Designation: D4794 – 94 (Reapproved 2009)

Standard Test Method for Determination of Ethoxyl or Hydroxyethoxyl Substitution in Cellulose Ether Products by Gas Chromatography[1]

This standard is issued under the fixed designation D4794; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method is applicable to the determination of ethoxyl or hydroxyethoxyl substitution in cellulose ether products by a Zeisel gas chromatographic technique.

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

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 5 and Note 3.

2. Summary of Test Method

2.1 When a cellulose ether containing ethyl or hydroxyethyl substitutes is allowed to react with hydriodic acid, one mole of iodoethane is liberated for each mole of ethoxyl or hydroxyethoxyl ether substituted on the cellulose chain. The iodoethane is extracted in situ with o-xylene and quantitated by gas chromatography using an internal standard technique. It is recommended to run duplicate samples.

3. Apparatus

3.1 *Gas Chromatograph* with thermal conductivity detector and heated injection port.

3.2 *Electronic Integrator.*

3.3 *Column*—stainless steel, 1829 mm in length, 3.2 mm in outside diameter, packed with the reagent in 4.6, coiled to fit the chromatograph used; or equivalent column and packing as appropriate.

3.4 *Syringe,* 10 µL.

3.5 *Reaction Vials, Caps, and Heating Block.* [2]

3.6 *Syringe,* 100 µ L.

3.7 *Cover,* stainless steel, fabricated to cover the heating block.

4. Reagents and Materials

4.1 *Purity of Reagents*—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.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 *Iodoethane,* 99 % minimum.

4.3 *O-xylene.*

4.4 *Toluene.*

4.5 *Hydriodic Acid,* 57 % (sp gr 1.69 to 1.70).

4.6 *Column Packing,* 10 % methyl silicone stationary phase USP code [G1] coated on inert diatomite solid support USP code [S1A], 100/120 mesh.

5. Hazards

5.1 Safety precautions must be taken for handling of hydriodic acid.

5.2 During the reaction, the glass vials are under pressure. Exercise precaution in handling the hot vials.

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

Current edition approved Feb. 1, 2009. Published February 2009. Originally approved in 1988. Last previous edition approved in 2003 as D4794 – 94 (2003). DOI: 10.1520/D4794-94R09.

[2] The sole source of supply of a heating block, Silli-Therm Heating Module, Reacti-Block 21, Reacti-Vials, and Minnert valve tops, known to the committee at this time is the Pierce Chemical Company P.O. Box 117, Rockford, IL 61105–9976. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[3] *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 Preparation and Conditioning

6.1 *Column* (Note 1)—Columns are packed with reagent under vacuum and mechanical vibration using silanized glass wool to contain the packing. Install each in the gas chromatograph to facilitate on column injection. Condition the column at 200°C for 12 h, then allow it to come to equilibrium under the conditions described below:

Oven temperature, °C	130 isothermal
Injection port temperature, °C	200
Detector temperature, °C	250
Detector current, ma	175 ma
Attenuation	1
Polarity	A
Carrier gas	helium
Column A, mL/min	30
Column B, mL/min	30

NOTE 1—The conditions used here were determined to be optimum for the column. Optimum conditions should be determined for each column on an individual basis.

6.2 *Integrator:*

6.2.1 *Settings* (Note 2):

Attenuation	3
Chart speed	1.0
Peak width	0.04
Threshold	4

NOTE 2—These settings were used with a Hewlett-Packard 3390A Integrator. Other units may require different settings.

6.2.2 *Approximate Component Retention Times:*

Relative Retention Time	Component
0.38	iodoethane
0.59	toluene (internal standard)
1.00	o-xylene

7. Preparation of Standard Solutions

7.1 *Internal Standard Solution* (25 mg toluene/mL o-xylene):

7.1.1 Weigh 25.00 ± 0.01 g of toluene into a 1000-mL volumetric flask.

7.1.2 Dilute with o-xylene to 1000 mL.

7.2 *Calibration Standard Solution:*

7.2.1 Pipet 2.0 mL of 57 % hydriodic acid into a 5-mL vial.

7.2.2 Pipet 2.0 mL of the internal standard solution (prepared in 7.1) into the vial and seal with the mininert valve.

7.2.3 Weigh the vial and contents to the nearest 0.1 mg.

7.2.4 Add 50 µL of iodoethane to the vial with a syringe.

7.2.5 Weigh and record the amount of iodoethane added.

7.2.6 Shake for 30 s and allow to stand for 20 minutes.

8. Calibration of Electronic Integrator

8.1 Inject 1.0 µL of the upper solvent layer of the standard solution prepared in 7.2 into the gas chromatograph and record the chromatogram.

8.1.1 Calibrate the integrator according to the manufacturer's instructions.

8.2 If an integrator is not available peak areas and response factors can be determined manually as follows:

$$RF = \frac{A \times w \times P_1 \times F}{0.05 \times B \times P_2} \quad (1)$$

where:

RF = response factor,
A = peak height of internal standard (toluene),
w = weight of iodoethane, g,
P_1 = purity of iodoethane,
F = factor of 0.289 for ethoxyl $\left(\frac{45}{156}\right)$, 0.391 for hydroxyethoxyl,
0.05 = weight of toluene, g,
B = peak height of iodoethane, and
P_2 = purity of toluene.

9. Procedure

9.1 *Specimen Preparation:*

9.1.1 Dry the specimen at 105°C for 1 h and store in a dessicator until cool.

9.1.2 Weigh 60 to 80 mg of the specimen prepared in dry 9.1.1 into a clean, tared 5-mL reaction vial (see 3.5).

9.1.3 For a cellulose ether that is not soluble in o-xylene, add 2.0 mL of the internal standard solution prepared in 7.1 to the vial.

9.1.4 Add 2.0 mL of hydriodic acid to the vial.

9.1.5 For a cellulose ether that is soluble in o-xylene, reverse the order of addition of 9.1.3 and 9.1.4.

9.1.6 Cap tightly and weigh the vial.

9.1.7 Shake the specimen for 30 s.

9.1.8 Place the vial in a heated block at 180 ± 5°C for 2 h.

NOTE 3—**Warning:** Vials contain a hot corrosive acid under pressure.

9.1.9 Remove the vial and cool in the hood to room temperature. The specimen will separate into two layers.

9.1.10 Reweigh to determine any loss due to leakage. Discard any specimen with loss greater than 25 mg.

9.1.11 Shake the sample vigorously and allow to stand for 20 minutes.

9.2 *Analysis:*

9.2.1 Enter the weight of the toluene (internal standard) and the weight of the specimen into the integrator if an integrator is being used.

9.2.2 Inject 1.0 µL of the upper layer of the specimen into the gas chromatograph.

10. Calculation

10.1 If an integrator is not available, calculate the peak areas and concentrations using the following equation:

$$\text{ethoxyl, \% or hydroxyethoxyl, \%} = \frac{B \times 0.05 \times P_2 \times RF}{A \times \text{sample weight (g)}} \quad (2)$$

where:

B = peak height of iodoethane,
0.05 = weight of toluene, g,
P_2 = purity of toluene,
RF = response factor determined for calibration standard solution, and
A = peak height of toluene.

11. Precision and Bias[4]

11.1 *Precision*—The relative precision was found to be 0.64 % at the 95 % confidence level.

11.2 *Bias*—No justifiable statement can be made on the bias of the procedure in this test method because no suitable reference material for determining the bias exists.

12. Keywords

12.1 cellulose ether; ethoxyl or hydroxyethoxyl substitution; gas chromatography

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report: RR:D01-1058.