Designation: D1166 – 21

Standard Test Method for Methoxyl Groups in Wood and Related Materials[1]

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 milled wood or sawdust, or 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 6.

1.3 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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:

$$CH_3 I + Br_2 \rightarrow CH_3 Br + IBr \quad (1)$$

$$IBr + 2Br_2 + 3H_2 O \rightarrow HIO_3 + 5HBr$$

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

$$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2 O \quad (2)$$

From the above equations, it follows that one methoxyl group (CH_3 O) 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,*

4.1.2 *Heat Source*—A temperature controlled heating mantle,

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 *Hydroiodic Acid (HI) (57 % in water sp gr 1.70)*—This best reagent grade HI, should be stored in the absence of light and at a low temperature to keep its purity.

6.2 *Phenol.*

6.3 *Cadmium Sulfate Solution (50 g $CdSO_4$ /L)*—Dissolve 67.2 g of $CdSO_4 \cdot 4H_2 O$ in water and dilute to 1 L.

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

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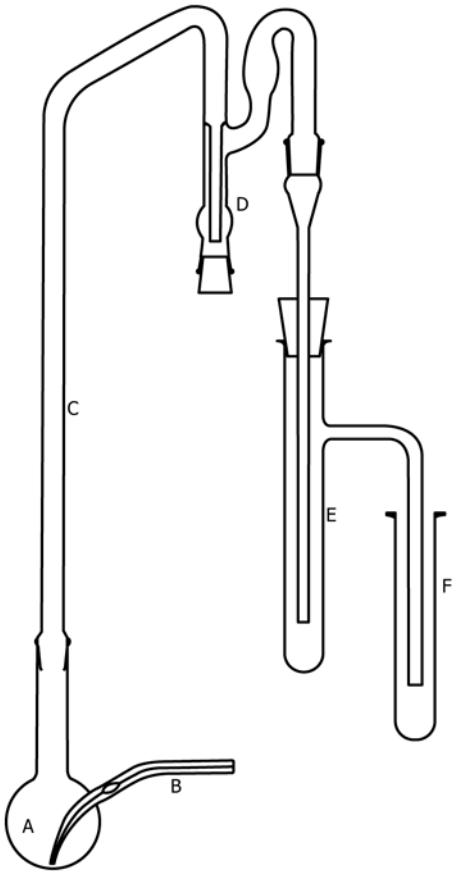
[2] The boldface numbers in parentheses refer to the references listed at the end of this test method.

[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—CO_2 inlet tube.
C—Vertical air-cooled condenser.
D—Trap or scrubber.
E and *F*—Absorption vessels or receivers.

FIG. 1 Apparatus for Methoxyl Determination

6.4 *Sodium Thiosulfate Solution (50 g Na_2 S_2 O_3 /L)*—Dissolve 78.5 g of Na_2 S_2 O_3 ·$5H_2$ O in water and dilute to 1 L (Note 1).

6.5 *Carbon Dioxide Gas*—The CO_2 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 $NaHCO_3$ solution and the second containing H_2 SO_4 (sp gr 1.84). Solid CO_2, 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 Na_2 S_2 O_3, a fresh solution should be prepared.

6.11 *Sulfuric Acid (1 + 9)* —Mix one volume of H_2 SO_4 (sp gr 1.84) with nine volumes of water.

6.12 *Standard Sodium Thiosulfate Solution (0.1 N)*—Dissolve 25 g of Na_2 S_2 O_3 ·$5H_2$ 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 $KMnO_4$ 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* $KMnO_4$ or 10.0 mL of 0.18 *N* $KMnO_4$, 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 Na_2 S_2 O_3 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 Na_2 S_2 O_3 required in the blank determination from that required in the other titration, and calculate the normality of the Na_2 S_2 O_3, based on the normality of the $KMnO_4$.

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 or milled wood that has been ground to pass a 420 µm (40 mesh) 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 weighing 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 or milled wood 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.

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 Na_2 S_2 O_3