Kraft lignins – Lignin and carbohydrate content – Acid hydrolysis method

0 Introduction
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1 Scope
This Innventia Test Method document describes a method for the determination of lignin content and carbohydrate content in kraft lignins.

The procedure is based on the sulphuric acid hydrolysis of the samples. This method makes it possible to determine concentrations of individual anhydrous monosaccharides down to 1 mg/g oven-dry sample and lignin content, measured as the sum of the amount of acid-insoluble matter and acid-soluble matter after sulphuric acid hydrolysis, down to 10 mg/g oven-dry sample.

2 Normative references
The following referenced documents are indispensable for the application 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.

Innventia Test Methods Kraft lignins – Dry matter content – Oven-drying method
L 1:2016

3 Terms and definitions
For the purposes of this Innventia Test Method, the following definitions apply:

3.1 Kraft lignin
Solid matter containing mainly degraded lignin isolated from a kraft pulping process (e.g. isolated from a kraft black liquor).

3.2 Lignin content
The sum of the amount of acid-insoluble matter and acid-soluble matter, absorbing at 205 nm, after sulphuric acid hydrolysis, as determined by gravimetry and spectrophotometry according to this method, in a sample, in milligrams per gram.

3.3 Carbohydrate content
The sum of the amounts of the five principal, neutral monosaccharides; arabinose, galactose, glucose, mannose and xylose in anhydrous form, in a sample, in milligrams per gram.

4 Principle
The samples are hydrolyzed with sulphuric acid using a two-step technique.

The amounts of the different monosaccharides are determined using ion chromatography (IC).

The amount of lignin is determined using gravimetry and spectrophotometry.

5 Reagents
All chemicals must be of analytical grade.
5.1 Water
Water, of high purity, distilled or deionized.

5.2 Monosaccharide standards
Monosaccharide standards, for calibration: arabinose, galactose, glucose, mannose and xylose.
Prepare standard solutions of appropriate concentrations.

5.3 Sulphuric acid
72% H₂SO₄. Add 300 ml of water to 1000 ml volumetric flask. Add slowly 670 ml of concentrated sulphuric acid (H₂SO₄ sp gr 1.84) while cooling under a cold water tap. When the temperature has reached equilibrium with the ambient temperature, dilute to the mark and mix.

5.4 Eluent solution (for IC determination)
The composition of this solution depends on the type of IC column to be used. Therefore, follow the recommendations given by the IC column supplier.

6 Apparatus
Ordinary laboratory equipment and the following:

6.1 Analytical balance, accurate to 0.1 mg.

6.2 Water bath at a temperature of (30 ± 0.5) ˚C.

6.3 Autoclave at a temperature of (120 ± 5) ˚C.

6.4 Drying oven, (105 ± 3) ˚C.

6.5 Ion-chromatograph (IC) with a suitable column and detector for monosaccharide determination.

6.6 Glass fibre filters (or equivalent).

6.7 Spectrophotometer capable of measuring the absorption at 205 nm.

7 Sampling
The sampling procedure is not covered by this method. Make sure that the test portions taken are representative of the sample received.

8 Procedure

8.1 Determination of dry matter content
Weigh a portion of the sample material and determine the dry matter content in accordance with Innventia Test Method L 1:2016.

Note
Samples with high moisture content (ie. dry matter content less than approximately 90%) should be air-dried prior to the analysis.

8.2 Test material preparation
Carry out the preparation and testing in duplicate.

Weigh a test portion of (100 ± 10) mg to the nearest 0.1 mg into a glass beaker with a volume of at least 150 ml.

Calculate and record the oven-dry weight \( W \) of the test portion, in grams.

8.3 Hydrolysis
To the test material in the beaker, add exactly 1 ml of 72% sulphuric acid (5.3) with a pipette. Stir the contents of the beaker with a glass rod until the test material begins to dissolve. Place the beaker in a (30 ± 0.5) ˚C water bath for 1 h. Stir occasionally. Add 28 ml of water (5.1).

Cover the beaker with aluminium foil and place it in autoclave (6.3) at (120 ± 5) ˚C for 1 h. Allow the beaker and its contents to cool to approx. 80 ˚C.

8.4 Determination of acid-insoluble residue (AIR)
Filter the content of the beaker while still hot through a single or double pre-weighed glass fibre filters. Transfer the filtrate to a separate beaker (this filtrate is used for the determination of acid-soluble lignin). Wash the retained residue with hot water until acid free (check with pH-indicator paper). Remove the filter with residue from the filter container carefully and allow it to dry overnight at 105°C, cool down in exsiccator and determine weight increase (ie. the acid-insoluble residue).

8.5 Determination of acid-soluble lignin (ASL)
Determine the content of acid-soluble lignin in the first filtrate (in step 4) by spectrophotometry at 205 nm. Dilute the filtrate until the absorption is in the range 0.2–0.7 AU.
8.6  Determination of saccharides

8.6.1  Solution preparation
Transfer the test solution from the beaker to a 250 ml volumetric flask, allow it cool to room temperature and fill up to the mark with water.

8.6.2  Calibration
Calibrate the device using the monosaccharide standard solutions. Use the conditions recommended by the manufacturer or determine the optimum conditions empirically. The optimum conditions depend on the apparatus and the column.

Determine the calibration factor \( k_i \) for each monosaccharide as the chromatographic area per milligram of monosaccharide

8.6.3  Determination
Filter the test solution and inject an aliquot into the instrument. Record the dilution factor \( D \).

Run the determination according to the manufacturer’s instructions.

Check from the chromatogram that the separation is adequate. If necessary, dilute the sample further until the concentration is within the calibration range and record the new dilution factor, \( D \). Run a new determination.

Determine the chromatographic area \( A_i \) for each monosaccharide

9  Calculations

9.1  Acid-insoluble residue (AIR)

\[
AIR = \frac{m}{M} \cdot 1000 \text{ mg/g}
\]

where:

\( m \) is the weight (ie. the residue after drying), in g;

\( M \) is the oven-dry weight of sample (ie. as 100% dry matter) before acid hydrolysis/suspension, in g.

9.2  Acid-soluble lignin (ASL)

\[
ASL = \frac{A \cdot D \cdot V}{a \cdot b \cdot M} \cdot 1000 \text{ mg/g}
\]

where:

\( A \) is the absorption at 205 nm;

\( D \) is the dilution factor;

\( V \) is the volume of the filtrate, in l (here: 0.029 l);

\( a \) is the extinction coefficient of lignin, in g/l cm (here: 110 g/l cm, according to TAPPI UM 250);

\( b \) is the cuvette path length, in cm (here: 1 cm);

\( M \) is the oven-dry weight of sample (ie. as 100% dry matter) before acid hydrolysis/suspension, in g;

9.3  Total lignin content

Total lignin content = AIR + ASL

9.4  Saccharides

Calculate the anhydrous content of each monosaccharide from the expression:

\[
X_i = A_i \cdot C_i \cdot D / (W \cdot k_i)
\]

where:

\( X_i \) is the content of anhydrous monosaccharide \( i \) in the oven-dry sample, in milligrams per gram;

\( A_i \) is the chromatographic area of monosaccharide \( i \), in area units (i.e. signal ∙time);

\( C_i \) is the anhydrous factor for monosaccharide \( i \) (0.88 for xylose and arabinose, 0.90 for glucose, mannose and galactose);

\( D \) is the dilution factor (depending on procedure chosen);

\( W \) is the oven-dry weight of the sample, in grams;

\( k_i \) is the calibration factor for monosaccharide \( i \), in chromatographic area per milligram of monosaccharide.

Report the results to the nearest whole number.
Calculate the relative content of each monosaccharide from the expression:

\[ Y_i = 100\% \cdot \frac{X_i}{X_{tot}} \]  

(2)

where:

- \( Y_i \) is the relative content of anhydrous monosaccharide \( i \), in per cent;
- \( X_i \) is the content of anhydrous monosaccharide \( i \) in the oven-dry sample, in milligrams per gram;
- \( X_{tot} \) is the total content of anhydrous monosaccharides in the oven-dry sample, in milligrams per gram.

Report the results to the first decimal place.

10 Report

The test report shall include the following information:

a) A reference to this test method;

b) Date and place of testing;

c) Identification of the sample tested;

d) The results expressed as the contents of acid-insoluble residue (in milligrams per gram);

e) The content of acid-soluble lignin (in milligrams per gram);

f) The extinction coefficient used for calculation of the content of acid-soluble lignin (here: 110 g/l cm, according to TAPPI UM 250);

g) The contents of the individual anhydrous monosaccharides in the oven-dry sample (in milligrams per gram);

h) The relative contents of the anhydrous monosaccharides (in per cent);

i) The reference monosaccharides used for calibration;

j) Information regarding any departure from the procedure described in this test method and/or any other circumstances that may have affected the result.

11 Precision

11.1 Repeatability

The carbohydrate and lignin content of a lignin sample isolated from softwood kraft black liquor was determined using the procedure described. The mean values and coefficients of variation of the reported contents (here, based on six parallel determinations during repeatability conditions) are given in Table 1.

<table>
<thead>
<tr>
<th>Monosaccharide</th>
<th>Mean content, mg/g</th>
<th>Relative standard deviation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arabinose</td>
<td>2</td>
<td>1.7%</td>
</tr>
<tr>
<td>Galactose</td>
<td>5</td>
<td>3.1%</td>
</tr>
<tr>
<td>Glucose</td>
<td>1</td>
<td>2.6%</td>
</tr>
<tr>
<td>Xylose</td>
<td>2</td>
<td>2.1%</td>
</tr>
<tr>
<td>Mannose</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Total carbohydrate content</td>
<td>10</td>
<td>2.4%</td>
</tr>
</tbody>
</table>

n.d. = not determined (<1 mg/g)

11.2 Reproducibility

Reproducibility information is currently not available for this test method.

12 References

- F Aldaeus, H Schweinebarth, P Törngren, A Jacobs, Simplified determination of total lignin
content in kraft lignin samples and black liquors,
Holzforschung 65 (2011) 601–604