WI 060802.06

T 222

DRAFT NO. 2

DATE June 16, 2006

TAPPI

WORKING GROUP
CHAIRMAN Method reaffirmed

SUBJECT
CATEGORY Chemical Properties

RELATED
METHODS See "Additional Information"

CAUTION:
This Test Method may include safety precautions which are believed to be appropriate at the time of publication of the method. The intent of these is to alert the user of the method to safety issues related to such use. The user is responsible for determining that the safety precautions are complete and are appropriate to their use of the method, and for ensuring that suitable safety practices have not changed since publication of the method. This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this method, the user must determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

Acid-insoluble lignin in wood and pulp

(Reaffirmation of T 222 om-02)

1. Scope

1.1 This method describes a procedure which can be applied to the determination of acid-insoluble lignin in wood and in all grades of unbleached pulps. In semi-bleached pulp the lignin content should not be less than about 1% to provide a sufficient amount of lignin, about 20 mg, for an accurate weighing. The method is not applicable to bleached pulps containing only small amounts of lignin.

1.2 Some of the lignin dissolves in acid solution during the test and is not included in the test result. In softwoods (coniferous woods) and in sulfate pulps, the amount of soluble lignin is small, about 0.2 to 0.5%. In hardwoods (deciduous woods), non-wood fibers, and in sulfite pulps, the content of soluble lignin is about 3 to 5%. In semi-bleached pulps, soluble lignin could amount to about one-half or more of the total lignin content.

NOTE 1: The acid-soluble lignin can be determined in a solution, after filtering off the insoluble lignin, by a spectrophotometric method based on absorption of ultraviolet radiation. The most often used wavelength is 205 nm (*1*).

1.3 The total lignin content in pulps can be estimated fairly closely by rapid, indirect methods based on chlorination of the lignin (TAPPI T 253 “Hypo Number of Pulp” - method withdrawn in 1998) or oxidation of the lignin (TAPPI T 236 “Kappa Number of Pulp”).

2. Summary of method

The carbohydrates in wood and pulp are hydrolyzed and solubilized by sulfuric acid; the acid-insoluble lignin is filtered off, dried, and weighed.

3. Significance

Wood contains from about 20 to 30% lignin, removal of which is a main objective of pulping and bleaching processes. Determination of lignin content in wood and pulps provides information for evaluation and application of the processes. Hardness, bleachability, and other pulp properties, such as color, are also associated with the lignin content.

4. Definitions

4.1 Lignin represents what is called the “incrusting material” forming a part of the cell wall and middle lamella in wood. It is an aromatic, amorphous substance containing phenolic methoxyl, hydroxyl, and other constituent groups; its chemical structure has not been fully elucidated.

4.2 In this method of determination, lignin (also known as “Klason lignin”) is defined as a wood or pulp constituent insoluble in 72% sulfuric acid.

5. Apparatus

5.1 *Filtration apparatus* (Fig. 1), consisting of a filtering flask, 2000 mL, a filtering crucible, about 30 mL, an adapter, and a siphon tube. Other types of filtration apparatus may also be used.

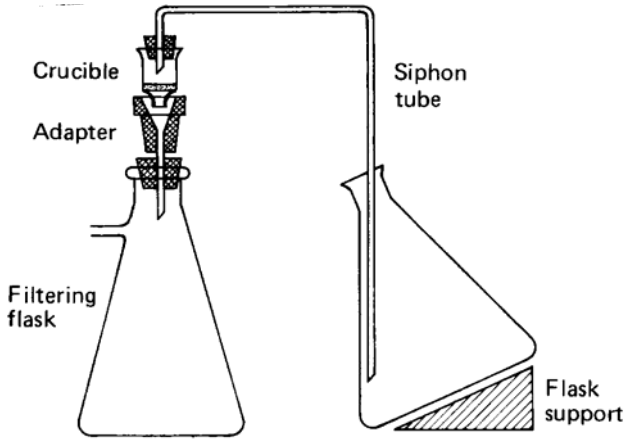

Fig. 1. Lignin filtration apparatus.

NOTE 2: Various types of filtering crucibles can be used, provided that the filtration is reasonably fast and all of the lignin is retained on the filter, resulting in a clear filtrate. Glass filtering crucibles with a sintered glass disc of a fine (*F*), or medium (*M*) porosity can be used on wood and on most of the pulps. Lignin in low-yield sulfite pulps forms a fine dispersion, which often clogs the pores of the sintered glass discs and slows the filtration. A disc of a glass fiber paper, fitted in the crucible, facilitates the filtration. Alundum or porous porcelain crucibles, with a mat of glass fibers, may also be used.

5.1.1 Dry the filtering crucibles in an oven at 105 ± 3°C for about 2 h, cool, and weigh before use.

5.2 *Constant temperature bath*, to maintain a temperature of 20 ± 1°C.

5.3 *Flasks*, Erlenmeyer, 1000 mL, with a mark added at 575 mL volume (for wood specimens; and 2000 mL, with a mark added at 1540 mL volume (for pulp specimens).

5.4 *Reflux condenser* (optional), to be attached to the flask. If used, flasks and condenser should be equipped with ground glass connectors. If ground glass connectors are not available, a rubber stopper may be used.

5.5 *Drying oven*, forced circulation type, maintained at 105 ± 3°C.

5.6 *Hot plate*, electric.

5.7 *Wiley mill*, with a 10 or 20-mesh screen, or a Waring-type blender.

5.8 *Other glassware*: buret, 50 mL; beakers, 100 mL; glass stirring rods.

6. Reagents

6.1 *Sulfuric acid*, 72% H_2SO_4 solution, 24 ± 0.1*N*, sp gr 1.6338 at 20°/4°C, prepared as follows:

6.1.1 Carefully pour 665 mL of concentrated H_2SO_4 (95.5 to 96.5%, sp gr 1.84) into 300 mL of water, and after cooling, make up to 1000 mL. Adjust the strength to 24 ± 0.1*N* by titration with a standard alkali, or by measuring specific gravity. A variation of 0.1% in the strength of acid at this concentration causes a change of 0.0012 in specific gravity.

6.1.2 Cool the acid solution in a refrigerator or under tap water to 10 to 15°C before use.

6.2 *Ethanol-benzene mixture.* Mix one volume of approximately 95% ethanol and two volumes of C.P. benzene.

6.3 Safety information.

6.3.1 Benzene has been identified as a hazardous substance and a confirmed carcinogen (long-term exposure). It must be handled carefully using proper ventilation in an approved fume hood.

6.3.2 Sulfuric acid is corrosive and can cause burns to the skin. It must always be cautiously added to water to prevent splashing.

7. Sampling

7.1 Obtain a sample of wood in accordance with TAPPI T 257 "Sampling and Preparing Wood for Analysis" and prepare about 5 g of extractive-free wood in accordance with TAPPI T 264 "Preparation of Wood for Chemical Analysis."

7.2 For pulp obtain a sample equivalent to about 10 g oven-dry, in accordance with a predetermined sampling procedure. If the pulp is wet, dry it in air or in an oven at 60°C or less.

7.2.1 Disintegrate the pulp in a blender or grind in a mill to pass a 10 or 20 mesh screen. Pulps which do not contain coarse fibers or shives and which can be dispersed in sulfuric acid readily could be used without prior disintegration.

7.2.2 Extract groundwood and high-yield pulps containing a significant amount of resins with ethanol-benzene in accordance with TAPPI T 204 "Solvent Extractives of Wood and Pulp." Wash with ethanol and hot water and dry thoroughly in air or in an oven at 60°C or less.

NOTE 3: Resins, if allowed to remain in pulp, remain insoluble in acid and would be weighed as lignin.

8. Test specimens

8.1 Allow the sample to reach moisture equilibrium in the atmosphere near the balance, and weigh out two test specimens to the nearest 0.1 mg as follows: for wood, 1.0 ± 0.1 g; for pulp, 2.0 ± 0.1 g, equivalent to oven-dry weight. Place the test specimens in 100-mL beakers.

NOTE 4: Groundwood and very-high-yield pulps, with their high lignin content, may be regarded as being the same as wood and the same weight, 1 g, and the same procedure as on wood specimens can be applied.

8.2 At the same time weigh another specimen for moisture determination.

9. Procedure

9.1 Add to the beakers containing the test specimens cold (10 to 15°C) 72% sulfuric acid, 15.0 mL for a wood and 40.0 mL for a pulp specimen. Add the acid gradually in small increments while stirring and macerating the material with a glass rod. Keep the beaker in a bath at 2 ± 1°C during dispersion of the material.

NOTE 5: Some pulps do not absorb the acid and therefore do not disperse readily. In such cases, place the beaker after addition of the acid in a vacuum desiccator for a few minutes to facilitate wetting and dispersion.

9.2 After the specimen is dispersed, cover the beaker with a watch glass and keep it in a bath at 20 ± 1°C for 2 h. Stir the material frequently during this time to ensure complete solution.

9.3 Add about 300 to 400 mL of water to a flask (see 5.3) and transfer the material from the beaker to the flask. Rinse and dilute with water to 3% concentration of sulfuric acid, to a total volume of 575 mL for wood, and to 1540 mL for pulps.

9.4 Boil the solution for 4 h, maintaining constant volume either by using a reflux condenser or by frequent addition of hot water.

NOTE 6: Do not use a reflux condenser if the acid-soluble lignin is being determined in the solution.

9.5 Allow the insoluble material (lignin) to settle, keeping the flask in an inclined position. If the lignin is finely dispersed, it may require an "overnight" or a longer period to settle.

9.6 Without stirring up the precipitate, decant or siphon off the supernatant solution through a filtering crucible (see Note 7). Then transfer the lignin quantitatively to the filter, using hot water and a rod with rubber policeman.

NOTE 7: If required, take a portion of the filtrate before dilution with water, for determination of the acid-soluble lignin using appropriate method from the literature.

9.7 Wash the lignin free of acid with hot water.

9.8 Dry the crucible with lignin in an oven at 105 ± 3°C to constant weight. Cool in a desiccator and weigh.

9.9 If a correction for ash in lignin is desired, transfer the lignin to a small platinum or porcelain crucible and proceed in accordance with TAPPI T 211 "Ash in Wood and Pulp."

NOTE 8: Lignin may be ashed also directly in porcelain or alundum filtering crucibles that have been ignited to a constant weight before filtering. Glass crucibles cannot be used for ashing.

10. Calculation

For each determination, calculate the lignin content in the test specimen as follows:

$$\text{Lignin, \%} = A\ 100 / W$$

where:

A = weight of lignin, g
W = oven-dry weight of test specimen, g

11. Report

Report the lignin content as the average of two determinations, to the nearest 0.1%.

12. Precision

12.1 The data on precision are summarized in Table 1, where the repeatability and reproducibility obtained on wood and on pulps with different lignin content are shown.

Table 1. Precision data

Material	*Lignin content, %*	*Repeatability*	*Reproducibility*
Wood	From 19 to 30	0.34	0.79
Sulfate pulps	From 2.6 to 19.1	0.17	0.45
Sulfite pulps	From 6.5 to 28.0	0.48	1.04

12.2 Comparability (between materials) is not known.

12.3 The data on repeatability and reproducibility are in accordance with the definition of these terms in TAPPI T 1200 “Interlaboratory Evaluation of Test Methods to Determine TAPPI Repeatability and Reproducibility.”

12.4 These dates were obtained in an interlaboratory study conducted by nine laboratories on 6 wood and 10 pulp samples (6 sulfate and 4 sulfite pulps). It was found that the precision of the lignin test, both within and between laboratories, depends mainly on the type of the material but is approximately constant throughout the range of lignin content.

13. Keywords

Lignin, Acid insolubles, Wood, Pulp

14. Additional information

14.1 Effective date of issue: to be assigned.

14.2 Related methods: ASTM D 1106; PAPTAC G.8 and G.9; Australian and New Zealand AS/NZS P 11.

Reference

1. Schoening, A. G., and Johansson, G., "Absorptiometric Determination of Acid-Soluble Lignin in Semichemical Bisulfite Pulps and in Some Woods and Plants," *Svensk Papperstid* **68** (18): 607 (1965).

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Director of Quality and Standards. ■

WI 060802.06

T 222

DRAFT NO. 1

DATE May 10, 2006

TAPPI

WORKING GROUP
CHAIRMAN to be assigned

SUBJECT
CATEGORY Chemical Properties

RELATED
METHODS See "Additional Information"

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Acid-insoluble lignin in wood and pulp

(Five-year review of T 222 om-02)

1. Scope

1.1 This method describes a procedure which can be applied to the determination of acid-insoluble lignin in wood and in all grades of unbleached pulps. In semi-bleached pulp the lignin content should not be less than about 1% to provide a sufficient amount of lignin, about 20 mg, for an accurate weighing. The method is not applicable to bleached pulps containing only small amounts of lignin.

1.2 Some of the lignin dissolves in acid solution during the test and is not included in the test result. In softwoods (coniferous woods) and in sulfate pulps, the amount of soluble lignin is small, about 0.2 to 0.5%. In hardwoods (deciduous woods), non-wood fibers, and in sulfite pulps, the content of soluble lignin is about 3 to 5%. In semi-bleached pulps, soluble lignin could amount to about one-half or more of the total lignin content.

NOTE 1: The acid-soluble lignin can be determined in a solution, after filtering off the insoluble lignin, by a spectrophotometric method based on absorption of ultraviolet radiation. The most often used wavelength is 205 nm (*1*).

1.3 The total lignin content in pulps can be estimated fairly closely by rapid, indirect methods based on chlorination of the lignin (TAPPI T 253 “Hypo Number of Pulp” - method withdrawn in 1998) or oxidation of the lignin (TAPPI T 236 “Kappa Number of Pulp”).

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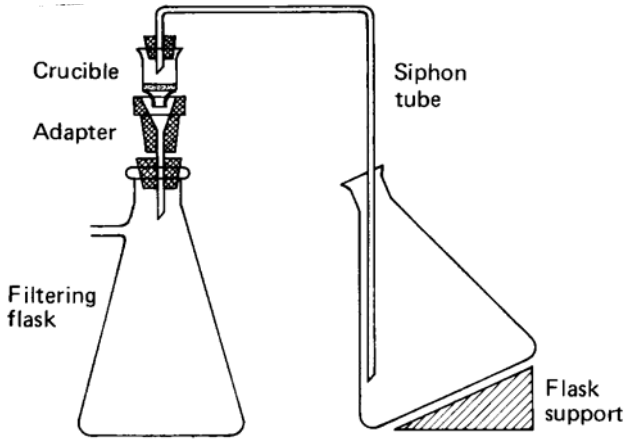

Fig. 1. Lignin filtration apparatus.

NOTE 2: Various types of filtering crucibles can be used, provided that the filtration is reasonably fast and all of the lignin is retained on the filter, resulting in a clear filtrate. Glass filtering crucibles with a sintered glass disc of a fine (*F*), or medium (*M*) porosity can be used on wood and on most of the pulps. Lignin in low-yield sulfite pulps forms a fine dispersion, which often clogs the pores of the sintered glass discs and slows the filtration. A disc of a glass fiber paper, fitted in the crucible, facilitates the filtration. Alundum or porous porcelain crucibles, with a mat of glass fibers, may also be used.

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9.7 Wash the lignin free of acid with hot water.

9.8 Dry the crucible with lignin in an oven at 105 ± 3°C to constant weight. Cool in a desiccator and weigh.

9.9 If a correction for ash in lignin is desired, transfer the lignin to a small platinum or porcelain crucible and proceed in accordance with TAPPI T 211 "Ash in Wood and Pulp."

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