standard is referenced on www.astm.org.

[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.

8. Reagents

8.1 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

8.2 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfuric acid (H_2SO_4).

9. Procedure

9.1 Weigh to the nearest 0.01 g about 2 g of the sample (previously dried for ½ h at 105°C) into a tared Coors No. 1, high-form, porcelain crucible. Add 5 drops of H_2SO_4 around the inside surface of the crucible. Place the crucible inside of a loosely fitting aluminum ring (approximately 32 mm (1¼ in.) high, with 6.4-mm (¼-in.) sidewall, and 44-mm (1¾-in.) inside diameter, cut from a piece of aluminum pipe) on a hot plate. Loosely cover with a crucible cover. Carefully char the hydroxypropyl methylcellulose until all the volatiles are removed.

9.2 Cool the crucible, add 1 ml of H_2SO_4 and 2 ml of HNO_3 so that it completely wets the charred residue. Cautiously heat to dense white fumes on a hot plate. Place the uncovered crucible in a muffle furnace at 600°C and ignite until all the carbon is gone (for about 1 h). Transfer to a dessicator until cool, then weigh. (Save the residue for the Heavy Metals determination.)

10. Calculation

10.1 Calculate the percent of ash, *C*, as follows:

$$C = (A/B) \times 100 \tag{2}$$

where:

A = sulfated ash, g, and
B = sample used, g.

CHLORIDES—AS SODIUM CHLORIDE

11. Scope

11.1 This test method covers the determination of the total percent of chloride (bromide included if present) calculated as sodium chloride (NaCl) in hydroxypropyl methylcellulose. The sample is dispersed and the chloride titrated volumetrically with 0.100 *N* silver nitrate solution.

12. Reagents

12.1 *Ferric Alum Indicator Solution*—Add 100 g of ferric ammonium sulfate $FeNH_4(SO_4)_2 \cdot 12H_2O$ to 250 mL of water. Heat to boiling and add NHO_3 (sp gr 1.42) slowly until the red color is removed. This will usually require about 6 to 15 mL of HNO_3. Filter the solution and store in a glass bottle.

12.2 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

12.3 *Potassium Thiocyanate Standard Solution (0.1 N)*—Dissolve 10 g of potassium thiocyanate (KCNS) in 1 L of water. By means of a pipet, measure 25 mL of 0.100 *N* silver nitrate ($AgNO_3$) solution into a 400-mL beaker. Add 100 mL of water, 10 mL of HNO_3 (sp gr 1.42), and 5 mL of ferric alum indicator solution. Titrate with the KCNS solution, while stirring, until a faint persistent red color is produced. Calculate the normality, *N*, of the KCNS solution as follows:

$$N = (A/B) \times 0.1 \tag{3}$$

where:

A = 0.100 N $AgNO_3$ solution added, mL, and
B = KCNS solution required for the titration, mL.

12.4 *Silver Nitrate-Standard Solution (0.100 N)*—Grind silver nitrate ($AgNO_3$) crystals fine enough to pass through a No. 20 (850-μm) sieve and then dry for 2 h at 110°C. Prepare a 0.100 *N* solution by dissolving 16.989 g of dry $AgNO_3$ in chloride-free water and diluting to 1 L in a volumetric flask.

13. Procedure

13.1 Weigh to the nearest 0.01 g about 1.0 g of the sample (previously dried for ½ h at 100 to 105°C) and transfer to a 500-mL, wide-mouth Erlenmeyer flask. Add 250 mL of hot water and swirl for a few minutes; then cool to dissolve.

13.2 Add 5 mL of 0.100 *N* $AgNO_3$ solution and 5 mL of ferric alum indicator solution, and back-titrate with 0.1 *N* KCNS solution to the first appearance of a faint pink color.

14. Calculation

14.1 Calculate the percent of chlorides as NaCl as follows:

$$\text{Chlorides, \%} = ([(AB - CD) \times 0.0585]/E) \times 100 \tag{4}$$

where:

A = $AgNO_3$ solution added, mL,
B = normality of the $AgNO_3$ solution,
C = KCNS solution required to back-titrate the excess $AgNO_3$, mL,
D = normality of the KCNS solution, and
E = sample used, g.

ALKALINITY—AS SODIUM CARBONATE

15. Scope

15.1 This test method covers the determination of the total alkalinity of hydroxypropyl methylcellulose expressed as sodium carbonate (Na_2CO_3).

16. Reagents

16.1 *Methyl Purple Indicator Solution.*

16.2 *Sulfuric Acid, Standard (0.01 N)*—Prepare and standardize a 0.01 *N* solution of sulfuric acid (H_2SO_4).

17. Procedure

17.1 Weigh to the nearest 0.01 g about 1.0 g of the sample (previously dried for ½ h at 100 to 105°C) and transfer to a 500-ml, widemouth Erlenmeyer flask. Add 250 mL of hot water and swirl for a few minutes; then cool to dissolve.

17.2 Add 4 drops of methyl purple indicator solution and titrate to the first faint pink color with 0.01 *N* H_2SO_4.

18. Calculation

18.1 Calculate the percent alkalinity as Na_2CO_3, *S*, as follows:

$$S = [(AB \times 0.053)/C] \times 100 \quad (5)$$

where:

A = H_2SO_4 required for titration of the sample, mL,
B = normality of the H_2SO_4, and
C = sample used, g.

IRON

19. Scope

19.1 This test method covers the determination of total iron content in samples of hydroxypropyl methylcellulose. The iron is converted to ferric sulfate which reacts with the indicator to form a pink color that can be quantitatively measured.

20. Apparatus

20.1 *Photometer*—Any photoelectric filter photometer or spectrophotometer suitable for measurements at 430 nm.

20.2 *Kjeldahl Flasks*—Calibrated to contain 50 mL, and made of heat- and chemical-resistant glass.

21. Reagents

21.1 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH_4OH).

21.2 *Buffer Solution*—Dissolve 20 g of sodium bicarbonate ($NaHCO_3$) and 10 g of sodium carbonate (Na_2CO_3) in water and dilute to 1 L.

21.3 *Disodium-1,2-Dihydroxybenzene-3,5-Disulfonate Solution*—Prepare an aqueous solution containing 25 g/L.

21.4 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

21.5 *Hydrogen Peroxide (30 %)*—Concentrated hydrogen peroxide (H_2O_2).

21.6 *Iron Standard Solution (0.0001 g Fe/ml)*—Dissolve 0.01 g of iron powder containing not less than 99.9 % iron in HCl (sp gr 1.19). Oxidize the solution with bromine water and expel the excess by boiling. Dilute to 1 L in a volumetric flask.

21.7 *Phenolphthalein Indicator Solution (1 g/100 mL)*—Dissolve 1 g of phenolphthalein in 100 mL of ethanol (95 %).

21.8 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfuric acid (H_2SO_4).

21.9 *Sulfuric Acid (1+4)*—Carefully mix 1 volume of H_2SO_4 (sp gr 1.84) with 4 volumes of water, adding the H_2SO_4 gradually while mixing.

22. Preparation of Calibration Curve

22.1 Following the procedure given in Section 23, and using varied amounts of the standard iron solution prepared in accordance with 21.6, prepare a calibration curve showing iron content in parts per million and the corresponding photometer readings.

23. Procedure

23.1 Weigh to the nearest 0.01 g about 2 g of the sample (previously dried for ½ h at 100 to 105°C). Transfer by means of a funnel to a Kjeldahl flask. Place the flask at a 20° angle in the furnace at 500°C and heat until some charring of the sample has taken place. (Care must be taken not to char too much.) Remove and allow to cool.

23.2 Add 3 mL of H_2SO_4 to the flask. Place on the digestion rack and digest. Cool and add H_2O_2 dropwise until the solution is clear. Heat over a Meker burner to a volume of 2 mL. Cool, and wash the sides of the flask with water. Add 3 drops of phenolphthalein indicator solution. Add NH_4OH to a red end point. Wash the neck of the flask. The solution should be clear and not greater than 20 mL in volume.

23.3 Add 2 mL of the color-forming solution described in 21.3, and mix. Adjust pH to 7.0 and then dilute to mark with buffer. Transfer a small portion to an absorption cell and determine the photometer reading at 480 nm.

23.4 *Blank*—Make a blank determination, using the same amount of reagents and the same procedure as for the sample.

24. Calculation

24.1 Read the iron content, in parts per million, directly from the calibration curve (Section 22). Subtract the parts per million of iron due to iron in the blank.

HEAVY METALS

25. Scope

25.1 This test method covers the determination of whether or not the heavy metals content of hydroxypropyl methylcellulose is below a given level based on a lead standard.

26. Summary of Test Method

26.1 The ash residue from the sulfated ash test is digested with dilute hydrochloric acid. A standard containing a known amount of lead is prepared, and the heavy metals content is determined qualitatively by comparing the sample to the standard.

27. Apparatus

27.1 *Nessler Tubes,* 50-mL.

27.2 *Volumetric Flasks,* 50-mL.

28. Reagents

28.1 *Acetic Acid*—Glacial acetic acid.

28.2 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH_4OH).

28.3 *Ammonium Hydroxide (2+3)*—Dilute 400 mL of NH_4OH (sp gr 0.90) with sufficient water to make 1000 mL.

28.4 *Buffer Solution*—Dissolve 60 mL of acetic acid in about 500 mL of water, add 10 mL of NH_4OH, and dilute to 1 L.

28.5 *Hydrochloric Acid (1+2)*—Dilute 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 2 volumes of water.

28.6 *Hydrogen Sulfide TS*—Saturate a convenient volume of water with hydrogen sulfide (H_2S) in a narrow-neck, glass-stoppered, amber bottle. This solution must be made fresh.

28.7 *Hydroxylamine Hydrochloride Solution (200 g/L)*—Dissolve 20 g of hydroxylamine hydrochloride ($NH_2OH·HCl$) in 100 mL of water.

28.8 *Lead Nitrate Stock Solution*—Dissolve 159.8 mg of lead nitrate ($Pb(NO_3)_2$) in 100 mL of water containing 1 mL of HNO_3 (sp gr 1.42). Dilute with water to 1000.0 mL and mix. This solution should be prepared and stored in glass containers that are free from lead salts.

28.9 *Lead Standard Solution (1 mL = 1 µg Pb)*—Dilute 10 mL of the lead nitrate stock solution, accurately measured, with water to 100.0 mL. Each millilitre of the solution so prepared contains 10 µg of lead.

29. Procedure

29.1 Pipet into a 50-mL Nessler tube 0.15 mL of HCl (1+2), 2 mL of the buffer solution, and a volume of the standard lead solution containing the quantity of lead equivalent to the specified heavy metals limit. Add water to make 40 mL and label as Solution A. Make sure that the final pH of these solutions is between 3 and 4. This can be tested by pH indicator paper or pH meter. For visual comparison make sure that the optimum lead content is between 20 and 40 µg.

29.2 To the crucible containing the sulfated ash residue add 4 mL of HCl (1+2). Cover and carefully digest on a steam bath for 10 min. Uncover and slowly evaporate to dryness. Moisten the residue with 0.15 mL of HCl (1+2), 0.5 mL of hydroxylamine hydrochloride solution, and 10 mL of hot water. Carefully digest for 2 min. Add 2 mL of the buffer solution. Filter if necessary. Thoroughly wash the crucible and filter with water into a 50-mL Nessler tube that matches the one used for Solution A. If necessary, adjust the pH to 3 to 4 with NH_4OH (2+3) or HCl (1+2) using pH indicator paper. Dilute to 40 mL and label this Solution B.

29.3 Add 10 mL of H_2S solution to each tube: Solution A and Solution B. Mix and view downward over a white surface. The color of Solution B shall be no darker than that of Solution A. Make the comparison within 10 min.

METHOXYL CONTENT

30. Scope

30.1 This test method covers the determination of the methoxyl content of hydroxypropyl methylcellulose. Total alkoxyl is first determined and the methoxyl content found by subtracting the hydroxypropyl content from the total alkoxyl figure.

31. Summary of Test Method

31.1 The hydroxypropyl methylcellulose is heated with a strong solution of hydriodic acid to form an alkyl iodide, which by means of a carbon dioxide stream is swept through a condenser and finally absorbed in a mixture of bromine, acetic acid, and sodium acetate. The alkyl iodide absorbed in the aforementioned mixture is oxidized to an alkyl iodate. The excess bromine is reduced with formic acid, and the iodate is determined iodometrically using potassium iodide and standard thiosulfate.

32. Apparatus

32.1 *Distillation Apparatus,* as illustrated in Fig. 1, consisting of a boiling flask with a side arm for admission of carbon dioxide or nitrogen, an air condenser with a trap, and a receiver.

32.2 *Oil Bath,* equipped with a heating device, preferably electrical, so that the bath can be maintained at 145 to 150°C.

33. Reagents

33.1 *Bromine Solution*—Dissolve 5 mL of bromine in 145 mL of the potassium acetate solution. Prepare the bromine solution fresh daily in a hood to remove bromine vapors.

33.2 *Carbon Dioxide*—This may be obtained by the interaction of marble and hydrochloric acid (HCl, 1+1) in a Kipp generator or preferably from a cylinder of the gas equipped with a suitable needle valve. The carbon dioxide (CO_2) shall be passed through a bubble counter and a dry trap, and then through a pressure regulator consisting of a glass tee whose vertical arm extends almost to the bottom of a 254-mm (10-in.) column of water. A screw clamp shall be attached to the thin-walled rubber tubing connecting the horizontal arm of the tee with the boiling flask. This arrangement permits regulation of the flow of gas and allows any excess gas to escape. Nitrogen may be used in place of CO_2.

33.3 *Formic Acid (90 %).*

33.4 *Gelatin Capsules*—Gelatin capsules of a suitable size to hold 50 to 60 mg of the dried sample.

33.5 *Hydriodic Acid (57 %, sp gr 1.70)*—Hydriodic acid (HI) forms with water a constant-boiling mixture (boiling point 126 to 127°C) that contains 57 % HI. The concentration of HI in the reagent used should be not less than 56.5 %. The blank determination, which is affected primarily by free iodine in the reagent should require not more than 0.5 mL of 0.1 *N* sodium thiosulfate ($Na_2S_2O_3$) solution.[5] If necessary, the acid may be purified by adding to it a small amount of red phosphorus and boiling for 20 to 30 min in a hood, while passing a stream of CO_2 into the liquid. Distillation shall then be carried out behind a safety glass shield in a hood, using an all-glass apparatus with a slow stream of CO_2 running through the receiver. (**Warning**—See 33.5.1) Put the purified HI in small, brown, glass-stoppered bottles, previously swept out with CO_2, and seal the stoppers with molten paraffin. Store in a dark place. To minimize decomposition of HI due to contact with air, run CO_2 into the bottle while withdrawing portions of the acid for use.

33.5.1 **Warning:**Under some conditions the poisonous gas phosphine (PH_3) is formed during distillation, and this may unite with molecular iodine to form phosphorus triodide (PI_3), which may explode on contact with air. It is, therefore, advisable to keep the current of CO_2 going after the distillation is ended and until the apparatus has cooled.

33.6 *Phosphorus Slurry*—Add about 0.06 g of red phosphorus to 100 mL of water. Shake well before using.

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[5] Hydriodic acid suitable for methoxyl determination may be prepared by the method of Samsel, E. P., and McHard, J. A., "Determination of Alkoxyl Groups in Cellulose Ethers," *Industrial and Engineering Chemistry*, Analytical Edition, IECHA, Vol 14, 1942, p. 750.

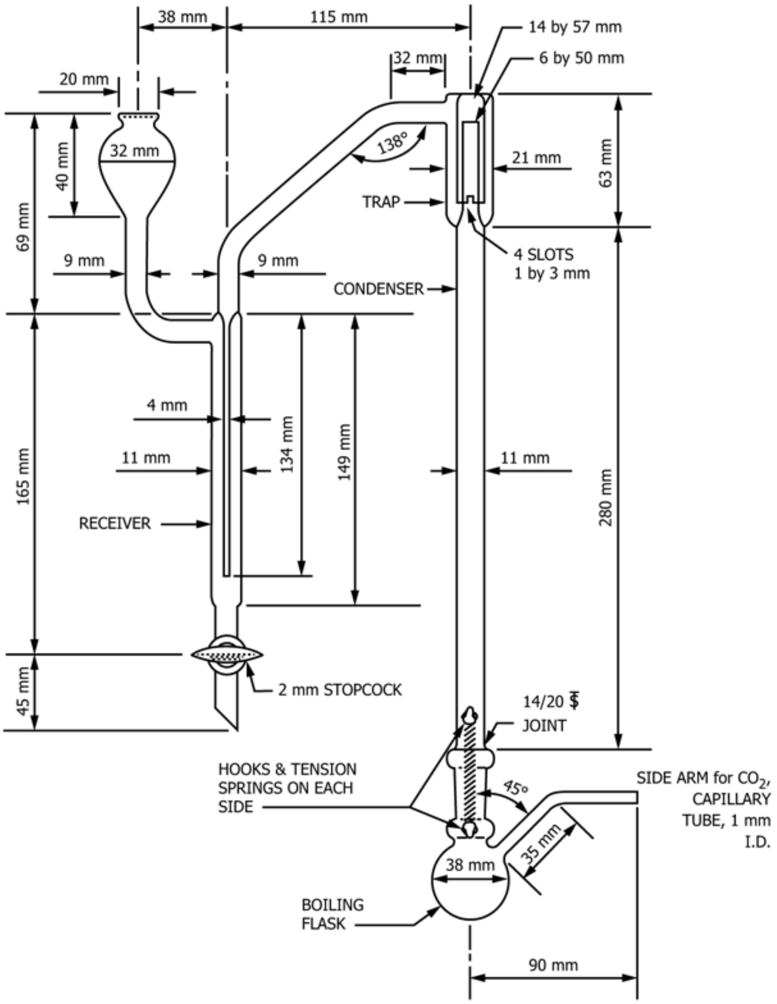

FIG. 1 Distillation Apparatus for Methoxyl Determination

33.7 *Potassium Acetate Solution (100 g/L)*—Dissolve 100 g of anhydrous potassium acetate crystals in 1 L of a solution containing 900 mL of glacial acetic acid and 100 mL of acetic anhydride.

33.8 *Potassium Iodide (KI).*

33.9 *Sodium Acetate Solution (220 g/L)*—Dissolve 220 g of anhydrous sodium acetate in water and dilute to 1 L.

33.10 *Sodium Thiosulfate Standard Solution (0.1 N)*—Dissolve 25 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 200 ml of water and dilute to 1 L. Use freshly boiled and cooled water. It is preferable to allow the solution to stand for a few days before standardization. Standardize the solution against 0.1000 *N* potassium dichromate ($K_2Cr_2O_7$) prepared by dissolving exactly 4.9037 g of $K_2Cr_2O_7$ (National Institute of Standards and Technology Standard Sample No. 136) in water and diluting to a 1 L in a volumetric flask. By means of a buret, measure accurately 35 to 45 mL of the $K_2Cr_2O_7$ solution into a 250-mL Erlenmeyer flask. Add 2 g of KI and 50 mL of H_2SO_4 (1+9) and allow to stand for about 5 min. The flask should be stoppered during the standing period to avoid loss of iodine. Titrate the liberated iodine with the $Na_2S_2O_3$ solution, using starch indicator solution near the endpoint. At the end point, the blue color of the starch indicator will be destroyed, leaving the pale green color of the chromate ion. The normality of the $Na_2S_2O_3$ solution should be checked at least once a week. Calculate the normality of the $Na_2S_2O_3$ solution, *N*, as follows:

$$N = (A/B) \times 0.1 \tag{6}$$

where:

A = 0.1000 N $K_2Cr_2O_7$ solution added, mL, and
B = $Na_2S_2O_3$ solution required for the titration, mL.

As an alternative procedure, the $Na_2S_2O_3$ solution may be standardized against arsenic trioxide (As_2O_3) (National Institute of Standards and Technology standard sample No. 83) or potassium iodate (KIO_3).

33.11 *Starch Indicator Solution.*

33.12 *Sulfuric Acid (1+9)*—Carefully mix 1 volume of concentrated H_2SO_4 (sp gr 1.84) with 9 volumes of water, adding the H_2SO_4 gradually while mixing.

34. Procedure

34.1 Dry the sample at 105°C for at least 30 min. Through the condenser, add to the trap in the distillation apparatus (Fig.

1) enough of the phosphorus slurry to make the trap about half full (Note 1). Add 19 to 20 mL of the bromine solution to the receiver. Weigh 50 to 60 mg of the dry sample, to the nearest 0.1 mg, into a gelatin capsule and drop it into the boiling flask. (Do the weighing as rapidly as possible without sacrificing accuracy, since dry hydroxypropyl methylcellulose picks up moisture rapidly.)

NOTE 1—Water may be used in the trap to scrub out entrained vapors of iodine quite successfully. If the test method is to be used as a routine control test, this may be advisable for safety purposes. If so, check the accuracy of the apparatus with the water trap against samples that have been run using the phosphorus slurry trap.

34.2 Add a few small glass beads or chips of clay plate and then 6 mL of the HI. Moisten the ground-glass joint with 2 drops of the HI, then fasten to the distillation assembly. Connect the source of CO_2 to the side arm of the flask. Pass a current of CO_2 into the apparatus at the rate of about 2 bubbles/s. Immerse the flask in the oil bath, maintained at 150°C, and heat for 40 min.

34.3 Add 10 mL of sodium acetate solution to a 500-mL Erlenmeyer flask and wash into it the contents of the receiver; dilute to 125 mL with water. Add formic acid dropwise, with swirling, until the brown color of bromine is discharged, and then add about 6 drops more. A total of 12 to 15 drops is usually required. After about 3 min add 3 g of KI and 15 mL of H_2SO_4 (1 + 9) and titrate immediately with 0.1 *N* $Na_2S_2O_3$ solution to a light straw color. Add a little starch indicator solution and continue the titration to the disappearance of the blue color.

34.4 *Blank*—Make a blank determination, using the same amounts of reagents and the same procedure as for the sample. (Usually, about 0.1 mL of 0.1 *N* $Na_2S_2O_3$ solution is required.)

35. Calculation

35.1 Calculate the percent of methoxyl as follows:

$$M = ([(A - B)C \times 0.00517]/D) \times 100 \tag{7}$$

where:

M = Methoxyl, total (methyl + hydroxypropyl groups calculated as methoxyl),
A = $Na_2S_2O_3$ solution required for titration of the sample, mL,
B = $Na_2S_2O_3$ solution required for titration of the blank, mL,
C = normality of the $Na_2S_2O_3$ solution, and
D = sample used, g.

35.2 In 35.1 the percent OCH_3 represents the total of methyl and hydroxypropyl groups calculated as methoxyl. To obtain the corrected methoxyl content, the total alkoxyl must be corrected for the percent OC_3H_6OH obtained in Section 41. The percent OC_3H_6OH shall be first corrected by a factor of 0.93 (an average obtained by running Morgan determinations on a large number of samples) for the propylene produced from the reaction of HI with the hydroxypropyl group as follows:

$$A = B - (C \times 0.93 \times 31/75) \tag{8}$$

where:

A = corrected OCH_3, %,
B = total OCH_3,% , and
C = OC_3H_6OH,%.

HYDROXYPROPOXYL CONTENT[6]

36. Scope

36.1 This test method covers the determination of the hydroxypropoxyl content of hydroxypropyl methylcellulose. The figure obtained from this analysis is used in determining the corrected percent methoxyl content.

37. Summary of Test Method

37.1 The hydroxypropoxyl group of hydroxypropyl methylcellulose is oxidized by hot chromic acid to acetic acid and this in turn is titrated with 0.02 *N* sodium hydroxide solution. Procedures are also given for (*1*) eliminating the error resulting from oxidation of the cellulose backbone, which yields an apparent hydroxypropyl value, and (*2*) preparing a synthetic hydroxypropyl methylcellulose standard using methylcellulose and propylene glycol.

38. Apparatus

38.1 *Chromic Acid Oxidation Apparatus,* as illustrated in Fig. 2.

38.2 *Oil Bath,* equipped with an electrical heating device so the bath can be maintained at 155°C.

38.3 *pH Meter,* expanded scale, capable of giving reproducible results within ±0.1 pH units and equipped with glass and calomel electrodes.

39. Reagents

39.1 *Chromium Trioxide Solution (30 %)*—Dissolve 60 g of chromic trioxide (CrO_3) in 140 mL of organic-free water.

39.2 *Nitrogen.*

39.3 *Potassium Iodide (KI).*

39.4 *Sodium Bicarbonate ($NaHCO_3$).*

39.5 *Sodium Hydroxide, Standard Solution (0.02 N), carbon dioxide-free*—Standardize against primary standard potassium hydrogen phthalate ($KHC_8H_4O_4$) using a pH meter to an end point of pH 7.0 ± 0.1.

39.6 *Sodium Thiosulfate Standard Solution (0.1 N)*—Dissolve 24.8 g of sodium thiosulfate ($Na_2S_2O_3$) and 0.2 g sodium bicarbonate ($NaHCO_3$) in freshly boiled water. Dilute to 1 L with water. Standardize against potassium iodate (KIO_3) using starch indicator to determine the end point.

39.7 *Sodium Thiosulfate Standard Solution (0.02 N)*—Dilute 200 ml of 0.1 *N* sodium thiosulfate standard solution to 1 L with water. Prepare fresh solutions daily as needed.

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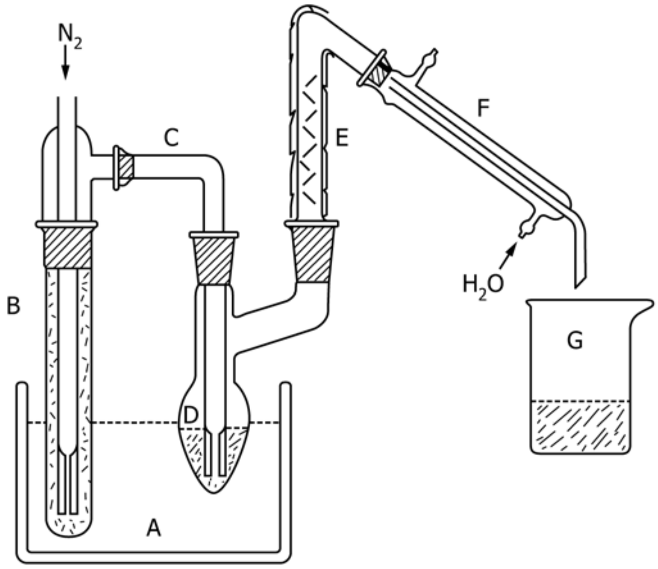
[6] References for the hydroxypropoxyl determination are as follows:

Dow Method No. MC-15, "The Determination of the Hydroxypropyl Group in the Presence of an Alkyl Group in Hydroxypropyl Methylcellulose."

Lemieux, R. U., and Purves, C. B., "Quantitative Estimation as Acetic Acid of Acetyl, Ethylidene, Ethoxy, and Hydroxyethyl Groups," *Canadian Journal of Research*, Vol B-25, 1947, p. 485.

Morgan, P. W., "Determination of Ethers and Esters of Ethylene Glycol," *Industrial and Engineering Chemistry*, Analytical Edition, IECHA, Vol 18, 1946, p. 500.



A—Oil bath equipped with an electric heater capable of heating the bath at the desired rate and maintaining the temperature at 155°C.
B—Steam generator consisting of a 25 by 150-mm test tube and a gas inlet tube with a ¾ to 1¼-mm capillary tip.
C—Adapter bleeder tube with a ¾ to 1¼-mm capillary tip.
D—Reaction flask consisting of a 25-mL conical bottom micro boiling flask modified to provide a sidearm outlet.
E—Vigreaux column, 95 mm long, wrapped with aluminum foil.
F—Micro condenser with a 100-mm jacket.
G—Beaker, 150-mL, Berzelius, graduated.

FIG. 2 Oxidation and Distillation Apparatus.

39.8 *Sulfuric Acid (1 + 165)*—Carefully add, while stirring 10 mL of concentrated H_2SO_4 (sp gr 1.84) to 165 mL of distilled water.

39.9 *Methylcellulose,* free of foreign material such as other substituted celluloses or glycols that will break down to acetic acid.

39.10 *Propylene Glycol.*

39.11 Water, organic-free, obtained by distillation or by ion-exchange treatment and to pass the following test: To 100 mL of water add 10 mL of dilute H_2SO_4 (1+16.5), heat to boiling, and add 0.1 mL of potassium permanganate ($KMnO_4$) solution (approximately 0.1 *N*). The water must retain a pink coloration after boiling for 10 min.

40. Procedure

40.1 Weigh to the nearest 0.0001 g about 100 mg of the sample (previously dried at 105°C for ½ h) and transfer to flask, *D*, and add 10 mL of 30 % CrO_3 solution. Fill the steam generator, *B*, to the bottom of the standard-taper joint and then assemble the apparatus as shown in Fig. 2. Immerse the steam generator and sample flask in the oil bath to the level of the CrO_3 solution. Start the condenser cooling water and pass nitrogen gas through the flask at a rate of 1 bubble per second. Raise the temperature of the bath to 155°C within ½ h and maintain it at this temperature until the end of the determination. Too rapid an initial rise in temperature results in high blanks. Distill until 50 mL of distillate has been collected. Detach condenser, *F*, from the Vigreaux column, *E*, and wash with water, collecting the washings in the beaker containing the distillate. Titrate the solution with standard 0.02 *N* NaOH solution to a pH of 7.0 ± 0.1 using the expanded-scale pH meter. Record the volume, *V*, of standard NaOH used. Add approximately 0.5 g of $NaHCO_3$ followed by 10 mL dilute H_2SO_4 (1+165). After evolution of carbon dioxide (CO_2) has ceased, add 1 g of KI, mix well, and allow the solution to stand in the dark for 5 min. Titrate the liberated iodine with 0.02 *N* $Na_2S_2O_3$ to the disappearance of the yellow color. Record the volume, *Y*, of standard $Na_2S_2O_3$ used. This titration, *Y* mL, when multiplied by the empirical factor, *K*, appropriate to the particular apparatus and reagents in use, gives the acid equivalent not caused by acetic acid. The acetic acid equivalent is $(V - KY)$ mL of 0.02 *N* NaOH solution.

40.2 *Empirical Factor, K*—The empirical factor, *K*, for each apparatus is obtained by running a blank determination in which the cellulose ether is omitted. The acidity of a blank run for a given apparatus and given reagents is in a fixed ratio to the oxidizing equivalent of the distillate in terms of $Na_2S_2O_3$ solution as follows:

$$K = (V_b \times N_1)/(Y_b \times N_2) \tag{9}$$

where:

V_b = 0.02 N NaOH solution required in blank run, mL,
N_1 = normality of the 0.02 N NaOH solution,
Y_b = 0.02 N $Na_2S_2O_3$ required in blank run, mL, and

N_2 = normality of the 0.02 N $Na_2S_2O_3$ solution.

40.3 *Methylcellulose Blank*—Conduct several determinations using methylcellulose according to the given procedure.

40.4 *Hydroxypropoxyl Standard*—Since primary standards of hydroxypropyl methylcellulose are not available, a synthetic standard may be prepared by weighing 100 mg of methylcellulose into the reaction flask and adding 1.0 mL of an aqueous solution containing 1.0 g of propylene glycol in 100 mL. Thus, a secondary standard hydroxypropyl methylcellulose can be established by repeated analysis by this method using properly standardized conditions.

41. Calculation

41.1 Calculate the percent of uncorrected hydroxypropoxyl as follows:

$$A_U = ([(V_aN_1 - KY_aN_2) \times 0.075]/W) \times 100 \qquad (10)$$

where:

A_U = OC_3H_6OH (uncorrected), %
V_a = 0.02 N NaOH solution required for titration of the sample, mL,
N_1 = normality of the 0.02 N NaOH solution,
K = empirical factor,
Y_a = 0.02 N $Na_2S_2O_3$ solution required for titration of the sample, mL,
N_2 = normality of the 0.02 N $Na_2S_2O_3$ solution, and
W = sample used, g.

41.2 Calculate the percent of corrected hydroxypropoxyl as follows:

$$A_C = A_U - B \qquad (11)$$

where:

A_C = OC_3H_6OH (corrected), %, and
B = OC_3H_6OH obtained from the methylcellulose blank determination, % (40.3).

VISCOSITY

42. Scope

42.1 This test method covers the determination of the apparent viscosity of 2 % water solutions of hydroxypropyl methylcellulose. The viscosities found by this test method do not necessarily correspond to values obtained from other possible test methods.

43. Summary of Test Method

43.1 A 2 % water solution of hydroxypropyl methylcellulose is measured by use of an Ubbelohde tube viscometer. This 2 % solution is based on a dry mass of the product, for example, corrected mass for moisture found in the moisture analysis.

44. Apparatus

44.1 *Viscometer,* as shown in Fig. 3.

NOTE 2—If a viscometer has been repaired, it should be recalibrated

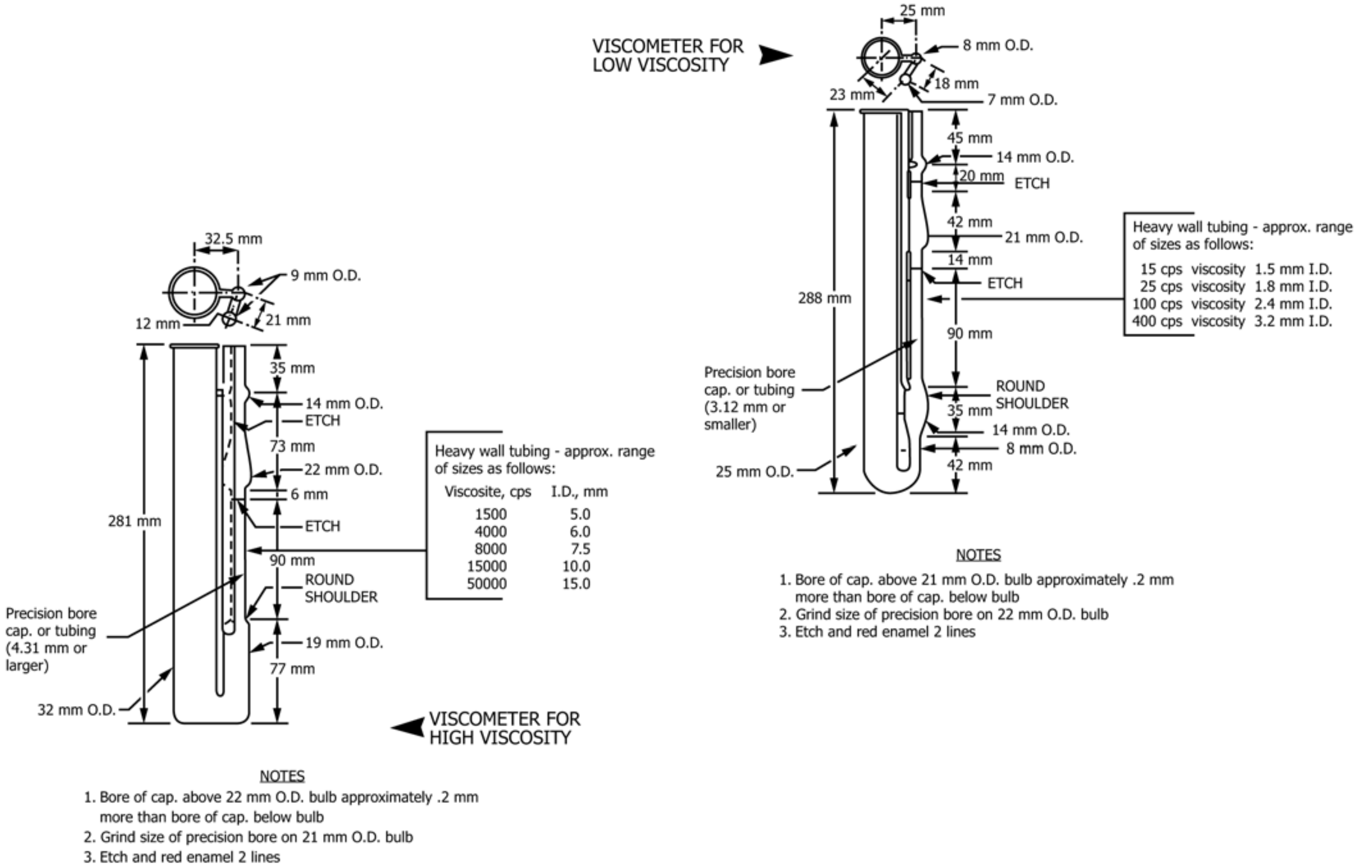


FIG. 3 Hydroxypropyl Methylcellulose Viscometers

before it is used again. Even minor repairs can cause significant changes in the K value.

44.2 *Mechanical Stirrer.*

45. Procedure

45.1 Determine the moisture content of a portion of the sample. Since cellulose and its water-soluble derivatives are hygroscopic, keep the exposure of the sample to the atmosphere to a minimum. Changes in moisture content can introduce large errors into the accuracy of the determination, and this step should never be omitted if precise results are desired. The suggested method is to weigh out a 2-g portion in a suitable dish, dry at 105°C for 1 h, or until constant mass is obtained after cooling in a desiccator.

45.2 Correcting for the moisture content, weigh out enough of the undried sample to give 2.000 g of solids, calculated as follows:

$$\text{Mass of sample, g} = [100/(100 - \text{moisture content, \%})] \times 2 \quad (12)$$

Place the sample in an 250-mL (8-oz) wide-mouth bottle. This weighing step is critical in obtaining good checks and make sure that it is done on a good balance sensitive to 1 mg. Masses to the nearest 0.01 g will be sufficiently accurate.

45.3 Add 98.0 g of hot water (85 to 90°C) to the 250-mL (8-oz) bottle containing the 2-g sample.

45.4 Agitate with a mechanical stirrer for 10 min, then place the bottle in an ice bath (0 to 5°C) until solution is complete (at least 20 min). Equip the stirrer assembly with a one-hole stopper or bottle cap so that no water vapor is lost during agitation. De-air the solution by some means such as centrifuging.

45.5 When solution is complete, as evidenced by the absence of partially swollen or undispersed particles, determine the viscosity in a methylcellulose viscometer at 20 ± 0.1°C. Observe two precautions at this point: (*1*) Make sure that the solution is essentially free of air bubbles, and (*2*) check that the temperature of the material in the tube in order to make certain that it is actually at the bath temperature. The methylcellulose viscosity tube (Fig. 3) consists of three parts: a large filling tube with a reservoir at its lower extremity, A; the orifice tube, B; and an air vent to the reservoir, C; when B is filled, close C to prevent the sucking of air bubbles into the orifice tube. Before the sample is allowed to flow through the orifice for the viscosity determination, open the vent C so that the column of solution in B will flow into the reservoir against atmospheric pressure. Failure to open C before running the viscosity will result in false values.

46. Calculation

46.1 Calculate the viscosity as follows:

$$V = Kdt \quad (13)$$

where:

V = viscosity, cP,
K = viscometer constant (Note 3),
d = density of the sample solution at 20/20°C (Note 4), and
t = time for the solution to pass from the upper to the lower mark of the viscometer, s.

NOTE 3—The viscometer constant is determined by passing a standard oil of known viscosity through the tube and determining the time of flow. The above equation can then be solved for K.

NOTE 4—For routine work, the density of solutions of hydroxypropyl methylcellulose may be assumed to be 1.00.

pH

47. Procedure

47.1 Determine the pH of the viscosity solution from 45.4, using any suitable pH meter which is standardized according to Test Method E70.

SOLIDS

48. Scope

48.1 This test method covers the determination of the level of water-insoluble matter in hydroxypropyl methylcellulose.

49. Summary of Test Method

49.1 Hydroxypropyl methylcellulose is dispersed in hot water and then cooled to complete solution. Water-insoluble matter is settled by centrifugal force and measured volumetrically.

50. Apparatus

50.1 *Oil Tubes,* graduated, long-form, 100-mL tapered ASTM, conforming to the requirements prescribed in Section 3 and Fig. 1 of Test Method D96.

50.2 *Centrifuge,* capable of whirling filled centrifuge tubes at a speed that will produce a centrifugal force of 725 times gravity.

51. Procedure

51.1 Add 1.50 g of bone-dry hydroxypropyl methylcellulose to 148.5 g of 90°C water in a 57 by 152-mm (2¼ by 6-in.) bottle and agitate vigorously for about 15 min or until the material has become finely divided. Place an ice bath around the bottle and agitate the mixture until the solution is effected. This usually requires about 15 min.

51.2 Place 100 mL of this 1 % solution in an oil tube, cool to 10°C, and centrifuge at 725 times gravity for 5 min. Make sure that the solution temperature is below 20°C when finished. Read the percent by volume of solids from the graduations on the tube.

DENSITY

52. Scope

52.1 This test method covers the determination of the bulk density of hydroxypropyl methylcellulose.

53. Summary of Test Method

53.1 A weighed amount of hydroxypropyl methylcellulose is transferred to a 250-mL volumetric graduated cylinder and the graduate vibrated to settle the powder.

54. Apparatus

54.1 *Vibrator*—A magnetic-type electric vibrator attached to the vertical support rod of a ring stand approximately 0.6 n (1 ft) above the base. A condenser clamp of sufficient size to hold a 250-mL graduated cylinder also shall be attached to the above rod. The base of the stand should be weighted.

55. Procedure

55.1 Place 50.0 g of powdered hydroxypropyl methylcellulose in a 250-mL graduated cylinder and clamp to the ring stand support. Allow the cylinder to vibrate for 3 min; then observe the level to which the powder has contracted.

56. Calculation

56.1 Calculate the density, D, as follows:

$$D = 50/r \tag{14}$$

where:

r = observed reading.

57. Keywords

57.1 alkalinity; ash; chlorides; density; hydroxypropyl; metals; methylcellulose; moisture; ph

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