
Pulps — Determination of lignin content — Acid hydrolysis method

*Pâtes — Détermination de la teneur en lignine — Méthode
d'hydrolyse acide*

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Contents

Page

Foreword	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Terms and definitions	1
4 Principle	2
5 Apparatus	2
6 Reagents	2
7 Sampling	3
8 Test Specimens	3
9 Procedure	3
9.1 Hydrolysis.....	3
9.1.1 General.....	3
9.1.2 Hydrolysis procedure A.....	4
9.1.3 Hydrolysis procedure B.....	4
9.2 Filtration.....	5
9.3 Acid-insoluble lignin determination.....	5
9.4 Acid-soluble lignin determination.....	5
10 Calculation	5
11 Precision	6
12 Test Report	6
Annex A (informative) Precision	8
Bibliography	12

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 6, *Paper, board and pulps*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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Introduction

The main objective of measuring lignin in pulp is to assess the effect of a particular pulping or bleaching process on the degree of delignification. In chemical pulping, the goal is to remove lignin from wood with minimum degradation of the carbohydrates. The higher the level of residual lignin in any type of unbleached pulp, the greater the amount of bleaching chemicals that is applied in order to achieve a target brightness.

Comprehensive textbooks and reviews have been written on methods of lignin determination^{[1]-[3]}. This document specifies one such method, commonly used for the determination of the total lignin content of pulp. In this method, a pulp sample is treated with sulfuric acid, in a two-step (primary and secondary) hydrolysis process, to solubilize the carbohydrates. Most of the lignin remains insoluble at the end of the treatment and is filtered off, dried and weighed. This acid-insoluble lignin is also referred to as “Klason lignin”.

A small portion of lignin is dissolved during acid hydrolysis of the pulp. This so-called acid-soluble lignin is determined spectrophotometrically, from the UV absorbance at 205 nm of the filtrate from the acid-insoluble lignin determination^{[4]-[6]}. The total lignin content is determined as the sum of the acid-insoluble and acid-soluble lignin.

Two hydrolysis procedures are described in this document. In procedure A^{[7]-[9]}, the primary hydrolysis is performed with 72 % sulfuric acid at 30 °C for one hour, followed by dilution with water to 4 % sulfuric acid, and secondary hydrolysis in an autoclave at 120 °C for one hour. In procedure B^{[10][11]}, the primary hydrolysis is done at 15-20 °C for two hours, followed by secondary hydrolysis at 3 % sulfuric acid in a water bath at 100 °C for four hours. In procedure A, the use of 4 % sulfuric acid, instead of 3 %, for secondary hydrolysis has no impact on the lignin analysis and is accepted when both lignin and carbohydrates need to be analysed in the same sample.

Both procedures have been shown to give the same results; thus, either one can be used for determining acid-insoluble lignin. However, procedure A is considerably more rapid, and the use of an autoclave allows multiple samples to be hydrolysed simultaneously with minimum supervision. As such, it is now more commonly used in laboratories equipped with an autoclave. It is therefore the preferred method and should be used when analysis of carbohydrates is required in addition to the determination of lignin.

Pulps — Determination of lignin content — Acid hydrolysis method

WARNING — This method involves the use of hazardous chemicals. Care should be taken to ensure that the relevant precautions are taken.

1 Scope

The method is applicable to unbleached, bleached and semi-bleached wood pulp with a lignin content above 1 %. It is not generally intended for fully bleached chemical pulp, because the lignin content in these pulps is too low to be determined accurately.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 638, *Paper, board and pulps — Determination of dry matter content — Oven-drying method*

ISO 1762, *Paper, board, pulps and cellulose nanomaterials — Determination of residue (ash content) on ignition at 525 °C*

ISO 7213, *Pulps — Sampling for testing*

ISO 14453, *Pulps — Determination of acetone-soluble matter*

3 Terms and definitions

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For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at <https://www.iso.org/obp>

— IEC Electropedia: available at <http://www.electropedia.org/>

3.1

lignins

class of complex, organic macromolecules, containing aromatic sub-units, that play a key role in the formation of cell walls in wood and bark, conferring mechanical strength and rigidity to cell walls and to plants as a whole

Note 1 to entry: Lignin is the main non-carbohydrate constituent of wood.

3.2

acid-insoluble (Klason) lignin

residue after treating wood or pulp with sulfuric acid in a two-step hydrolysis procedure to solubilize the carbohydrates into monosaccharides

3.3

acid-soluble lignin

portion of *lignin* (3.1) which is soluble during the acid-insoluble lignin determination

3.4 acetone-soluble matter
amount of material that can be extracted with acetone from a sample of pulp by the method specified in ISO 14453

4 Principle

A pulp sample is treated with sulfuric acid in a two-step (primary and secondary) hydrolysis process to dissolve the carbohydrates. The residue after hydrolysis is filtered off, dried, and weighed, and referred to as acid-insoluble or Klason lignin. A small amount of lignin is dissolved during acid hydrolysis. This so-called acid-soluble lignin is determined by measuring the absorbance at 205 nm of the filtrate from the acid-insoluble lignin determination. The total lignin content is determined as the sum of the acid-insoluble lignin and acid-soluble lignin.

5 Apparatus

5.1 Filtration equipment: filtering flask; filtering crucible, fritted glass, medium or fine porosity, 30 ml; adapter for the filtering crucible, siphon tube (optional).

NOTE The choice of fritted glass porosity depends on the rate of filtration of the particular type of sample. For slow filtering samples, the use of medium (M) porosity is preferable. In low-yield sulfite pulps especially, lignin forms a fine dispersion and clogs the pores of the filter. Filtration can be facilitated by using a medium porosity crucible with a disc of fine porosity glass-fibre filter paper fitted over the sintered glass in the crucible.

Other types of filtering crucibles, such as alundum or porous porcelain crucibles lined with a mat of glass fibres can also be used.

5.2 Constant temperature water bath, capable of maintaining a temperature of 30 ± 1 °C (Procedure A); or 20 ± 1 °C (Procedure B).

5.3 Flask, Erlenmeyer, 1 000 ml, or smaller depending on the size of the pulp specimen.

5.4 Procedure A only: Autoclave, capable of maintaining a temperature of 120 ± 3 °C.

5.5 Drying oven, convection type, maintained at 105 ± 2 °C.

5.6 Analytical balance, accurate to 0,1 mg.

5.7 Spectrophotometer, UV-visible, diode array or simple wavelength, with high purity quartz cuvettes of pathlength 1 cm.

6 Reagents

6.1 Water, distilled or deionized.

6.2 Sulfuric acid, 72 % w/w (specific gravity 1,633 8 at 20 °C). 72 % sulfuric acid is available commercially. It can also be prepared from concentrated sulfuric acid as follows:

Slowly add 650 ml of concentrated sulfuric acid (H_2SO_4 sp gr 1,84) to 400 ml of water, while cooling under a cold water trap. When the temperature has reached equilibrium with the ambient temperature, adjust the specific gravity of the sulfuric acid solution to 1,633 8, with the use of a hydrometer, by careful addition of concentrated sulfuric acid or water.

6.3 Acetone, only if extraction of the sample is required prior to hydrolysis with sulfuric acid.

7 Sampling

If the analysis is being made to evaluate a lot of a consignment of pulp, the sample shall be taken in accordance with ISO 7213. If the analysis is made on another type of sample, report the origin of the sample, and if possible the sampling procedure.

Obtain a representative sample of pulp equivalent to about 10 g moisture-free pulp. Air dry the pulp and disintegrate in a household blender, or grind in a Wiley mill to pass a No. 20 (0,85 mm) screen. Groundwood and high yield pulps containing a significant amount of resins shall be extracted with acetone (6.3) according to ISO 14453 before testing.

NOTE Resins, if not extracted from the pulp prior to analysis, would remain insoluble in acid and be weighed as lignin.

NOTE Acetone is considered an effective solvent for extracting resin from pulp. Dichloromethane and ethanol/benzene (1:2), as specified in other methods, are not recommended due to health hazards. In particular, benzene is a confirmed carcinogen.

Determine the moisture content of the pulp according to ISO 638 by drying a 2-3 g specimen in an oven at 105 ± 3 °C to constant weight. If the pulp shall be pre-extracted, the moisture content shall be determined on the extracted pulp.

8 Test Specimens

Weigh (5.6) a test specimen, equivalent to 300 mg to 1,0 g of oven-dried mass of pulp to the nearest 0,1 mg (see NOTE) and transfer to a 200 ml beaker. Make sure that the test specimens taken are representative of the sample received.

The mass of the test specimen is such as to provide a minimum of 20 mg of lignin in the residue remaining after acid hydrolysis, for accurate weighing. The following can be used as a guide to the amount of pulp that should be selected for analysis, based on the lignin content:

— >10 % lignin: 300 mg pulp

— 5-10 % lignin: 500 mg pulp

— <5 % lignin: 1,0 g pulp

NOTE The amount of pulp selected for analysis also depends on whether hydrolysis procedure A or hydrolysis procedure B is used.

9 Procedure

Run the entire procedure in duplicate.

9.1 Hydrolysis

9.1.1 General

Two hydrolysis procedures are described in this Standard. In procedure A^{[7]-[9]}, the primary hydrolysis is performed at 30 °C for 1 h, followed by secondary hydrolysis in an autoclave at 120 °C for 1 h. In procedure B^{[10][11]}, the primary hydrolysis is performed at 15 - 20 °C for 2 h, followed by secondary hydrolysis in a water bath at 100 °C for 4 h.

NOTE Boiling under reflux is not allowed if acid-soluble lignin is to be determined in the solution (TAPPI T222, Section 9.4, NOTE 6). This is due to the possible contribution of furfural compounds to the acid-soluble lignin, if not removed in this step (Ref.2, p. 192).

Both procedures have been shown to give the same results^[7]; thus either one can be used for determining acid-insoluble lignin. However, procedure A is considerably more rapid, and the use of

an autoclave allows multiple samples to be hydrolysed simultaneously with minimum supervision. As such, it is now more commonly used in laboratories equipped with an autoclave.

NOTE Procedure A is therefore the preferred method and is used when analysis of carbohydrates is required, in addition to the determination of lignin.

9.1.2 Hydrolysis procedure A

Hydrolysis procedure A is based on the use of 300 mg of pulp. This procedure is more commonly used in laboratories equipped with an autoclave, and is similar to that described in other methods^{[7]-[9]} in situations in which analysis of carbohydrates is required, in addition to analysis of lignin.

For larger pulp specimens, the acid concentrations for both primary and secondary hydrolysis must remain the same as those used for 300 mg of pulp; thus the volume of solutions must be adjusted accordingly.

Add 3,0 ml of 72 % sulfuric acid (6.2) to the test specimen in the beaker. Add the acid gradually in small increments while stirring and macerating the material with a glass rod. To avoid losses, ensure that no material is sticking to the glass rod when it is removed.

NOTE Some pulps do not absorb the acid and therefore do not disperse readily. In such cases, after addition of acid, place the beaker under vacuum, in a vacuum desiccator for at least 15 minutes to facilitate wetting and absorption.

Place the beaker in a water bath adjusted to $30 \pm 1,0$ °C for 1 h. Stir occasionally.

Add 84,0 ml of water. Mix, cover the beaker with aluminium foil and place it in an autoclave at (120 ± 3) °C for 1 h. Allow the insoluble lignin to settle and for the beaker and contents to cool to approximately 80 °C.

NOTE In some cases, the lignin requires an overnight or a longer period to settle, especially if it is finely dispersed.

9.1.3 Hydrolysis procedure B

Hydrolysis procedure B is based on the use of 1,0 g of pulp, and is similar to that described in other methods^{[10][11]}. This procedure is also used in some laboratories.

NOTE Hydrolysis procedure B is not used when carbohydrate analysis is also required.

For smaller pulp specimens, the acid concentrations for both primary and secondary hydrolysis must remain the same as those used for 1,0 g of pulp; thus the solution volumes shall be adjusted accordingly.

Place the beaker with the test specimen in a water bath (5.2) at 20 ± 1 °C and add gradually 20,0 ml of 72 % sulfuric acid (6.2), maintaining a reaction temperature of 20 ± 1 °C. Stir thoroughly with a glass rod for about 1 min. To avoid losses, ensure that no material is sticking to the glass rod when it is removed.

NOTE Some pulps do not absorb the acid and therefore do not disperse readily. In such cases, after addition of acid, place the beaker under vacuum, in a vacuum desiccator for at least 15 min to facilitate wetting and absorption.

Keep the beaker in the bath for 120 ± 10 min with occasional stirring.

Transfer the material quantitatively from the beaker into a 1 000 ml Erlenmeyer flask and dilute with water to 750 ml.

Boil the solution for 4 h, maintaining a constant volume of solution by frequent addition of hot (80-90 °C) water. Allow the insoluble lignin to settle and for the flask and contents to cool to approximately 80 °C.

NOTE In some cases, the lignin requires an overnight or a longer period to settle, especially if it is finely dispersed.