

Methoxyl Group Content Analysis of Lignin

The methoxyl content of the residual lignin was measured using a modification of a suggested TAPPI method T 209 su-72 “Methoxyl Content of Pulp and Wood.”¹ This principle of this method is based on the reaction of the methoxyl group with hydroiodic acid to generate methyl iodide. The organic iodide is oxidized by bromine to form iodic acid, which is determined by the titration of iodine after it is reduced by KI. Figure shows the reactions occurring during the experimental procedure to determine the methoxyl content of wood, pulp, or residual lignin.

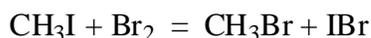
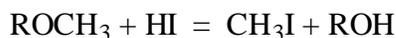


Figure 1. Reactions occurring during the experimental protocol for determining the methoxyl content of wood, pulp, and residual lignin

The procedure used for analyzing the methoxyl content in residual lignin is as follows:

1. Approximately 10 mL of a bromine-potassium acetate solution is added to a reaction flask. The sample is weighed out accurately to the nearest 0.10 mg and placed in the reaction flask with several boiling stones.
2. Exactly 2.00 mL propionic anhydride and 6.00 mL hydroiodic acid is delivered to the reaction flask.
3. The flask is immediately attached to the condenser. Helium gas is attached to another inlet of the flask.
4. The gas flow rate is adjusted to give two bubbles every second.
5. The flask is then submerged in a silicon oil bath, which is adjusted to and maintained at 145°C.
6. The reaction is continued for 30.0 minutes.

¹ T 209 su-72 *Methoxyl Content of Pulp and Wood*, In TAPPI Test Methods. TAPPI Press: Atlanta, Georgia. (1972).

7. Approximately 10 mL of a sodium acetate solution is added to a 500 mL Erlenmeyer flask. The contents of the reaction flask are washed into the Erlenmeyer flask. The contents of the Erlenmeyer flask are diluted to 125 mL and formic acid is added drop-wise, with stirring, until the yellow color of the bromine is discharged. Six additional drops of formic acid are added at this point. A total of 12 to 15 drops is usually required.
8. After about 3 minutes, 3 g KI and 15 mL of 4 N sulfuric acid is added to the flask.
9. Immediately titrate the solution with 0.1 N Na₂S₂O₃.

The methoxyl content is calculated by the relationship shown in Equation 1.

$$\text{Percentage methoxyl content} = \frac{(A - B) \times N \times 0.00517 \times 100}{W}$$

Equation 1. Calculation to determine the methoxyl content in wood, pulp, and residual lignin samples

In Equation 1, *A* is the volume of Na₂S₂O₃ required for the specimen; *B* is the volume of Na₂S₂O₃ required for the blank; *N* is the normality of the Na₂S₂O₃ solution; and *W* is the weight of the lignin sample, in grams. Typical standard deviations for the methoxyl content analysis were 0.3%.