



Designation: D914 – 12

## Standard Test Methods for Ethylcellulose<sup>1</sup>

This standard is issued under the fixed designation D914; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

### 1. Scope

1.1 These test methods cover the testing of ethylcellulose.

1.2 The test procedures appear in the following order:

	Sections
Moisture	4 to 6
Sulfated Ash	7 to 11
Chlorides (as Sodium Chloride)	12 to 16
Ethoxyl Content	20 to 24
Viscosity	25 to 39

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

1.4 **Warning**—Mercury has been designated by EPA and many state agencies as a hazardous material that can cause central nervous system, kidney and liver damage. Mercury, or its vapor, may be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury-containing products. See the applicable product Material Safety Data Sheet (MSDS) for details and EPA's website (<http://www.epa.gov/mercury/faq.htm>) for additional information. Users should be aware that selling mercury or mercury-containing products, or both, in your state may be prohibited by state law.

1.5 *This standard may involve hazardous materials, operations, and equipment. 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:*<sup>2</sup>

<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](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

D362 Specification for Industrial Grade Toluene (Withdrawn 1989)<sup>3</sup>

D446 Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers

D841 Specification for Nitration Grade Toluene

D4794 Test Method for Determination of Ethoxyl or Hydroxyethoxyl Substitution in Cellulose Ether Products by Gas Chromatography

E2251 Specification for Liquid-in-Glass ASTM Thermometers with Low-Hazard Precision Liquids

### 3. Purity of Reagents and Materials

3.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all of the reagents used shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>4</sup> Where such specifications have not been established, reagents of the best grade available shall be used. 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 ethylcellulose.

### 5. Significance and Use

5.1 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.

5.2 Moisture analysis (along with sulfated ash) is used to calculate the amount of active polymer in the material and shall be considered when determining the amount of ethylcellulose in various functions.

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

## 6. Apparatus

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

6.2 *Weighing Bottles*.

6.3 *Analytical Balance*.

## 7. Procedure

7.1 Weigh accurately 2 to 5 g of the sample to the nearest 0.001 g into a tared dish (fitted with a lid) and dry for 2 h in an oven at 100 to  $105^\circ\text{C}$ . Remove the dish from the oven, cover with a lid, cool in a desiccator, and weigh.

## 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 intralaboratory (repeatability) test results indicates a precision of  $\pm 5\%$  at the 95 % confidence level.

9.2 *Bias*—No statement of bias can be made as no suitable reference material is available as a standard.

### SULFATED ASH

## 10. Scope

10.1 This test method covers the determination of the residue on ignition of ethylcellulose after a specimen has been treated with sulfuric acid.

## 11. Significance and Use

11.1 This test method (along with moisture) is used to calculate the active polymer in the material. It shall be used when testing ethylcellulose in United States government regulated applications. Excessive ash may also affect solution clarity and film properties.

## 12. Apparatus

12.1 *Muffle Furnace*.

12.2 *Crucibles*, either porcelain, 30-mL high, form cracked, platinum.

## 13. Reagent

13.1 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ).

## 14. Procedure

14.1 Ignite a crucible for 10 to 15 min at  $800 \pm 25^\circ\text{C}$ , cool in a desiccator, and weigh to the nearest 0.001 g.

14.2 Weigh about 5 g of sample to the nearest 0.001 g (previously dried for 3 h at  $105^\circ\text{C}$ ) into the crucible. Burn off the bulk of the carbonaceous material directly over a flame.

After cooling, add 1 mL of  $\text{H}_2\text{SO}_4$  in such a way as to moisten the entire ash; then cautiously heat with the burner to dense white fumes. Ignite in a muffle furnace at  $800 \pm 25^\circ\text{C}$  until all signs of carbon are gone. Cool in a desiccator and reweigh to the nearest 0.001 g.

## 15. Calculation

15.1 Calculate the percent ash (as sulfate),  $C$ , as follows:

$$C = (A/B) \times 100 \quad (2)$$

where:

$A$  = ash, g, and

$B$  = sample used, g.

## 16. Precision and Bias

16.1 *Precision*—Statistical analysis of interlaboratory (reproducibility) test results indicates a precision of  $\pm 10\%$  at the 95 % confidence level.

16.2 *Bias*—No statement of bias can be made as no suitable reference material is available as a standard.

### CHLORIDES (as Sodium Chloride)

## 17. Scope

17.1 This test method covers the determination of the chloride content of ethylcellulose.

## 18. Significance and Use

18.1 Sodium chloride is a major by-product of the ethylcellulose manufacturing process. This test is a measure of the purity of ethylcellulose. Chlorides may also affect solution properties.

## 19. Apparatus

19.1 *Titration pH Meter*.

19.2 *Mercury-Mercurous Sulfate Reference Electrode*—The electrode uses a potassium sulfate electrolyte to avoid chloride contamination from a chloride electrolyte.

19.3 *Silver-Silver Chloride Electrode*—The electrode is coated with silver chloride periodically. Prepare the electrode by polishing with fine steel wool, briefly soaking it in 5 % potassium cyanide solution, and rinsing it with water. Coat the electrode with silver chloride by electrodeposition from 0.1  $N$  potassium chloride solution using a 3-V dry cell and a platinum wire electrode. Connect the silver electrode to the positive pole of the battery and electrolyze for 20 s; then reverse the connections for 5 s. Repeat these operations twice, and finally, chloridize the silver electrode for 20 s at the positive terminal. Store the silver electrode in 0.1  $N$  potassium chloride solution. Rinse the electrode with water and wipe it with a soft tissue before each titration.

19.4 *Salt Bridge for Reference Electrode*—**Fig. 1** shows one configuration in use. Exact dimensions are not important. The salt bridge is used to keep the reference electrode from plugging with the ethylcellulose slurry.

19.5 *Air-Driven Stirrer*.

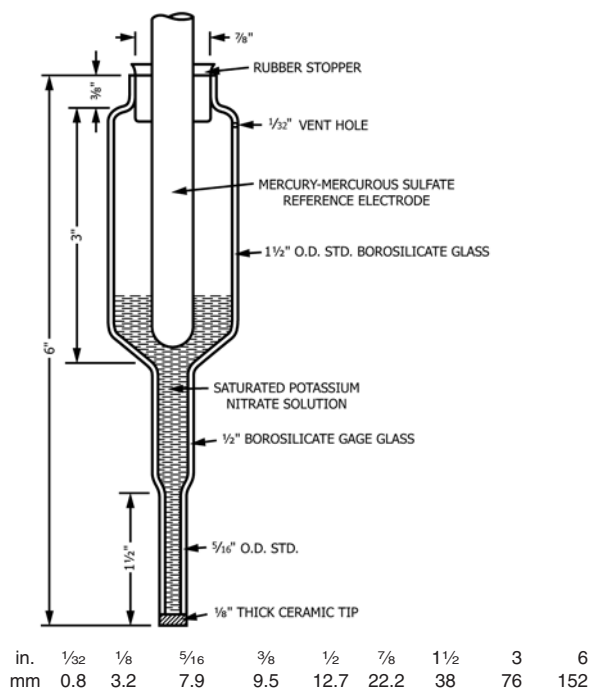


FIG. 1 Salt Bridge and Reference Electrode for Chloride Determination

20. Reagents

20.1 Ethanol (95 volume %), undenatured or specially denatured conforming to Formula 2B of the U.S. Bureau of Internal Revenue.

20.2 Ethanol-Distilled Water Solvent Mixture (80 + 20)—Mix 800 g of 2B ethanol with 200 g of water. Add 7.5 g of aerosol OT 100 % surface-active agent per 3000 g of ethanol-water mixture.

20.3 Potassium Nitrate (KNO<sub>3</sub>) Solution (saturated) for salt bridge (Fig. 1).

20.4 Silver Nitrate, Standard Solution (0.02 N)—Dissolve 3.4 g of silver nitrate (AgNO<sub>3</sub>) in water, dilute to 1 L with water in a volumetric flask, and mix. Weigh exactly 0.5845 g of dry, primary standard sodium chloride (NaCl), dissolve in 25 mL of water, and dilute to 1 L with water in a volumetric flask. Add 10 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 16) to each aliquot before titrating. Titrate aliquots of this solution potentiometrically with the AgNO<sub>3</sub> solution. Calculate the normality, N, of the AgNO<sub>3</sub> solution as follows:

$$N = (A/B) \times 0.01 \quad (3)$$

where:

- A = 0.01 N NaCl solution added, mL, and
- B = AgNO<sub>3</sub> solution required for the titration, mL.

20.5 Sulfuric Acid (1 + 16)—Add 1 volume of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, sp gr 1.84) slowly with stirring into 16 volumes of water.

20.6 Toluene, meeting the requirements of Specification D362.

20.7 Toluene-Ethanol Solvent Mixture (90 + 10)—Mix 900 g of toluene with 100 g of ethanol.

21. Procedure

21.1 Weigh accurately 10 g of sample to the nearest 0.001 g (previously dried for 2 h at 100 to 105°C) and transfer to a 600-mL beaker containing 200 mL of the toluene-ethanol solvent mixture. Stir with an air-driven stirrer until solution is complete.

21.2 Add 200 mL of the ethanol-water mixture and agitate for 5 min to form a uniform emulsion. Immerse the electrodes in the emulsion using an air-driven stirrer for mixing. Add 10 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 16) and agitate for 3 to 4 min to allow the system to reach equilibrium.

21.3 Titrate slowly with the 0.02 N AgNO<sub>3</sub> solution. Make intermittent additions of 0.1 mL. It is advisable to allow longer periods of time between additions of titrant as the end point is approached to avoid passing the equivalence point. Run a blank by the same procedure.

22. Calculation

22.1 Calculate parts per million of chlorides as NaCl, C, as follows:

$$C = [(VN \times 0.05845)/W] \times 1\,000\,000 \quad (4)$$

where:

- V = AgNO<sub>3</sub> solution, mL,
- N = normality of AgNO<sub>3</sub> solution,
- W = sample used, g, and
- 0.05845 = milliequivalent mass of NaCl.

23. Precision and Bias

23.1 Precision—Statistical analysis of interlaboratory (reproducibility) test results indicates a precision of ±5 % at the 95 % confidence level.

23.2 Bias—No statement of bias can be made as no suitable reference material is available as a standard.

ETHOXYL CONTENT

24. Scope

24.1 This test method covers the determination of the ethoxyl content of ethylcellulose.

24.2 For an alternative method see Test Method D4794.

25. Significance and Use

25.1 This test method determines the amount of substituent groups added to the cellulose backbone. The level can greatly affect solution properties, rheology, solubility parameters, and film properties.

26. Apparatus

26.1 Distillation Apparatus, as illustrated in Fig. 2, consisting of a boiling flask with a side arm for admission of carbon dioxide (CO<sub>2</sub>) or nitrogen, an air condenser with a trap, and a receiver.

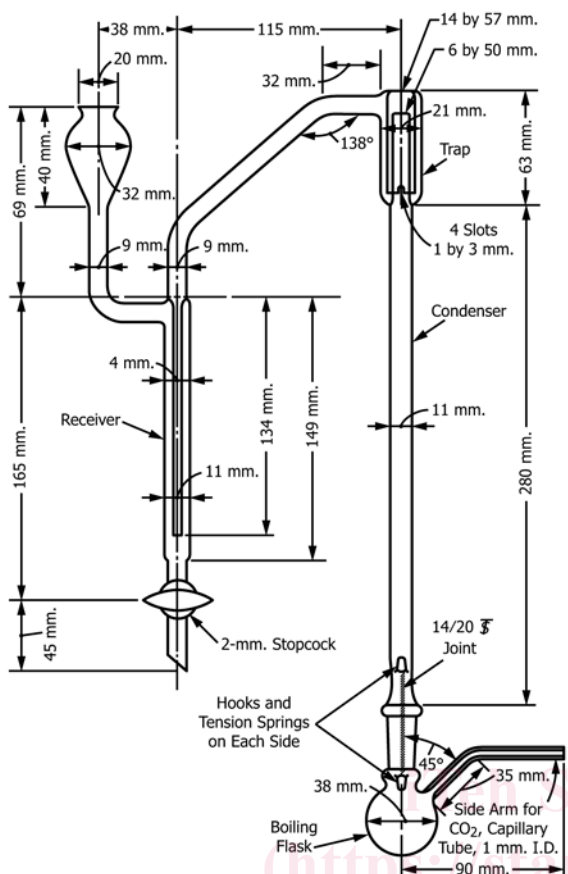


FIG. 2 Distillation Apparatus for Ethoxyl Determination

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

27. Reagents

27.1 *Bromine Solution*—Dissolve 5 mL of bromine in 145 mL of the potassium acetate (KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) solution. Prepare the bromine solution fresh daily in a hood to remove bromine vapors.

27.2 *Carbon Dioxide*—Pass the CO<sub>2</sub> 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<sub>2</sub>.

27.3 *Formic Acid (90 %)*.

27.4 *Gelatin Capsules*—Gelatin capsules of a suitable size to hold from 50 to 60 mg of the dried sample will be required.

27.5 *Hydriodic Acid (sp gr 1.70)<sup>5</sup>*—Hydriodic acid (HI) forms with water a constant-boiling mixture (boiling point 126

<sup>5</sup> Hydriodic acid suitable for ethoxyl determination may also be prepared by the method of Samsel, E. P., and McHard, J. A., *Industrial and Engineering Chemistry, Analytical Edition*, Vol 14, 1942, p. 750.

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 no more than 0.5 mL of 0.1 N sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) standard solution. 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<sub>2</sub> into the liquid. Distillation is then carried out behind a safety-glass shield in a hood, using an all-glass apparatus with a slow stream of CO<sub>2</sub> running through the receiver. Under some conditions, the poisonous gas phosphine (PH<sub>3</sub>) is formed during distillation, and this may unite with molecular iodine to form phosphorus triiodide (PI<sub>3</sub>) which may explode on contact with air. It is, therefore, advisable to keep the current of CO<sub>2</sub> going after the distillation is ended and until the apparatus has cooled; this will prevent air from being sucked into the apparatus. Put the purified HI in small, brown, glass-stoppered bottles, previously swept out with CO<sub>2</sub>, and seal the stoppers with molten paraffin. Store in a dark place. To minimize decomposition of HI due to contact with air, run CO<sub>2</sub> into the bottle while withdrawing portions of the acid for use.

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

27.7 *Potassium Acetate Solution (100 g/L)*—Dissolve 100 g of anhydrous potassium acetate (KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) crystal in 1 L of a solution containing 900 mL of glacial acetic acid and 100 mL of acetic anhydride.

27.8 *Potassium Iodide (KI)*.

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

27.10 *Sodium Thiosulfate, Standard Solution (0.1 N)*—Dissolve 25 g of sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O) 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<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) solution prepared by dissolving exactly 4.9037 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (National Institute of Standards and Technology Standard Sample No. 136) in water and diluting to 1 L in a volumetric flask. By means of a buret, measure accurately 35 to 45 mL of the K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution into a 250-mL Erlenmeyer flask. Add 2 g of KI and 50 mL of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 1 + 9) and allow to stand for about 5 min. Titrate the liberated iodine with the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, using starch indicator solution near the end point. 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<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution should be checked at least once a week. Calculate the normality, N, of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution as follows:

$$N = (A/B) \times 0.1 \tag{5}$$

where:

- A = 0.1000 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution added, mL, and
- B = Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution required for the titration, mL.

As an alternative procedure, the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution may be standardized against 0.1 N iodine that has been standardized in