



# Standard Test Methods for Sodium Carboxymethylcellulose<sup>1</sup>

This standard is issued under the fixed designation D1439; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope\*

1.1 These test methods cover the testing of sodium carboxymethylcellulose.

1.2 The test procedures appear in the following order:

	Sections
Moisture	4 – 9
Degree of Etherification:	
Test Method A—Acid Wash	10 – 17
Test Method B—Nonaqueous Titration	10, 12, 18 – 23
Viscosity	24 – 29
Purity	30 – 37
Sodium Glycolate	38 – 46
Sodium Chloride	47 – 54
Density	55 – 61

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 specific hazard statements, see 15.1 and 20.

## 2. Referenced Documents

2.1 *ASTM Standards*:<sup>2</sup>

D1347 Test Methods for Methylcellulose (Withdrawn 2003)<sup>3</sup>

E1 Specification for ASTM Liquid-in-Glass Thermometers

## 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,<sup>4</sup> where such specifications are available. 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 sodium carboxymethylcellulose.

4.2 The results of this test are used for calculating the total solids in the sample; and, by common usage, all materials volatile at this test temperature are designated as moisture.

## 5. Significance and Use

5.1 Moisture analysis (along with purity) is used to calculate the amount of active polymer in the material and must be considered when determining the amount of sodium carboxymethylcellulose to use in various formulations.

## 6. Apparatus

6.1 *Oven*—Gravity convection oven, capable of maintaining a temperature of  $105 \pm 3^\circ\text{C}$ .

6.2 *Weighing Bottles*, low-form, 50-mm inside diameter by 30-mm height, or equivalent.

6.3 *Analytical Balance*.

## 7. Procedure

7.1 Weigh 3 to 5 g of the sample to the nearest 0.001 g in a tared and covered weighing bottle.

7.2 Place the bottle in an oven at  $105^\circ\text{C}$  for 2 h with the cover removed. Cool the bottle in a desiccator, replace the cover, and weigh.

<sup>1</sup> 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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<sup>2</sup> 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.

<sup>3</sup> The last approved version of this historical standard is referenced on www.astm.org.

<sup>4</sup> *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.

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

7.3 Replace the sample in the oven for 30 min, cool, and reweigh.

7.4 Continue this procedure to a mass loss of not more than 5 mg for 30 min drying time.

## 8. Calculation

8.1 Calculate the percent moisture,  $M$ , as follows:

$$M = (A/B) \times 100 \quad (1)$$

where:

$A$  = mass loss on heating, g, and

$B$  = sample used, g.

## 9. Precision and Bias

9.1 *Precision*—Statistical analysis of interlaboratory reproducibility test results on samples containing 2 to 10 % moisture indicates a precision of  $\pm 0.2$  % absolute at the 95 % confidence level.

9.2 *Bias*—No justifiable statement can be made on the bias of the procedure for measuring moisture because no suitable reference material exists.

## DEGREE OF ETHERIFICATION

### 10. Scope

10.1 These test methods cover the determination of the degree of etherification (D.E.) of sodium carboxymethylcellulose.

10.2 Two test methods are included as follows:

10.2.1 *Test Method A (Acid Wash)*, for crude grades of sodium carboxymethylcellulose with degrees of etherification up to 0.85. Above 0.85 degree of etherification, slightly low results may be obtained.

10.2.2 *Test Method B (Nonaqueous Titration)*, for purified grades of sodium carboxymethylcellulose of all degrees of etherification. It is not applicable to the crude grades.

### 11. Significance and Use

11.1 These test methods determine the amount of substituent groups added to the cellulose backbone. The level can greatly affect solution properties, rheology, viscosity, hygroscopicity, salt tolerance, and many other properties of the polymer.

#### *Test Method A—Acid Wash*

### 12. Summary of Test Method

12.1 The water-soluble sodium carboxymethylcellulose is converted to the insoluble acid form, purified by washing, dried, and then a weighed sample is reconverted to the sodium salt with a measured excess of sodium hydroxide.

### 13. Apparatus

13.1 *Stirrer*, air-driven.

13.2 *Buchner Funnel*, 75-mm, fitted with a 70-mm fine-texture, heavy-duty filter paper. A 60-mm medium-porosity, fritted glass funnel may also be used.

13.3 *Drying Oven*, maintained at 105°C.

### 14. Reagents

14.1 *Diphenylamine Reagent*—Dissolve 0.5 g of diphenylamine in 120 mL of sulfuric acid ( $H_2SO_4$ , 9 + 2). The reagent should be essentially water-white. It will give a deep blue coloration with traces of nitrate or other oxidizing agents.

14.2 *Ethyl Alcohol (95 volume %)*—Denatured ethyl alcohol conforming to either Formula 2B, 3A, or 30 of the U. S. Bureau of Internal Revenue.

14.3 *Ethyl Alcohol (80 % by volume)*—Dilute 840 mL of Formula 2B, 3A, or 30 denatured alcohol to 1 L with water.

14.4 *Hydrochloric Acid, Standard* (HCl, 0.3 to 0.5 N).

14.5 *Methanol*, anhydrous.

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

14.7 *Sodium Hydroxide, Standard Solution(0.3 to 0.5 N)*—Prepare and standardize a 0.3 to 0.5 N solution of sodium hydroxide (NaOH).

14.8 *Sulfuric Acid (9 + 2)*—Carefully mix 9 volumes  $H_2SO_4$  with 2 volumes of water.

### 15. Procedure

15.1 Weigh approximately 4 g of the sample into a 250-mL beaker and add 75 mL of ethyl alcohol (95 %). Stir the mixture with an air-driven stirrer until a good slurry is obtained. Add 5 mL of  $HNO_3$ , while agitating, and continue agitation for 1 to 2 min. Heat the slurry and boil for 5 min. (**Warning**—Exercise care to avoid fire.) Remove the heat and continue agitation for 10 to 15 min.

15.2 Decant the supernatant liquid through the filter and transfer the precipitate to the filter with 50 to 100 mL of ethyl alcohol (95 %). Wash the precipitate with ethyl alcohol (80 %) that has been heated to 60°C, until all of the acid has been removed.

15.3 Test for the removal of acid and salts (ash) by mixing a drop of the acid carboxymethylcellulose slurry from the filter with a drop of diphenylamine reagent on a white spot plate. A blue color indicates the presence of nitrate and the necessity for further washing. If the first drop of reagent does not produce a blue color, further drops should be added until an excess of reagent is known to be present, noting the color after each drop. Four to six washings will usually suffice to give a negative test for nitrate.

15.4 Finally, wash the precipitate with a small amount of anhydrous methanol and draw air through it until the alcohol is completely removed. Transfer the precipitate to a glass or aluminum weighing dish provided with a cover. Heat the uncovered dish on a steam bath until the odor of alcohol can no longer be detected (in order to avoid fires due to methanol fumes in the oven), then dry the dish and contents, uncovered for 3 h at 105°C. Place the cover on the dish and cool to room temperature in a desiccator.

15.5 The sulfate ash content of the sample at this point should be less than 0.5 % when determined on 0.5 g of the

sample by the procedure given in the Ash as Sulfate section of Test Methods **D1347**. If the ash content is greater than 0.5 %, rewash the sample with ethyl alcohol (80 %). If necessary, repeat the procedure described in **15.1 – 15.4**.

15.6 Weigh, to the nearest 0.01 g, about 1 to 1.5 g of the dried acid carboxymethylcellulose (depending on the normality of the acid and base to be used) into a 500-mL Erlenmeyer flask. Add 100 mL of water and 25.00 mL of 0.3 to 0.5 *N* NaOH solution, while stirring. Heat the solution to boiling, and boil for 15 to 30 min.

15.7 Titrate the excess NaOH, while the solution is hot, with the 0.3 to 0.5 *N* HCl to a phenolphthalein end point.

## 16. Calculation

16.1 Calculate the degree of etherification, *G*, as follows:

$$A = (BC - DE)/F \quad (2)$$

$$G = 0.162A/(1 - 0.0584A) \quad (3)$$

where:

- A* = milliequivalents of acid consumed per gram of sample,
- B* = NaOH solution added, mL,
- C* = normality of the NaOH solution,
- D* = HCl required for titration of the excess NaOH, mL,
- E* = normality of the HCl,
- F* = acid carboxymethylcellulose used, g,
- 162 = gram molecular mass of the anhydroglucose unit of cellulose, and
- 58 = net increase in molecular mass of anhydroglucose unit for each carboxymethyl group substituted.

## 17. Precision and Bias

17.1 *Precision*—Statistical analysis of intralaboratory (repeatability) test results indicates a precision of  $\pm 0.04$  D.E. units at the 95 % confidence level.

17.2 *Bias*—No justifiable statement can be made on the bias of the procedure for measuring degree of etherification because no suitable reference material exists.

### *Test Method B—Nonaqueous Titration*

## 18. Summary of Test Methods

18.1 This measurement is based upon a nonaqueous acid-base titration. The sample is refluxed with glacial acetic acid, and the resulting sodium acetate is titrated with a standard solution of perchloric acid in dioxane, to a potentiometric end point. Impurities containing alkaline sodium will also be titrated under these conditions. Sodium chloride does not interfere.

## 19. Apparatus

19.1 *pH Meter*, equipped with a standard glass electrode and a calomel electrode modified as follows:

19.1.1 Discard the aqueous potassium chloride solution, then rinse and fill with the calomel electrode solution as described in **20.2**.

19.1.2 Add a few crystals of potassium chloride and silver chloride or silver oxide to the electrode.

19.2 *Buret*, micro, 10-mL capacity.

## 20. Reagents

20.1 *Acetic Acid*, glacial.

20.2 *Calomel Electrode Solution*—Add 2 g of potassium chloride (KCl) and 2 g of silver chloride (AgCl) or silver oxide (Ag<sub>2</sub>O) to 100 mL of methanol and shake thoroughly to saturate. Use the supernatant liquid.

20.3 *1,4-Dioxane*.

20.4 *Perchloric Acid* (0.1 *N*)—Add 9 mL of concentrated perchloric acid (HClO<sub>4</sub>, 70 % to 1 L of dioxane, with stirring (**Warning**—The solution of perchloric acid in dioxane should never be heated or allowed to evaporate.). Store in an amber glass bottle. Any slight discoloration that appears on standing may be disregarded.

20.4.1 Standardize the solution as follows: Dry potassium acid phthalate for 2 h at 120°C. Weigh 2.5 g to the nearest 0.0001 g into a 250-mL volumetric flask. Add glacial acetic acid, shake to dissolve, and then make up to volume and mix thoroughly. Pipet 10 mL into a 100-mL beaker and add 50 mL of acetic acid. Place on a magnetic stirrer and insert the electrodes of the pH meter. Add nearly the required amount of HClO<sub>4</sub> from a buret, then decrease the increments to 0.05 mL as the end point is approached. Record the millilitres of titrant versus millivolts, and continue the titration a few millilitres beyond the end point. Plot the titration curve and read the volume of titrant at the inflection point. Calculate the normality, *N*, as follows:

$$N = (A \times 10 \times 1000)/(B \times 204.22 \times 250) \quad (4)$$

where:

- A* = potassium acid phthalate used, g,
- B* = HClO<sub>4</sub> added, mL,
- 204.22 = gram molecular mass of potassium acid phthalate,
- 10 = potassium acid phthalate solution added, mL, and
- 250 = glacial acetic acid used to dissolve potassium acid phthalate, mL.

20.5 *Potassium Acid Phthalate*, primary standard, National Institute of Standards and Technology Standard Sample No. 84.

## 21. Procedure

21.1 Weigh 0.2 g of the sample, to the nearest 0.0001 g, into a 250-mL Erlenmeyer flask with ground-glass joint. Add 75 mL of acetic acid, connect to a water-cooled condenser, and reflux gently on a hot plate for 2 h.

21.2 Cool, and transfer the solution to a 250-mL beaker with the aid of 50 mL of acetic acid. Place on the magnetic stirrer and titrate to a potentiometric end point with 0.1 *N* HClO<sub>4</sub> in accordance with **20.4**.

## 22. Calculation

22.1 Calculate the degree of etherification, *H*, as follows (**Note 1**):

$$M = (AN \times 100)/(G \times (100 - B)) \quad (5)$$

$$H = 0.162 M/(1.000 - (0.080 M)) \quad (6)$$

where:

- $M$  = milliequivalents of acid consumed per gram of sample,
- $A$  =  $\text{HClO}_4$  added, mL,
- $N$  = normality of  $\text{HClO}_4$ ,
- $G$  = sample used, g,
- $B$  = percent moisture, determined on a separate sample, in accordance with Sections 4 – 7,
- 162 = gram molecular mass of an anhydroglucose unit of cellulose, and
- 80 = net increase in molecular mass of an anhydroglucose unit for each sodium carboxymethyl group added.

NOTE 1—The result calculated in accordance with Section 18 includes the alkaline sodium from sodium glycolate; however, if the latter is less than 0.5 %, the interference is negligible.

### 23. Precision and Bias

23.1 *Precision*—Statistical analysis of interlaboratory test results indicates the precision of this test method as shown below:

Approximate D.E. Level	Precision, D.E. Units (95 % Confidence Level)
0.40	±0.010
0.80	±0.012
1.35	±0.038

23.2 *Bias*—No justifiable statement can be made on the bias of the procedure for measuring degree of etherification because no suitable reference material exists.

## VISCOSITY

### 24. Scope

24.1 This is an arbitrary test method for determining the viscosity of aqueous solutions of sodium carboxymethylcellulose in the viscosity range from 10 to 10 000 mPa·s (cP) at 25°C.

24.2 The concentration to be used for the test should be agreed upon between the purchaser and the seller. It should be such that the viscosity of the solution will fall within the range of this test.

24.3 The results for the viscosity of sodium carboxymethylcellulose by this test method will not necessarily correlate with results from other types of instruments used for viscosity measurements.

24.4 The determinations are run on a calculated dry basis; that is, the amount of sodium carboxymethylcellulose required for the desired concentration on a dry basis is calculated from the known moisture content.

24.5 This test method is intended for referee purposes. The rotational elements and speeds given in Table 1 are recommended for this purpose. Slight deviations from the table may occasionally be convenient for an individual application.

### 25. Significance and Use

25.1 This test method determines the relative ability of the polymer to thicken water. This is the primary function of sodium carboxymethylcellulose.

TABLE 1 Rotational Elements and Speeds

Rotational Element Selection (see Fig. 1)				
Viscosity Range, (mPa·s)	Length (mm)	Diameter (mm)	Speed (r/min)	Torque Scale Multiplier
10 to 100	19	65	60	1
100 to 200	19	65	30	2
200 to 1000	10	54	30	10
1000 to 4000	5.9	43	30	40
4000 to 10000	3.2	31	30	200

### 26. Apparatus

26.1 *Viscometer, Rotational*—The essential instrumentation required providing the minimum rotational viscometer analytical capabilities for this method include:

26.1.1 *A drive motor* to apply a unidirectional rotational displacement to the specimen at a rate from 0.5 to 60 r/min constant to 1 %.

26.1.2 *A force sensor* to measure the torque developed by the specimen to the rotational displacement of the rotational element.

26.1.3 *A coupling shaft*, or other means to transmit the rotational displacement from the motor to the specimen.

26.1.4 *A rotational element, spindle or tool* to fix the specimen between the drive shaft and a stationary position.

NOTE 2—Each rotational element typically covers a range of 2 decades. The rotational element shall be selected so that the measured torque is between 10 and 90 % of the range of the rotational element.

NOTE 3—Cylindrical spindles of the general shape shown in Fig. 1 have been found suitable for this measurement.

26.1.5 *A data collection device* to provide a means of acquiring, storing, and displaying measured or calculated

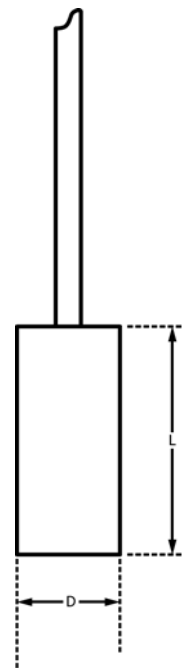


FIG. 1 Cylindrical Rotational Element

signals, or both. The minimum output signals required for rotational viscometry are torque, rotational speed, temperature, and time.

26.1.6 *A stand*, to support, level, and adjust the height of the drive motor, shaft, and rotational element.

26.1.7 Auxiliary instrumentation considered necessary or useful in conducting this method includes:

26.1.7.1 *Data analysis capability* to provide viscosity, stress or other useful parameters derived from measured signals.

26.1.7.2 *A level* to indicate the vertical plumb of the drive motor, shaft, and rotational element.

26.2 *Container*—Glass jar, approximately 64-mm (2½-in.) in diameter and 152 mm (6 in.) deep, unstricted at the top, capacity 340 g (12 oz).

26.3 *Analytical Balance*.

26.4 *Mechanical Stirrer*—Stirrer constructed of stainless steel (Fig. 2) attached to a variable speed motor capable of operating at 900 ± 100 r/min under varying load conditions.

26.5 *Water Bath*, constant-temperature, set at 25°C and capable of maintaining that temperature within ±0.2°C.

26.6 *Temperature Measurement Device* to provide an indication of specimen temperature over the range from 19 to 27°C to within ±0.1°C.

## 27. Procedure

27.1 Determine moisture in accordance with Sections 4 – 9.

27.2 Calculate the dry-basis sample mass,  $M$ , in grams necessary to make 240 g of test solution as follows:

$$M = 100A / (100 - B) \quad (7)$$

where:

$A$  = desired dry mass of sample, g, and

$B$  = moisture in the sample as received, %.

27.3 Calculate the quantity of distilled water required as follows:

$$V = 240 - S \quad (8)$$

where:

$V$  = volume of distilled water, mL, and

$S$  = mass of sample, g.

27.4 Add the calculated quantity of water to the jar. Position the stirrer in the jar allowing minimum clearance between the stirrer and the bottom of the container.

27.5 Begin stirring and slowly add the sodium carboxymethylcellulose specimen. Adjust the stirring speed to approximately 900 ± 100 r/min and mix for 120 ± 3 min.

NOTE 4—Do not allow the stirring speed to exceed 1200 r/min since higher speeds tend to affect viscosity on certain grades of sodium carboxymethylcellulose.

NOTE 5—If the specimen is added too rapidly, agglomeration will occur. This may prevent complete dissolution within the required mixing time.

27.6 Remove the stirrer and transfer the specimen container to the constant-temperature bath for 1 h. Check the specimen temperature with a thermometer at the end of 1 h to ensure that the test temperature has been reached.

27.7 Remove the specimen container from the bath and shake vigorously for 10 s.

27.8 Measure the viscosity with the rotational viscometer, after the rotational element has been in rotation for 3 min.

## 28. Report

28.1 Report the results as rotational viscosity at 25°C, stating the solution concentration and the spindle and speed used.

28.2 Complete description of the rotational viscometer including manufacturer, model, and rotational element.

28.3 Experimental conditions used including rotational speed and temperature of measurement.

## 29. Precision and Bias

29.1 *Precision*—Statistical analysis of interlaboratory (reproducibility) test results indicates a precision of ±10 % at the 95 % confidence level.

29.2 *Bias*—No justifiable statement can be made on the bias of the procedure for measuring viscosity because no suitable reference material exists.

## PURITY OF CRUDE SODIUM CARBOXYMETHYLCELLULOSE

## 30. Scope

30.1 This test method covers the determination of purity or percent of active ingredient in crude sodium carboxy-

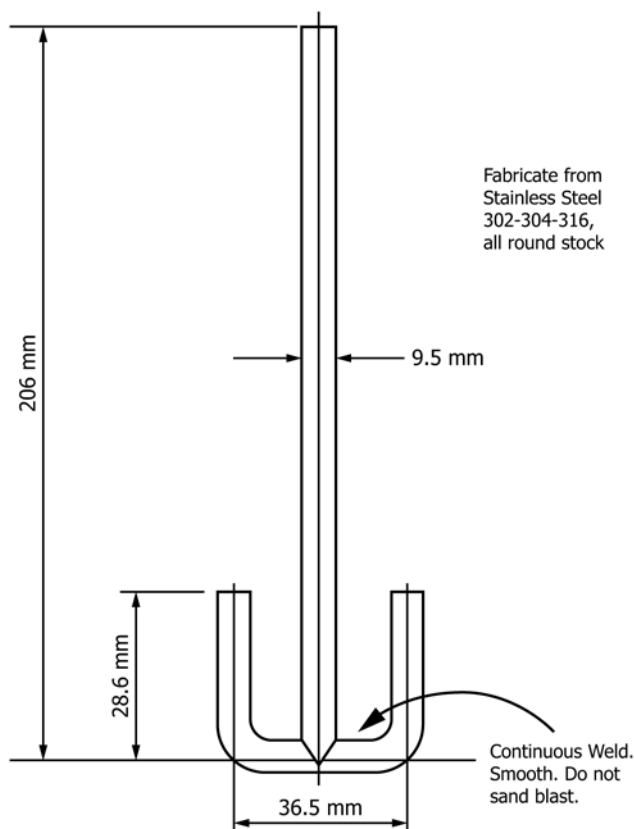


FIG. 2 Stirrer

methylcellulose containing no phosphate. The test method has been standardized on materials having a degree of etherification of about 0.85 or less.

30.2 For determination of purity of refined sodium carboxymethylcellulose (purity approximately 98 % or higher), analysis for individual or combined impurities and calculation of purity by difference will give more reliable results.

### 31. Summary of Test Method

31.1 A 3-g sample is stirred mechanically in a beaker for 15 min with each of two 150-mL portions of ethanol (80 % by volume) at a temperature of 60 to 65°C. The supernatant liquid is decanted through a tared filtering crucible after each treatment. The undissolved matter is transferred quantitatively to the crucible, dried, weighed, and calculated as percent of sodium carboxymethylcellulose. The temperature of the ethanol during the leaching need not be closely controlled, but the concentration of the ethanol must be closely controlled (sp gr within 0.001).

### 32. Significance and Use

32.1 This test method is intended for use in testing sodium carboxymethylcellulose for applications in which purity is not a critical property. If purity greater than 98 % is required, analysis for individual impurities (sodium chloride and sodium glycolate) is essential.

### 33. Apparatus

33.1 *Filtering Crucible*, fritted glass, medium-porosity, 50-mL capacity.

33.2 *Mechanical Stirring Motor*, electric or air-driven, with any convenient stirrer of appropriate size.

33.3 *Water Bath*, constant-temperature, maintained at 60 to 65°C.

33.4 *Cover*—A lid to keep a 400-mL beaker substantially covered during mechanical stirring in bath. A flanged lid, preferably of stainless steel, with a slot, wide enough to pass the shaft of the mechanical stirrer, cut from the rim to the center, has been found satisfactory. The center should be cut out somewhat larger than the shaft of the stirrer to permit free rotation of the stirrer. Such a lid serves to weight down the beaker as well as to minimize the evaporation losses during leaching.

### 34. Reagents

34.1 *Ethanol (95 volume %)*—Undenatured or specially denatured ethanol conforming to Formula 2B (Note 6) of the U. S. Bureau of Internal Revenue.

NOTE 6—Other grades of denatured alcohol, such as Formula 3A, are not satisfactory for this purpose.

34.2 *Ethanol (80 volume %)*—Dilute 840 mL of 95 % ethanol (30.1) to 1 L with water. The specific gravity should be  $0.857 \pm 0.001$  at 25/25°C. If necessary, add water or ethanol until the specific gravity is within the specified limits.

34.3 *Ethyl Ether*, anhydrous, ethanol-free.

### 35. Procedure

35.1 Weigh 3 to 5 g of the sample into a tared low-form, 65-mm diameter glass weighing dish fitted with a cover. Dry to constant mass at  $105 \pm 1^\circ\text{C}$  in either a gravity or a mechanical convection oven. Weigh at the end of an initial 2-h heating period, then continue with 30-min heating periods until the change in mass during a 30-min heating period is not more than 0.10 %. If there is an increase in mass of the sample during one or more drying periods, record the lowest mass observed as the mass for use in the calculation of moisture content. Calculate the loss in mass as the percent of moisture in the sample.

35.2 Weigh  $3 \pm 0.1$  g of the sample, in the “as-received” condition, to the nearest 0.001 g and transfer to a 400-mL beaker.

35.3 Add 150 mL of ethanol (80 %) that has been heated to between 60 and 65°C, and immediately place the beaker in a constant-temperature water bath maintained at 60 to 65°C. The level of the water in the bath should be somewhat higher than the level of the liquid in the beaker. Cover the beaker as completely as possible with a lid that will permit mechanical stirring. Lower a mechanical stirrer almost to the bottom of the beaker, and stir for 10 min at a rate suitable to provide good agitation without spattering material on the walls of the beaker above the liquid level.

35.4 Stop the stirrer. Allow the undissolved matter to settle with the beaker still in the bath, and then decant the hot supernatant liquid as completely as possible through a tared, fritted-glass filtering crucible.

35.5 Add 150 mL of ethanol (80 %), at 60 to 65°C to the beaker and proceed in accordance with 32.3 and 32.4.

35.6 After decanting the supernatant liquid as completely as possible, transfer the insoluble matter to the crucible with the aid of ethanol (80 %) at 60 to 65°C in a wash bottle, being careful to scrape all insoluble matter from the lid, the stirrer, and the beaker. A total of about 250 mL of ethanol (80 %) will normally be required to transfer the insoluble matter to the crucible and to further wash the insoluble matter in the crucible. During the operations prescribed in this paragraph, apply suction only while filtration is in progress. Make every effort to avoid drying-out of the filter cake. If fines appear to pass through the filter, use only gentle suction.

35.7 Wash the residue in the crucible with 50 mL of ethanol (95 %) at room temperature, and finally with several portions of ether at room temperature (Note 7). Without permitting suction to continue longer than necessary, place the crucible in a beaker or weighing bottle on the steam bath until no odor of ether can be detected.

NOTE 7—Thorough washing with ether is necessary to remove ethanol completely from the insoluble matter. If ethanol is not completely removed before oven drying, it may not be completely removed during the oven drying.

35.8 Place the crucible in an oven at  $105 \pm 1^\circ\text{C}$  for 1 h. Stir the contents of the crucible with a dissecting needle or thin rod (preferably of smooth-surfaced metal) to break up the cake and facilitate complete drying. Again, dry at  $105 \pm 1^\circ\text{C}$  for 1 h. Place the crucible in a desiccator. Cover it with a flat glass

plate, weighing bottle cover, or other suitable cover to minimize absorption of moisture from the atmosphere in the desiccator; and cool to room temperature (at least 30 min). Weigh the uncovered crucible as rapidly as possible.

35.9 Dry the crucible for additional 1-h periods until the change in mass during a 1-h drying period does not exceed 0.003 g. If increases in mass are observed after such additional drying periods, record the lowest mass observed as the mass of the crucible plus dry sodium carboxymethylcellulose.

### 36. Calculation

36.1 Calculate the percent sodium carboxymethylcellulose, *S*, on the dry basis as follows:

$$S = (A \times 10000)/(B(100 - C)) \quad (9)$$

where:

*A* = mass of dried residue, g,

*B* = mass of specimen used, g, and

*C* = moisture in the specimen as received, %.

### 37. Precision and Bias

37.1 *Precision*—Statistical analysis of interlaboratory (reproducibility) test results indicate a precision of  $\pm 0.6\%$  absolute at the 95 % confidence level.

37.2 *Bias*—No justifiable statement can be made on the bias of the procedure for measuring purity of crude sodium carboxymethylcellulose because no suitable reference material exists.

## SODIUM GLYCOLATE

### 38. Scope

38.1 This test method covers the determination of the sodium glycolate content of purified sodium carboxymethylcellulose containing not more than 2.0 % sodium glycolate.

### 39. Summary of Test Method

39.1 The sodium carboxymethylcellulose is dissolved in acetic acid (50 %), precipitated with acetone and sodium chloride and the insoluble material filtered off. The filtrate containing the sodium glycolate (as glycolic acid) is treated to remove the acetone and reacted with 2,7-dihydroxy naphthalene. The resulting color is measured at 540 nm with a spectrophotometer calibrated with known solutions.

### 40. Significance and Use

40.1 This test method (along with moisture and sodium chloride) is used to calculate the amount of active polymer in the material. It must be used when analyzing highly purified (>98 %) grades of sodium carboxymethylcellulose, especially in government-regulated applications (that is, food, pharmaceuticals, cosmetics, etc.).

### 41. Apparatus

41.1 *Spectrophotometer or Filter Photometer*, suitable for measuring absorbance at 540 nm.

41.2 *Absorption Cells*, for spectrophotometer, 1-cm light path.

41.3 *Aluminum Foil*—Cut to approximately 50-mm. (2-in) squares.

### 42. Reagents

42.1 *Acetic Acid*, glacial.

42.2 *Acetone*.

42.3 *Dihydroxy Naphthalene Reagent (0.100 g/L)*—Dissolve 0.100 g of 2,7-dihydroxy naphthalene in 1 L of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Before using, allow the solution to stand until the initial yellow color disappears. If the solution is very dark, discard it and prepare a new solution from a different supply of H<sub>2</sub>SO<sub>4</sub>. This solution is stable for approximately 1 month if stored in a dark bottle.

42.4 *Glycolic Acid, Standard Solution (1 mg glycolic acid/mL)*—Dry several grams of glycolic acid in a desiccator at room temperature overnight. Accurately weigh 0.100 g of the dried material, dissolve in water, and make up to volume in a 100-mL volumetric flask. This solution will contain 1 mg of glycolic acid/mL. The solution is stable for approximately 1 month.

42.5 *Sodium Chloride* (NaCl).

42.6 *Sulfuric Acid (sp gr 1.84)*—Concentrated H<sub>2</sub>SO<sub>4</sub>.

### 43. Preparation of Calibration Curve

43.1 Into a series of five 100-mL volumetric flasks accurately introduce 1, 2, 3, and 4-mL aliquots of the standard glycolic acid solution, reserving the fifth flask for a blank. Add sufficient water to each flask to give a total volume of 5 mL. Add 5 mL of glacial acetic acid, make up to volume with acetone and mix. These solutions will contain 0, 1, 2, 3 and 4 mg of glycolic acid, respectively.

43.2 Pipet 2 mL of each of these solutions into individual 25-mL volumetric flasks. Place the uncovered flasks upright in a boiling water bath for exactly 20 min to remove the acetone. Remove the flasks from the bath and cool.

43.3 To each flask add 20 mL of 2,7-dihydroxy naphthalene reagent as follows: Add 5 mL of reagent initially, mix thoroughly, then add the remaining 15 mL of reagent and mix. Cover the mouth of the flasks with a small piece of aluminum foil and place upright in the boiling water bath for 20 min. Remove from the bath, cool, and make up to volume with H<sub>2</sub>SO<sub>4</sub>.

43.4 Measure the absorbance of each solution at 540 nm against the blank solution. Plot the milligrams of glycolic acid in the original 100 mL of solution against absorbance to give a calibration curve.

### 44. Procedure

44.1 Weigh about 0.5 g of the sample (0.2 g for semirefined grades) to the nearest 0.001 g and transfer to a 100-mL beaker. Moisten the specimen thoroughly with 5 mL of acetic acid followed by 5 mL of water, and stir with a glass rod until solution is complete (usually about 15 min is required). Slowly add 50 mL of acetone, stirring during addition, followed by approximately 1 g of NaCl. Stir several minutes to ensure complete precipitation of the carboxymethylcellulose.

44.2 Filter through a soft, open-texture paper, previously wetted with a small amount of acetone, and collect the filtrate in a 100-mL volumetric flask. Use an additional 30 mL of acetone to facilitate transfer of the solids and to wash the filter cake. Make up to volume with acetone and mix.

44.3 Prepare a blank solution containing 5 mL of water and 5 mL of glacial acetic acid in another 100-mL volumetric flask. Make up to the mark with acetone and mix.

44.4 Pipet 2 mL of the solution from the specimen and 2 mL of the blank solution into separate 25-mL volumetric flasks. Develop the color and measure the absorbance in accordance with 43.2 – 43.4.

44.5 Using the observed absorbance, refer to the calibration curve and read the corresponding milligrams of glycolic acid.

#### 45. Calculation

45.1 Calculate the percent sodium glycolate content,  $C$ , as follows:

$$C = (B \times 12.9) / [W \times (100 - A)] \quad (10)$$

where:

- $B$  = glycolic acid, read from the calibration curve, mg,
- $W$  = sample used, g,
- $A$  = moisture in the sample as received, %, and
- 12.9 = (gram molecular mass of sodium glycolate per gram molecular mass of glycolic acid)  $\times$  10.

#### 46. Precision and Bias

46.1 *Precision*—Statistical analysis of intralaboratory (repeatability) data on material containing less than 0.50 % sodium glycolate indicate a precision of  $\pm 0.03$  % absolute at the 95 % confidence level.

46.2 *Bias*—No justifiable statement can be made on the bias of the procedure for measuring sodium glycolate because no suitable reference material exists.

### SODIUM CHLORIDE

#### 47. Scope

47.1 This test method covers the determination of the sodium chloride content of purified sodium carboxymethylcellulose.

#### 48. Summary of Test Method

48.1 The sodium carboxymethylcellulose is dissolved in water and titrated with a standard solution of silver nitrate to a potentiometric end point. Hydrogen peroxide is added to reduce the viscosity of the solution.

#### 49. Significance and Use

49.1 This test method (along with moisture and sodium glycolate) is used to calculate the amount of active polymer in the material. It must be used when analyzing highly purified (>98 %) grades of sodium carboxymethylcellulose, especially in government-regulated applications (that is, food, pharmaceuticals, cosmetics, etc.).

#### 50. Apparatus

50.1 *pH Meter*, equipped with a silver electrode and a mercurous sulfate-potassium sulfate electrode.

50.2 *Buret*, micro, 10-mL capacity.

#### 51. Reagents

51.1 *Hydrogen Peroxide (30 mass %)*—Concentrated hydrogen peroxide ( $H_2O_2$ ).

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

51.3 *Silver Nitrate, Standard Solution (0.1 N)*—Dissolve 17.0 g of silver nitrate ( $AgNO_3$ ) in 1 L of water. Store in an amber glass bottle. Standardize the solution as follows:

51.3.1 Dry the sodium chloride ( $NaCl$ ) for 2 h at 120°C. Weigh 0.65 g to the nearest 0.0001 g, into a 250-mL beaker and add 100 mL of water. Place on a magnetic stirrer, add 10 mL of  $HNO_3$ , and insert the electrodes of the pH meter. Add nearly the required amount of  $AgNO_3$  solution from a buret, then decrease the increments to 0.05 mL as the end point is approached. Record the millilitres of titrant versus millivolts, and continue the titration a few millilitres beyond the end point. Plot the titration curve and read the volume of titrant at the inflection point. Calculate the normality,  $N$ , as follows:

$$N = (A \times 1000) / (B \times 58.45) \quad (11)$$

where:

- $A$  =  $NaCl$  used, g,
- $B$  =  $AgNO_3$  solution added, mL, and
- 58.45 = gram molecular mass of  $NaCl$ .

51.4 *Sodium Chloride* ( $NaCl$ ).

#### 52. Procedure

52.1 Weigh 5 g of the sample, to the nearest 0.0001 g, into a 250-mL beaker. Add 50 mL of water and 5 mL of  $H_2O_2$  (30 %). Place the beaker on a steam bath, stirring occasionally to achieve a nonviscous solution. If solution is not complete after 20 min, add 5 mL more of  $H_2O_2$  and heat until solution is complete.

52.2 Cool the beaker, add 100 mL of water and 10 mL of  $HNO_3$ . Place it on the magnetic stirrer and titrate to a potentiometric end point with 0.1  $N$   $AgNO_3$  solution in 46.3.

#### 53. Calculation

53.1 Calculate the percent sodium chloride content,  $C$ , as follows:

$$C = (AN \times 584.5) / [G \times (100 - B)] \quad (12)$$

where:

- $A$  =  $AgNO_3$  solution added, mL,
- $N$  = normality of  $AgNO_3$  solution,
- $G$  = sample used, g,
- $B$  = moisture, determined on a separate sample, %, in accordance with Sections 4 – 7, and
- 584.5 = gram molecular mass of  $NaCl$   $\times$  10.



#### 54. Precision and Bias

54.1 *Precision*—The precision of this test method is estimated to be  $\pm 0.05\%$  absolute for material containing less than 0.50 % sodium chloride and  $\pm 0.10\%$  absolute for material containing greater than 0.59 % sodium chloride.

54.2 *Bias*—No justifiable statement can be made on the bias of the procedure for measuring sodium chloride because no suitable reference material exists.

### DENSITY

#### 55. Scope

55.1 This test method covers the determination of the bulk density of sodium carboxymethylcellulose.

#### 56. Summary of Test Method

56.1 A weighed amount of sodium carboxymethylcellulose is transferred to a 100-mL graduated cylinder and the graduate vibrated to settle the powder.

#### 57. Significance and Use

57.1 The density of the material can relate to dry flow properties, rate of dissolution, lumping, and package and storage space requirements.

#### 58. Apparatus

58.1 *Vibrator*—A magnetic-type electric vibrator attached to the vertical support rod of a ring stand approximately 1 ft (0.3 m) above the base. A condenser clamp of sufficient size to hold a 100-mL graduated cylinder also shall be attached to the above rod. The base of the stand should be weighted.

#### 59. Procedure

59.1 Place 50.0 g of sodium carboxymethylcellulose in a 100-mL graduated cylinder and place it in the condenser

clamp. Turn on the vibrator and allow the cylinder to vibrate for 3 min. Record the level (in millilitres) to which the specimen has compacted.

59.2 Alternatively, the specimen may be compacted manually. Tap it on a hard surface by dropping the cylinder repeatedly from a height of about 1 in. (25 mm) until the volume of the specimen remains constant. In order to prevent cylinder breakage, cover the tapping surface with a  $\frac{1}{8}$  to  $\frac{1}{4}$ -in. (3 to 6-mm) thick rubber sheet or use a plastic graduated cylinder.

#### 60. Calculation

60.1 Calculate the density,  $D$ , in grams per millilitre as follows:

$$D = 50/r \quad (13)$$

where:

$r$  = observed reading, mL.

#### 61. Precision and Bias

61.1 *Precision*—Statistical analysis of intralaboratory (repeatability) test results indicates a precision of  $\pm 0.04$  g/mL at the 95 % confidence level.

61.2 *Bias*—No justifiable statement can be made on the bias of the procedure for measuring density because no suitable reference material exists.

#### 62. Keywords

62.1 degree of etherification; density; moisture; purity; rotational viscometer; sodium carboxymethylcellulose; sodium chloride; sodium glycolate; viscosity

### SUMMARY OF CHANGES

Committee D01 has identified the location of selected changes to this standard since the last issue (D1439-03(2008<sup>e1</sup>)) that may impact the use of this standard. (December 1, 2015.)

(1) Sections 24 – 29 revised to include a generic apparatus description in accordance with Practice E1953.

(2) Figure 1 is added and Figure 2 is revised to include metric dimensions.

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