Designation: D3876 – 96 (Reapproved 2013)

Standard Test Method for Methoxyl and Hydroxypropyl Substitution in Cellulose Ether Products by Gas Chromatography[1]

This standard is issued under the fixed designation D3876; 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 methoxyl and hydroxypropyl substitution content in cellulose ether products by a Zeisel-gas chromatographic technique.

1.2 This test method is not suitable for use for the analysis of hydroxypropyl-cellulose due to its very high substitution level.

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 2, 11.1.4, and 11.1.7.

2. Summary of Test Method

2.1 When methyl cellulose or hydroxypropyl methyl cellulose is reacted with hydriodic acid, 1 mol of methyl iodide and 1 mol of isopropyl iodide are liberated for each mole of methoxyl and hydroxypropoxyl that is substituted on the cellulose chain. The methyl iodide and isopropyl iodide are extracted in situ with *o*-xylene and quantitated by gas chromatography using an internal standard technique.

3. Significance and Use

3.1 This test method determines the methoxyl and hydroxypropoxyl content of cellulose ethers by a Zeisel-gas chromatographic technique.

3.2 Substitution levels affect solution properties, rheology, viscosity, and many other properties of the polymer.

4. Apparatus

4.1 *Gas Chromatograph,*[2] with thermal conductivity detector and heated injection port.

4.2 *Electronic Integrator.*[3]

4.3 *Stainless Steel Tubing,*[4] 9.5 mm in outside diameter and 1981 mm in length, packed with reagent in 5.8.

4.4 *Syringes,* 10 and 100 µL.

4.5 *Reaction Vials, Caps, and Heating Block.*[5]

5. Reagents

5.1 *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.[6] 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.

5.2 *o-Xylene,* ACS.

5.3 *Toluene,* ACS.

5.4 *Iodomethane,* 99 % min.

5.5 *2-Iodopropane,* 97 % min.

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

5.7 *Acetone.*

5.8 *Packing Material.*[7]

6. Hazards

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

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[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.

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[2] Hewlett-Packard Model 5700, available from Hewlett-Packard, Route 41, Starr Rd, P.O. Box 900, Avondale, PA 19311, has been found satisfactory for this purpose.

[3] Hewlett-Packard Model 3380 has been found satisfactory for this purpose.

[4] Tubing from Supelco, Inc., Supelco Park, Bellefonte, PA 16823 has been found satisfactory for this purpose.

[5] Reacti-therm Heating module, Reacti-Block Reacti-vials and Mininert valve tops from Pierce Chemical Co., Box 117, Rockford, IL 61105 have been found satisfactory for this purpose.

[6] *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.

[7] Columns packed with 10 % SP2100 on 100/120 Supelcoport® have been found satisfactory for this purpose.

6.2 During the reaction, the glass vials are under pressure. Exercise caution in handling the hot vials.

7. Sampling

7.1 A specific sampling method is currently under study by the subcommittee.

8. Apparatus Preparation and Conditioning

8.1 Install prepackaged columns in the chromatograph and condition them by heating to 150°C over 1 h and then holding at temperature for 16 h. Then set the chromatograph as follows:[8]

Oven temperature	130°C isothermal
Injection port temperature	200°C
Detector temperature	250°C
Detector current	170 mA
Attenuation	1
Carrier gas	helium
Column A	20 mL/min
Column B	20 mL/min

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

8.2 *Integrator:*

8.2.1 *Settings:*[8]

Attenuation	3
Chart	auto
Chart speed	1.0 cm/in.
Area reject	off
Slope sensitivity	must be determined

8.2.2 *Approximate component retention times:*

Minutes	Component
3.00	methyl iodide
5.00	isopropyl iodide
7.00	toluene (internal standard)
13.00	*o*-xylene

9. Preparation of Standard Solutions

9.1 *Internal Standard Solution (25 mg toluene/ml o-xylene):*

9.1.1 Weigh a 100-mL volumetric flask containing 10 mL of *o*-xylene to the nearest 0.01 g.

9.1.2 Add 2.50 ± 0.01 g of toluene.

9.1.3 Dilute with *o*-xylene to 100 mL.

9.2 *Calibration Standard Solution:*

9.2.1 Add 2.0 mL of 57 % hydriodic acid.

9.2.2 Pipet 2.0 mL of the internal standard solution into the vial and cap with a serum stopper or septum top.[9]

9.2.3 Weigh vial and contents to nearest 0.1 mg.

9.2.4 Add 30 µL of isopropyl iodide to the vial through the septum top with a syringe. Weigh and record the amount of isopropyl iodide added to nearest 0.1 mg.

9.2.5 Add 90 µL of methyl iodide to the vial with a syringe. Weigh and record the amount added to nearest 0.1 mg.

9.2.6 Mix the contents well.

9.2.7 Convert the alkyl iodides into their respective alkoxyl equivalents using the following equations:

$$\text{mg methoxyl} = \text{g methyl iodide} \times \left(\frac{31 \times 1000}{142}\right) \quad (1)$$

$$\text{mg hydroxy propoxyl} = \text{g propyliodide} \times \left(\frac{75 \times 1000}{170}\right) \quad (2)$$

$$\text{mg toluene} = \text{internal standard solution concentrated} \times 4 \text{ ml} \quad (3)$$

10. Calibration of Electronic Integrator[10]

10.1 Inject 1 µL of the upper layer of the prepared standard solution (9.2) into the gas chromatograph and start the electronic integrator.

10.1.1 Calibrate in accordance with the manufacturer's instructions.

10.2 In the event an electronic integrator is not available the peak areas can be measured manually and a factor determined for each component can be obtained using the following equation:

$$F = \frac{A \times B}{C \times D} \quad (4)$$

where:

A = weight of the component in the standard solution, mg,
B = peak area of the internal standard solution, toluene from the standard run,
C = peak area of the component from the standard run,
D = weight of the internal standard solution, mg, and
F = component response factor.

11. Procedure

11.1 *Sample Preparation:*

11.1.1 Dry the sample at 105°C (221°F) for 60 min and store in a desiccator.

11.1.2 Weigh 60 to 80 ± 0.1 mg into a clean 5-mL reactor-vial.

11.1.3 Add 2.00 ± 0.01 mL of internal standard solution (9.1).

11.1.4 Add 2.00 ± 0.05 mL of 57 % hydriodic acid. (**Warning—**Use a hood, goggles, and other appropriate safety equipment. Hydriodic acid can cause systemic damage.)

11.1.5 Immediately cap tightly to prevent leakage.

11.1.6 Shake the specimen for approximately 30 s.

11.1.7 Place the reactor-vial into a 180°C (356°F) heated block for 2 h. (**Warning—**A possible safety hazard exists because the vials contain a hot corrosive acid under pressure.)

11.1.8 After 2-h heating time, remove the specimen and place in the hood to cool for about 45 min. The specimen will separate into two layers.

11.1.9 If leakage has occurred (which will be visibly obvious), discard the sample and repeat the analysis.

12. Analysis

12.1 Enter into the integrator the milligrams of specimen and toluene internal standard used in the preparation of the specimen.

[8] These settings were used with the Hewlett-Packard Model 3380 Integrator. Other units may require different settings.

[9] Mininert valve tops from Pierce Chemical Co., Box 117, Rockford, IL 61105 have been found satisfactory for this purpose.

[10] The Hewlett-Packard 3380 has been found satisfactory for this purpose. Other electronic integrators may require a different calibration technique.

12.1.1 This can be calculated from the concentration of the internal standard solution.

12.2 Inject 2 μL of the *upper* layer of the specimen into the gas chromatograph and immediately start the integrator.

13. Calculation

13.1 The integrator printout records the methoxyl or hydroxypropoxyl substitution, or both, in weight percent.

13.2 If an electronic integrator is not available the peak areas can be measured manually and the alkoxyl substitution may be calculated using the following equation:

$$\% = \frac{G \times F \times H \times 100}{I \times J} \quad (5)$$

where:

G = peak area of the component from the specimen run,
F = component response factor obtained in 13.2,
H = weight of the toluene internal standard in the specimen, mg,
I = peak area of the internal standard from the specimen run, and
J = specimen weight, mg.

14. Precision and Bias

14.1 *Precision*—The data using an electronic integrator show an average relative precision of 1.7 % for methoxyl substitution (26 % level) and 5.4 % for hydroxypropyl substitution (0.3 to 10 % level) at the 95 % confidence limit 2σ.

14.2 *Interlaboratory Test Data.*[11]

14.3 *Bias*—No justifiable statement on bias of this procedure can be made because no suitable reference material exists.

15. Keywords

15.1 cellulose ethers; gas chromatography; hydroxypropyl; methoxyl

[11] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D23-1000.