



Designation: D1166 – 84 (Reapproved 2013)

Standard Test Method for Methoxyl Groups in Wood and Related Materials¹

This standard is issued under the fixed designation D1166; 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.

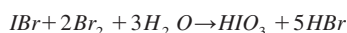
1. Scope

1.1 This test method covers the determination of methoxyl groups in wood and related materials (1-7).² The test method is applicable to wood sawdust and, by suitable adjustment in size of the test specimen, to fractions isolated from wood and lignin.

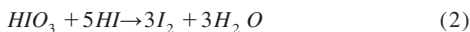
1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 6.

2. Principle of Method

2.1 The principle of the test method is the same as that in the original method of Zeisel (1), except that the methyl iodide is collected in an acetic acid solution of potassium acetate containing bromine. The following reactions then occur:



The iodic acid is determined by titration of iodine liberated by the reaction:



From the above equations, it follows that one methoxyl group (CH_3O) liberates six atoms of iodine.

3. Significance and Use

3.1 Most of the methoxyl in wood is attributable to the lignin. This test method is used extensively in the study of lignin.

4. Apparatus

4.1 The apparatus shall be similar to that illustrated in Fig. 1 and shall consist of the following:

¹ This test method is under the jurisdiction of ASTM Committee D07 on Wood and is the direct responsibility of Subcommittee D07.01 on Fundamental Test Methods and Properties.

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² The boldface numbers in parentheses refer to the references listed at the end of this test method.

4.1.1 *Reaction Flask,*

4.1.2 *Heat Source*—A microburner, provided with a cylindrical shield to eliminate the effect of air drafts,

4.1.3 *Vertical Air-Cooled Condenser,*

4.1.4 *Scrubber,* and

4.1.5 *Two Absorption Vessels.*

5. Purity of Reagents and Water

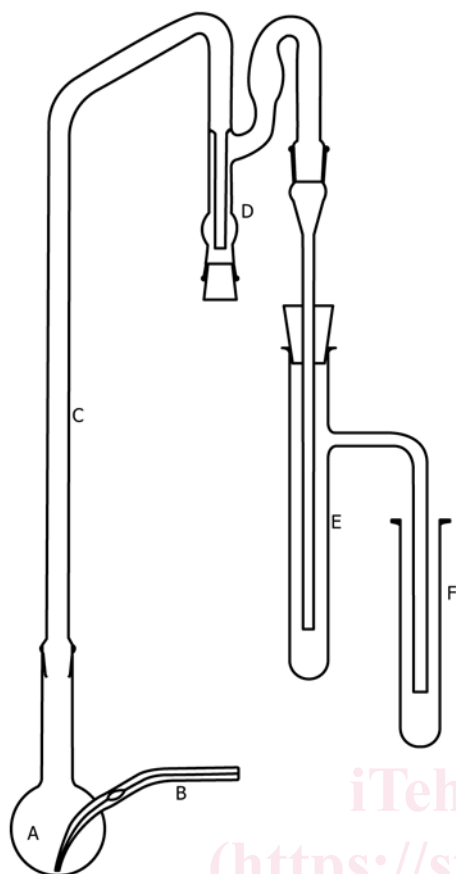
5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ Other grades 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.

5.2 *Water*—Unless otherwise indicated, references to water shall be understood to mean distilled water.

6. Reagents

6.1 *Hydriodic Acid (sp gr 1.70)*—The best reagent grade HI, if stored in the absence of light and at a low temperature, may be used without redistillation. If purification is necessary, the HI may be redistilled. If purification is necessary, the HI may be redistilled after addition of a few grams of red phosphorus, taking care not to overheat the sides of the flask above the liquid level, and collecting the distillate which comes over between 124 and 130°C. A slow stream of CO_2 should be maintained through the receiver during the distillation. (**Warning**—During the distillation, the poisonous gas phosphine, PH_3 , may be formed under certain conditions, and this may unite with molecular iodine to form the explosive PI_3 , similar in properties to NI_3 . The PI_3 may explode on contact with air. It is therefore advisable to keep the current of CO_2 going after the distillation has been finished, until the apparatus has cooled; this prevents air from being sucked into the apparatus. As a safety precaution, the distillation should be

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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.



A—Reaction flask.
 B—CO₂ inlet tube.
 C—Vertical air-cooled condenser.
 D—Trap or scrubber.
 E and F—Absorption vessels or receivers.

FIG. 1 Apparatus for Methoxyl Determination

conducted in a hood or behind a wire-glass shield.) A permanently colorless solution of hydriodic acid may be obtained if the liquid, heated to approximately 100°C, is treated with slightly more than the quantity of H₃ PO₂ (50 %) necessary to effect complete de-colorization.

6.2 Phenol.

6.3 Cadmium Sulfate Solution (50 g CdSO₄ /L)—Dissolve 67.2 g of CdSO₄ ·4H₂ O in water and dilute to 1 L.

NOTE 1—A water suspension of red phosphorus is equally satisfactory in the scrubber.

6.4 Sodium Thiosulfate Solution (50 g Na₂ S₂ O₃ /L)—Dissolve 78.5 g of Na₂ S₂ O₃ ·5H₂ O in water and dilute to 1 L (Note 1).

6.5 Carbon Dioxide Gas—The CO₂ may be drawn from a cylinder of the compressed gas. It may be obtained also by the use of a Kipp generator and washed, before introduction into the apparatus, through two wash bottles, the first containing saturated NaHCO₃ solution and the second containing H₂ SO₄ (sp gr 1.84). Solid CO₂, or “dry ice,” is a convenient source (5) and the gas requires no purification.

6.6 Potassium Acetate Solution in Acetic Acid—Dissolve 100 g of anhydrous potassium acetate in 1 L of glacial acetic acid. Traces of moisture are not significant.

6.7 Liquid Bromine.

6.8 Sodium Acetate Solution (250 g/L)—Dissolve 415 g of sodium acetate trihydrate in water and dilute to 1 L.

6.9 Formic Acid (90 %).

6.10 Potassium Iodide Solution (100 g KI/L)—Dissolve 100 g of KI in water and dilute to 1 L.

NOTE 2—The KI solution, on standing, develops a yellow color due to free iodine. If a blank titration on the solution consumes Na₂ S₂ O₃, a fresh solution should be prepared.

6.11 Sulfuric Acid (1 + 9) —Mix one volume of H₂ SO₄ (sp gr 1.84) with nine volumes of water.

6.12 Standard Sodium Thiosulfate Solution (0.1 N)—Dissolve 25 g of Na₂ S₂ O₃ ·5H₂ 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 an approximately 0.1 N solution of KMnO₄ that has been standardized against sodium oxalate oxidimetric standard furnished by the National Bureau of Standards (standard sample No. 40). In each of two glass-stoppered Erlenmeyer flasks put 2 g of KI and 100 mL of freshly boiled and cooled water. Shake to dissolve the KI and add 2 mL of HCl (sp gr 1.18). To one flask add slowly from a buret either 20.0 mL of 0.1 N KMnO₄ or 10.0 mL of 0.18 N KMnO₄, while swirling the flask gently. To the other flask add an equal volume of water. Stopper the flasks and let them stand in the dark for 10 min. Titrate the iodine that has been set free with the Na₂ S₂ O₃ until the solution is of a faint straw color. Add 2 mL of starch solution and continue the titration until the blue color has just been destroyed. Subtract the volume of Na₂ S₂ O₃ required in the blank determination from that required in the other titration, and calculate the normality of the Na₂ S₂ O₃, based on the normality of the KMnO₄.

6.13 Starch Indicator Solution (10 g/L)—Make a paste of 1 g of soluble starch in 5 mL of water and add to 100 mL of boiling water. Prepare fresh as needed.

7. Test Specimen

7.1 The test specimen of wood shall consist of about 0.1 g, weighed to the nearest 0.0001 g, of air-dry sawdust that has been ground to pass a 420-µm sieve. For analysis of isolated lignins or other preparations of high methoxyl content, it is recommended that the specimen not exceed 0.05 g. For specimens of very low methoxyl content, the specimen may be increased to 0.2 g.

7.2 The specimen may be weighed in a glass boat, in a gelatin capsule, or on a cigarette paper. The container shall be transferred with the specimen to the reaction flask. The paper or capsule shall contain no methoxyl groups, as determined by a separate analysis.

8. Moisture Determination

8.1 At the same time the test specimen is weighed, weigh 0.1 g of the air-dry sawdust in a tared, glass-stoppered