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Lignins — Determination of carbohydrate composition in kraft lignin, soda lignin and hydrolysis lignin

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Foreword

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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.

Introduction

There is a rapidly-growing worldwide interest in developing novel applications for lignin as a replacement for fossil-based raw materials in products including carbon fibre, adhesives, thermoplastics, resins, composites, and various chemicals. In addition, the use of lignin in these and other applications will offload recovery boilers in pulp mills, allowing more efficient recovery of pulping chemicals and increased pulp production. These benefits translate into reduced environmental impact and improved sustainability owing to the use of renewable materials.

In order to ensure harmonization of testing practices among lignin producers and to facilitate trade, the use of international standard methods is needed to characterize the lignin raw material for a wide range of properties such as general composition, functional groups, molecular weight distribution, particle size, structural features, and thermal behaviour and stability.

The carbohydrate composition - the contents of the five principal, neutral monosaccharides; arabinose, galactose, glucose, xylose and mannose - provides chemical information about the main polysaccharides in lignin. The total content and composition of carbohydrates also provide an indication of the purity of the lignin isolated from the kraft pulping process (kraft lignin) or the soda pulping process (soda lignin), or that obtained by hydrolysis of biomass (hydrolysis lignin).

The methods described in this document are based on those described in other publications[1][2]. Although the principle is similar to that described in ISO 21437[3] and other related methods[4][5][6] for the determination of carbohydrates in pulp, the properties and end-use applications of lignin, as well as several steps in the testing procedure, including sampling, sample preparation, and others, are different from those of pulp.

Lignins — Determination of carbohydrate composition in kraft lignin, soda lignin and hydrolysis lignin

1 Scope

This document describes a method for the determination of carbohydrate composition in kraft lignin, soda lignin and biorefinery lignin.

The method is applicable to lignin isolated from a kraft pulping process, a soda pulping process, or lignin obtained by hydrolysis of biomass.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

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

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

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

— IEC Electropedia: available at https://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 the cell walls and to plants as a whole

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

3.2
kraft lignin
depolymerized and chemically modified lignin isolated from a kraft pulping process, such as that originating from kraft black liquor

3.3
soda lignin
depolymerized and chemically modified lignin isolated from a soda pulping process, such as that originating from soda liquor

3.4
hydrolysis lignin
lignin produced for commercial applications by conversion of biomass, through enzymatic or acid hydrolysis, into sugars and lignin streams, followed by separation of the lignin fraction

3.5
biomass
biological material derived from living, or previously living organisms, such as wood, agricultural crops, and other plant-based biodegradable material

3.6
acid-insoluble lignin
Klason lignin
residue after treating wood or pulp with sulfuric acid in a two-step hydrolysis procedure to solubilize the carbohydrates into monosaccharides

3.7
acid-soluble lignin
portion of lignin that is soluble during the acid-insoluble lignin determination

3.8
carbohydrate composition
amounts of the five principal, neutral monosaccharides; arabinose, galactose, glucose, mannose and xylose, in a sample

4 Principle

A lignin sample is treated with sulfuric acid in a two-step (primary and secondary) hydrolysis process to dissolve the carbohydrates. The acid-insoluble lignin is filtered off. The filtrate consists of hydrolysed carbohydrates and a small amount of acid-soluble lignin. The amounts of the different monosaccharides in the filtrate are determined using either ion chromatography (IC) or gas chromatography (GC) in the presence of an internal standard to validate the results. If GC is used, the hydrolysed sample is reduced and acetylated, and the resulting alditol acetates of the monosaccharides are then separated and determined by GC.

5 Apparatus

5.1 Filtration equipment

5.1.1 Filtering flask, 250 ml.

5.1.2 Gooch filtering crucible, fritted glass, medium or fine porosity, 30 ml; adapter for the filtering crucible, siphon tube (optional).

NOTE 1 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. 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.

NOTE 2 Other types of filtering crucibles, such as alundum or porous porcelain crucibles lined with a mat of fine fibres can also be used.

5.2 Constant temperature water bath, capable of maintaining a temperature of (30 ± 1) °C.

5.3 Autoclave, capable of maintaining a temperature of (120 ± 3) °C.

5.4 Drying oven, conduction type, maintained at (105 ± 2) °C.

A convection oven shall not be used, as this could lead to increased flare-ups and fire hazard, as well as loss of sample due to material being ejected from the crucible.

5.5 Analytical balance, accurate to 0,1 mg.

5.6 Equipment specific to the determination method

5.6.1 IC determination

Ion chromatograph (IC) with an anion-exchange column for monosaccharide determination and pulsed amperometric detector (PAD)

5.6.2 GC determination

5.6.2.1 Water bath, maintained at a temperature of (40 ± 0,5) °C.

5.6.2.2 Gas chromatograph (GC) with a suitable column for monosaccharide determination and flame ionization detector (FID).

6 Reagents

All chemicals shall be of ACS or reagent grade.

6.1 Water, of high purity, distilled or deionized.

6.2 Monosaccharide standards

Monosaccharide standards, for calibration: arabinose, galactose, glucose, mannose and xylose. Prepare standard solutions of appropriate concentrations, each standard solution containing all five monosaccharides.

6.3 Sulfuric acid, 72 % (720 g/kg, 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 tap. 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.

6.4 Petroleum ether.

6.5 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.

Reagents 6.6. to 6.13 are required only for GC determinations:

NOTE Alternative reagents (to those in 6.6 to 6.13) and procedures (to those in 10.3.3.1, 10.3.3.2 and 10.3.3.3) for the neutralization, reduction and derivatization steps, such as those described in TAPPI T249[6] can also be used, provided that it is indicated in the report.

6.6 Ammonia, NH_3 conc. 25 % (g/100 g) 13 M (moles/l).

6.6.1 Ammonia, 12 M (moles/l). Mix 9 parts ammonia (25 %) with 1 part water.

6.7 Potassium hydroxide, KOH 7,5 M Weigh 105 g KOH pellets into a 250 ml beaker. Add approximately 150 ml water (6.1) while stirring. Transfer the solution into a 250 ml volumetric flask, using an additional 20 ml to 30 ml of water to rinse the beaker in order to complete the transfer. Allow the solution to cool to ambient temperature and dilute it to the mark with water.

6.8 Potassium borohydride, KBH_4 solution.

Dissolve 150 mg KBH_4 in 250 µl 13 M NH_3 and 750 µl distilled water in a septum vial (4 ml).

This solution shall be freshly prepared before use.

6.9 Acetic acid, CH_3COOH, concentrated.

6.10 Acetic acid anhydride, concentrated.

6.11 1-methylimidazole.

6.12 Ethanol, 95 ml/100 ml to 99 ml/100 ml (95 % to 99 %).

6.13 Sodium sulfate, Na_2SO_4, water-free.

6.14 2-Deoxy-galactose.

6.14.1 Internal standard solution, 2-deoxy-galactose 20 mg/ml.

Weigh 1,00 g 2-deoxy-galactose to the nearest 0,1 mg, transfer it quantitatively to a 50 ml volumetric flask, and dilute to the mark with distilled water.

Other internal standards than 2-deoxy-galactose, such as fucose or myo-inositol, can also be used. However, this shall be specified in the report.

7 Sampling

Obtain a representative sample of lignin equivalent to about 2 g to 3 g on an air-dry basis. Report the origin of the sample and the sampling procedure. In particular, if the sample is first ground to ensure its homogeneity, and/or a sieving step is required in order to obtain samples with a uniform particle size or narrow particle size distribution, this shall be reported.

Lignin samples can contain a significant amount of resins. The resins shall be extracted with petroleum ether before testing. The percentage resin in the sample and the extraction method shall be included in the test report.

Extraction with petroleum ether should be carried out by a method similar to that described in ISO 14453[7].

Although acetone is an effective solvent for extracting resin, it cannot be used here since it will also dissolve part of the lignin.

NOTE Resins, if not extracted from lignin samples prior to analysis, will remain insoluble in acid and be weighed as acid-insoluble lignin.

8 Drying

Prior to drying to complete dryness, lignin samples shall be air-dried to over 75 % (g/100 g) solids. This step is necessary in order to minimize the extent of lignin degradation reactions and the drying period.

Determine the dry matter content of the lignin by drying a 2 g to 3 g specimen in an oven (5.4) at (105 ± 2) °C initially for 2 h, and then for additional 1-h periods up to a maximum of 7 h, until the difference in mass between two successive dryings in a desiccator, does not exceed 0,5 % mass fraction (g/100 g) of the test piece before drying.

9 Test Specimens

Weigh (5.5) a test specimen, equivalent to about 100 mg of oven-dried lignin, to the nearest 0,1 mg and transfer to a 100 ml beaker. Calculate and record the oven-dry mass *W* of the test portion, in grams.

10 Procedure

10.1 General

Carry out the entire procedure in duplicate.

10.2 Hydrolysis

Add 1,0 ml of 72 % sulfuric acid (6.3) to the test specimen in the beaker. Stir the contents of the beaker with a glass rod. To avoid losses, ensure that no material is sticking to the glass rod when it is removed. Place the beaker in a (30 ± 1) °C water bath (5.2) for 1 h. Stir occasionally.

Add 28 ml of water (6.1). Mix, cover the beaker with aluminium foil and place it in autoclave (5.3) at (120 ± 3) °C for 1 h. Remove the beaker from the autoclave and allow the beaker and its contents to cool to approximately 80 °C.

NOTE If the lignin is finely dispersed, it can require overnight or longer to settle.

10.3 Determination of monosaccharides

10.3.1 General

Carry out the determination according to either 10.3.2 or 10.3.3.

NOTE The determination of carbohydrate composition can also be carried out by HPLC (High Performance Liquid Chromatography), as mentioned in Reference [4] for example, provided that the results have been validated against those obtained with this document.

10.3.2 Determination using an IC instrument

10.3.2.1 Solution preparation

Without stirring the residue remaining after hydrolysis (from 10.2), which consists primarily of insoluble lignin, decant or siphon off the supernatant solution through a filtering crucible (5.1.2) into a 250 ml filtering flask (5.1.1). Transfer the filtrate to a 250 ml volumetric flask. Wash the precipitate on the filtering crucible with 2 × 30 ml warm water and add the washings to the volumetric flask. Rinse the filtering flask with a small amount of water and add the rinsings to the 250 volumetric flask. Add an appropriate volume of the internal standard 2-deoxy-galactose solution (6.14.1). Allow to cool to room temperature and fill up to the mark with water.

NOTE 1 The acid-insoluble lignin and acid-soluble lignin can be determined from the residue after hydrolysis, and from the filtrate in the volumetric flask, respectively, as described in ISO 24196[8].

NOTE 2 Transfer of the filtrate to a volumetric flask is not necessary if the determination of acid-soluble lignin is not required.

NOTE 3 Addition of the internal standard at this stage ensures that the ratio of monosaccharides to internal standard remains fixed throughout the entire procedure.

10.3.2.2 Calibration

Calibrate the IC instrument (5.6.1) using the monosaccharide standard solutions (6.2) containing the internal standard 2-deoxy-galactose (6.14.1). Use the conditions recommended by the manufacturer or

determine the optimum conditions empirically. The optimum conditions depend on the apparatus and the column.

10.3.2.3 Determination of chromatographic areas of monosaccharides

Filter the test solution from 10.3.2.1 through a syringe filter, with a PVDF membrane with a pore size of 0,45 µm or equivalent. Dilute this sample to a concentration that is within the calibration range. Inject an aliquot into the instrument.

Run the determination according to the manufacturer's instructions.

Check from the chromatogram that the peak separation is adequate. If necessary, dilute the sample further until the concentration is within the calibration range. Run a new determination.

Determine the chromatographic area A_i for each monosaccharide.

10.3.3 Determination using a GC instrument

Without stirring the residue remaining after hydrolysis (from 10.2), consisting primarily of insoluble lignin, decant the supernatant from the hydrolysis step (10.2) through a filtering crucible (5.1.2) into a 100 ml filtering flask (5.1.1). Transfer the filtrate to a 100 ml volumetric flask. Wash the precipitate on the filtering crucible with 2 × 5 ml warm water and add the washings to the volumetric flask. Rinse the filtering flask with a small amount of water and add the rinsings to the volumetric flask. Add 2 ml of the standard 2-deoxy-galactose solution (6.14.1).

Allow the sample to cool and dilute with water to the mark.

NOTE 1 The acid-insoluble lignin and acid-soluble lignin can be determined from the residue after hydrolysis, and from the filtrate in the volumetric flask, respectively, as described in ISO 24196[8].

NOTE 2 Transfer of the filtrate to a volumetric flask is not necessary if the determination of acid-soluble lignin is not required.

NOTE 3 Addition of the internal standard at this stage ensures that the ratio of monosaccharides to internal standard remains fixed throughout the entire procedure.

NOTE 4 Alternative reagents (to those in 6.6-6.13) and procedures (to those in 10.3.3.1, 10.3.3.2, and 10.3.3.3) for the neutralisation, reduction and derivatization steps, such as those described in TAPPI T249,[6] can also be used provided this is indicated in the report.

10.3.3.1 Neutralization

Transfer 1 ml of the solution from the 100 ml volumetric flask (from 10.3.3) to a test tube.

Add 100 µl of 12 M ammonia (6.6.1). Check with a glass capillary and a pH indicator paper that the pH is at or close to 7.

The pH should be checked before adding the entire 100 µl of ammonia to ensure that it is at or close to 7. If the solution becomes alkaline, reversion of the monosaccharides can occur[6].

10.3.3.2 Reduction

Add 100 µl of freshly prepared KBH_4-solution (6.8) to the neutralized supernatant solution from 10.3.3.1, and place the test tube in a water bath (5.6.2.1) at 40 °C for 1 h.

The test tube shall not be sealed since hydrogen gas is generated during this step.

Add 100 µl of concentrated acetic acid (6.9) to eliminate the excess of KBH_4.

10.3.3.3 Derivatization

Transfer 500 µl of the sample to a 30 ml test tube with a screw cap. Add 500 µl of 1-methylimidazole (6.11) and 5 ml of acetic acid anhydride (6.10). Cool the tube under a cold-water tap during the addition of the acetic acid anhydride.

Tighten the cap and mix the solution carefully. Allow the tube to stand in a cold-water bath for 10 min. Add 1,0 ml of ethanol (6.12) while cooling the tubes. Mix the solution carefully. Allow the mixture to react for 10 min (when ethanol reacts with acetic acid anhydride, it gives ethyl acetate).

Add 5 ml of water, mix and place the tube in a cold-water bath. The level of the water in the water bath shall exceed the level of the mixture in the tube during the following step.

Add 5 ml of 7,5 M KOH solution (6.7), tighten the cap and mix. After a few minutes, add another 5 ml portion of 7,5 M KOH. Tighten the cap carefully and shake the tube vigorously. Allow the tubes to stand for at least 10 min until two clear phases have separated in the tube.

WARNING — It is important that the tube be cooled when the KOH solution is being added, otherwise the ethyl acetate formed will evaporate.

Transfer the upper phase (ethyl acetate) into a test tube containing a small amount of dry sodium sulfate (6.13). Do this carefully so that no water phase is transferred.

Shake the tube and allow it to stand for 5 min to10 min. Transfer the clear solution to a septum vial and seal the vial.

10.3.3.4 Calibration

Calibrate the device using the monosaccharide standard solutions containing the internal standard (6.14.1). Use the conditions recommended by the manufacturer or determine the optimum conditions empirically. The optimum conditions depend on the apparatus and the column.

10.3.3.5 Determination

Inject an aliquot of the test specimen prepared according to 10.3.3.3 into the GC instrument (5.6.2.2). Run the determination according to the manufacturer's instructions.

Check the integration of the chromatogram and the retention times for the different monosaccharides to be sure that they are adequate. If necessary, dilute the sample further until the concentration is within the calibration range. Run a new determination.

11 Calculation

Calculate the anhydrous content of each monosaccharide from Formula (1):

$$X_i = \frac{A_i \cdot W_s \cdot k_i \cdot C_i}{A_s \cdot W} \quad (1)$$

where

X_i is the content of anhydrous monosaccharide *i* in the oven-dry sample, in mg per g;

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

W_s is the mass of the internal standard, in the undiluted sample, in mg;

C_i is the anhydrous factor for monosaccharide *i* (0,88 for xylose and arabinose; 0,90 for glucose, mannose and galactose);

A_s is the chromatographic area of the internal standard;

W is the oven-dry mass of the sample, in grams;

k_i is the calibration factor for monosaccharide *i*, (dimensionless), calculated as Formula (2):

$$k_i = \frac{W_i^c \cdot A_s^c}{W_s^c \cdot A_i^c} \quad (2)$$

where

W_i^c is the mass of monosaccharide *i* in calibration mixture, in mg;

W_s^c is mass of internal standard in calibration mixture, in mg;

A_i^c is the chromatographic area of monosaccharide *i* in the calibration mixture, in area units (signal ·time);

A_s^c is the chromatographic area of the internal standard in the calibration mixture.

Report the results to the nearest whole number.

Calculate the relative content of each monosaccharide from Formula (3):

$$Y_i = \frac{100 \cdot X_i}{X_{tot}} \quad (3)$$

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 mg per g;

X_{tot} is the total content of anhydrous monosaccharides in the oven-dry sample, as the sum of the five monosaccharides, in mg per g.

Report the results to the first decimal place. In some cases, such as for arabinose, and galactose in kraft lignins, xylose in softwood kraft lignin, and mannose, the levels can be close to, or below the detection limit, and shall be reported as such.

No correction factors were used to take into account the possible degradation of monosaccharides in standard solutions during acid hydrolysis. There is no definitive evidence to support the use of such factors. In fact, it is believed that monosaccharides in standard solutions can undergo more extensive degradation during hydrolysis than the polysaccharides in the original pulp. As such, the use of correction factors in the calculation of monosaccharide concentration could overestimate the carbohydrate composition and is not recommended.

12 Precision

The precision of the method was determined by conducting a round robin study with several types of lignin samples. A description of the samples used in this study, and the repeatability and reproducibility results are presented in Annex A. Comparison of the GC/FID and IC/PAD results is shown in Annex B.

13 Test Report

The test report shall include the following information:

a) a reference to this document, i.e. ISO 24215:2022;

b) the date and place of testing;

c) all the information for complete identification of the sample;

d) the results expressed as the contents of the individual anhydrous monosaccharides in the oven-dry sample (in milligrams per gram);

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

f) the reference monosaccharides used for calibration;

g) percentage of resin in the sample and the extraction method used;

h) any departure from the procedure described in this document, or any other circumstances which may have affected the result.

Annex A
(informative)

Precision

A.1 General

In June 2020 an international round robin study was performed in which seven laboratories from four different countries: Canada (two laboratories), France, Japan (two laboratories) and Sweden (two laboratories) participated.

A total of four samples representing different types of lignins were included in the study, including a softwood kraft lignin, acid form; a hardwood kraft lignin, acid form; a hydrolysis hardwood lignin, washed; and a soda lignin, acid form. The samples were submitted to the participating laboratories for testing according to this document.

Four of the participating laboratories used ion chromatography and three used gas chromatography. There were no significant differences in results between the two methods (see Annex B).

The participants were also requested to extract the softwood kraft lignin sample with petroleum ether and to perform the carbohydrate analyses on the extracted sample.

NOTE 1 The percent petroleum ether extract of the unbleached softwood lignin sample was 1,2, based on the average values reported by six laboratories.

Repeatability and reproducibility data for arabinan, galactan, glucan, and xylan for each type of sample are shown in Tables A.1 to A.10. The anhydrous monosaccharides, as well as the Standard deviation and repeatability/reproducibility limits are all expressed in % (g/100 g) of lignin. The coefficient of variation is expressed as a percentage of the standard deviation. The levels of mannan were below the detection limits for all but the hydrolysis hardwood sample. The calculations were made according to ISO/TS 24498[9].

The repeatability and reproducibility limits reported are estimates of the maximum difference which would be expected in 19 of 20 instances, when comparing two test results for material similar to those described under similar test conditions. These estimates might not be valid for different materials or different test conditions.

NOTE 2 Repeatability and reproducibility limits are calculated by multiplying the repeatability and reproducibility standard deviations by 2,77, where 2,77 = 1,96 √2.

As noted by the data in Tables A.6 to A.10, there was considerable variability in results among laboratories, particularly for low levels of monosaccharides. Although seven laboratories participated in the round robin study, the results from fewer than seven labs were included in the statistics in a number of cases. This was due to one of several factors: the levels of monosaccharides were below the detection limits or listed as <0,5 %, duplicate measurements were not performed, or the results were considered as outliers and were not included in the average.

Other possible factors for the discrepancies between labs include minor errors in the procedure due to incomplete hydrolysis of the sample, differences in preparation of calibration standards, derivatization, column type and set up, signal integration, and differences in internal standards, among others. Due to the multitude of steps involved in the analysis, small errors in each step can compound to produce more significant differences in the final results.

It was also noted that even for lignin samples with high sugar contents, the reproducibility among some labs was quite poor. This confirmed that such poor reproducibility is not only due to low levels of sugars

but also to the inherent variability of chromatographic analyses between laboratories. Such variability has also been observed with other types of samples and in the analyses of other parameters.

A.2 Repeatability

Table A.1 — Estimation of the repeatability of the arabinan test

Type of lignin	Number of laboratories	Arabinan, % Mean	Standard deviation S_r, %	Coefficient of variation $C_{V,r}$, %	Repeatability limit r, %
Kraft softwood	6[a]	0,18	0,02	11,1	0,04
Kraft softwood, extracted	4[b]	0,19	0,0	0,0	0,01
Kraft hardwood	5[b]	0,22	0,01	4,5	0,02
Hydrolysis hardwood	6[c]	0,83	0,01	4,5	0,03
Soda	6[c]	0,48	0,02	4,2	0,04

[a] Below detection limit in one lab.

[b] Below detection limit in two labs.

[c] Only single determination reported by one lab.

Table A.2 — Estimation of the repeatability of the galactan test

Type of lignin	Number of laboratories	Galactan, % Mean	Standard deviation S_r, %	Coefficient of variation $C_{V,r}$, %	Repeatability limit r, %
Kraft softwood	6	0,83	0,03	3,6	0,08
Kraft softwood, extracted	5	0,80	0,04	5,0	0,11
Kraft hardwood	6	0,45	0,03	6,7	0,08
Hydrolysis hardwood	7	1,05	0,15	14,3	0,42
Soda	6	0,19	0,02	10,5	0,06

Table A.3 — Estimation of the repeatability of the glucan test

Type of lignin	Number of laboratories	Glucan, % Mean	Standard deviation S_r, %	Coefficient of variation $C_{V,r}$, %	Repeatability limit r, %
Kraft softwood	5[a]	0,18	0,01	5,6	0,03
Kraft softwood, extracted	4[a]	0,18	0,03	16,7	0,07
Kraft hardwood	5[a]	0,31	0,01	3,2	0,03
Hydrolysis hardwood	7	19,0	0,27	1,4	0,75
Soda	6[1]	0,54	0,06	11,1	0,17

[a] Below detection limit in one lab.