

Standard Test Method for Methoxyl Groups in Wood and Related Materials¹

This standard is issued under the fixed designation D 1166; 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.

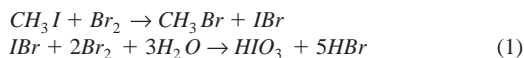
1. Scope

1.1 This test method covers the determination of methoxyl groups in wood and related materials (1 to 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.

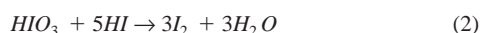
1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary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

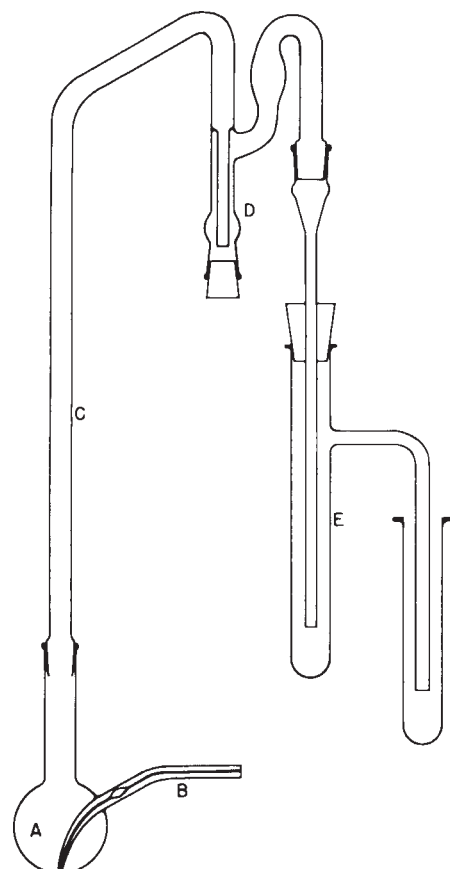
4.1 The apparatus shall be similar to that illustrated in Fig. 1 and shall consist of the following:

4.1.1 Reaction Flask,

¹ This test method is under the jurisdiction of ASTM Committee D7 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.



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

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 CO₂ should be maintained through the receiver during the distillation. (**Warning**—During the distillation, the poisonous gas phosphine, PH₃, may be formed under certain conditions, and this may unite with molecular iodine to form the explosive PI₃, similar in properties to NI₃. The PI₃ may explode on contact with air. It is therefore advisable to keep the current of CO₂ 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 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 weighing bottle. Dry in an oven for 12 h at 100 to 105°C, replace the stopper, and cool in a desiccator. Loosen the stopper to equalize the pressure and weigh. Continue the drying for 1-h periods until the weight is constant. Calculate the percentage of moisture-free wood.

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.

9. Procedure

9.1 Place in the reaction flask 15 mL of HI, 7 g of phenol, and a 10-mm length of Nichrome wire or a boiling tube (Note 3) to prevent bumping. Place in the scrubber a mixture of equal volumes of CdSO_4 solution (50 g CdSO_4 /L) and $\text{Na}_2 \text{S}_2 \text{O}_3$ solution (50 g $\text{Na}_2 \text{S}_2 \text{O}_3$ /L) (see Note 1). The volume of solution should be adjusted so that the inlet tube of the scrubber is covered to a depth of about 4 mm. Adjust the flow of CO_2 to about 60 bubbles per minute through the scrubber (Note 4).

NOTE 3—A boiling tube may be prepared by sealing off a piece of thin-wall capillary tubing of such length that it will remain vertical in the reaction flask, and inserting it with the open end down. If the CO_2 introduction tube extends to the bottom of the flask, no anti-bumping device is necessary.

NOTE 4—Two to four samples may be analyzed with one charge of reagents in the reaction flask and scrubber. The apparatus should then be thoroughly cleaned.

9.2 Bring the contents of the flask to reaction temperature. Adjust the rate of heating so that the vapors of the boiling HI rise about 100 mm into the condenser. Heat the flask at reaction temperature for 30 to 45 min, or longer if necessary, to remove methoxyl-containing or other interfering substances which are usually present in the reagents.

NOTE 5—An appreciable blank may rise from the reagents used. The greater part of this blank is removed by a preliminary “burning out” period. In normal work, the time required to remove interfering substances must be determined by a trial determination, in the absence of a test specimen, for a particular lot of reagents. For the highest accuracy, it is recommended that the residual blank be ascertained by “blank” determination before and after the determination on the test specimen. These blank determinations are made in the normal manner and their average is subtracted from the titration of the sample.

9.3 Let the reaction flask cool below 100°C . In the meantime, add to 20 mL of the potassium acetate solution, about 0.6 mL of bromine, and mix. Add approximately 15 mL of the mixture to the first receiver and 5 mL to the second, and attach the receiver to the apparatus. Seal the ground-glass joint with a small drop of water from the glass rod.

9.4 Remove the distilling flask and introduce the test specimen. Immediately reconnect the flask and seal the ground-glass joint with a drop of molten phenol from a glass rod. Bring the contents of the flask to reaction temperature while passing a uniform stream of CO_2 through the apparatus. Adjust the rate of heating so that the vapors of the boiling HI rise about 100 mm into the condenser. Continue the heating for a time sufficient to complete the reaction and sweep out the apparatus. Usually, not more than 50 min are required.

9.5 Wash the contents of both receivers into a 250-mL Erlenmeyer flask that contains 15 mL of sodium acetate solution. Dilute with water to approximately 125 mL and add 6 drops of formic acid. Rotate the flask until the color of the bromine is discharged, then add 12 more drops of formic acid and allow the solution to stand for 1 to 2 min. Add 10 mL of KI solution and 10 mL $\text{H}_2 \text{SO}_4$ (1 + 9), and titrate the liberated iodine with $\text{Na}_2 \text{S}_2 \text{O}_3$ solution, adding 1 mL of starch indicator solution just before the end point is reached and continuing the titration to the disappearance of the blue color.

10. Calculation and Report

10.1 Calculate the percentage of methoxyl groups, based on the weight of moisture-free wood, as follows:

$$\begin{aligned} \text{Methoxyl, \%} &= ((VN \times 31.03) \times 100) / (G \times 1000 \times 6) \\ &= (VN/G) \times 0.517 \end{aligned} \quad (3)$$

where:

V = millilitres of $\text{Na}_2 \text{S}_2 \text{O}_3$ solution required for the titration,

N = normality of $\text{Na}_2 \text{S}_2 \text{O}_3$ solution, and

G = grams of moisture-free wood in the test specimen.

10.2 Report the results to the second decimal place.

11. Precision and Bias

11.1 Sufficient data is not currently available to develop a precision and bias statement.

12. Keywords

12.1 lignin; methoxyl; sawdust

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