Protocol for round robin test of lignin content in lignin samples (COST FP0901)

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Introduction

This document is a protocol for a first round robin test of lignin content in lignin samples in the COST FP0901 action. The protocol describes two methods for the determination of total lignin content in lignin samples.

In the first method (Procedure 1), the sample is hydrolyzed similar to the standard methods for pulp samples [SCAN-CM 71:09, TAPPI T 249 cm-00], but scaled down with a factor 3 due to that the high lignin content in precipitated lignin samples cause prolonged filtering time. After the hydrolysis, the sample is filtered, the acid-insoluble residue (Klason lignin) is determined gravimetrically [TAPPI T 222 om-02], and the acid-soluble lignin is determined spectrophotometrically [TAPPI UM 250].

The second method (Procedure 2) is similar to the first method, but the hydolysis step is omitted [Aldaeus, *et al.* 2010].

Note that it is assumed that the total lignin is equal to the sum of the acid-soluble lignin and the acid-insoluble residue. No corrections for extractives or ash are included in these procedures.

Reagents

- Water, of high purity (distilled or deionized)
- Sulphuric acid (H_2SO_4), 72 %

Apparatus

Ordinary laboratory equipment and the following:

- Water bath at a temperature of (30 ± 0,5) °C .
- Autoclave at a temperature of (120 ± 5) °C
- Drying oven at a temperature of (105 ± 3) °C for the determination of dry matter content in accordance with ISO 638 and the determination of acid-insoluble residue.
- Laboratory balance
- Glass fibre filters (or equivalent)
- Spectrophotometer capable of measuring the absorption at 205 nm.

Procedure 1

Procedure 1

1. Determination of dry matter content
Weigh a portion of the sample material and determine the dry matter content by drying at 105 °C until constant weight is achieved [ISO 638].

> *Note 1*
> Samples with high moisture content (*ie.* dry matter content less than approximately 90%) should be air-dried prior to the analysis.

2. Test material preparation
Note: Carry out the preparation and testing in step 2 – 5 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 of the test portion, in grams.

3. Hydrolysis
To the test material in the beaker, add 1,0 ml of 72 % sulphuric acid 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 28,0 ml of water.
Cover the beaker with aluminium foil and place it in autoclave at (120 ± 5) °C for 1 h. Allow the beaker and its contents to cool to approx. 80 °C.

4 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).

5 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.

Procedure 2
Same as Procedure 1, but step 3 (Hydrolysis) is replaced by:

3. Acid suspension
To the test material in the beaker, add 1,0 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. Add 28,0 ml of water. Heat the beaker and its contents to approx. 80 °C, and filter the content of the beaker while still hot.

Calculations

Acid-insoluble residue (AIR)

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

where

m = the weight increase (*ie.* the residue after drying), in g
M = Oven-dry weight of sample (*ie.* as 100% dry matter) before acid hydrolysis/suspension, in g

Acid-soluble lignin (ASL):

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

where

A = Absorption at 205 nm
D = Dilution factor
V = Volume of the filtrate, in l (here: 0,029 l)
a = Extinction coefficient of lignin, in g/l cm (here: 110 g/l cm, according to TAPPI UM 250)
b = cuvette path length, in cm (here: 1 cm)
M = Weight of sample (as 100% dry matter) before acid hydrolysis/suspension, in g

Total lignin content:

$$Total\ lignin\ content = AIR + ASL$$

Report

For every sample, please report for each of the two procedures:

- the average *AIR*, in mg/g
- the average *ASL*, in mg/g
- the average *total lignin content*, in mg/g
- which filter that has been used for the determination of acid-insoluble residue
- deviations from the proposed protocol

References

- SCAN-CM 71:09, *Pulps – Carbohydrate content*, 2009, Scandinavian Pulp, Paper and Board testing Committee, Stockholm, Sweden.
- TAPPI T 222 om-02, *Acid-insoluble lignin in wood and pulp*, in: 2002-2003 TAPPI Test Methods, 2002, Tappi Press, Atlanta, GA, USA.
- TAPPI T 249 cm-00, *Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography*, in: 2002-2003 TAPPI Test Methods, 2002, Tappi Press, Atlanta, GA, USA.
- TAPPI UM 250, *Acid-soluble lignin in wood and pulp*, in: 1991 TAPPI Useful Methods, 1991, Tappi, Atlanta, GA, USA.
- F Aldaeus, H Schweinebarth, P Törngren, A Jacobs, *Investigation and simplification of the determination of lignin content in kraft lignin samples and black liquors using the Klason method*, submitted manuscript (in parts presented at 11th European workshop on Lignocellulosics and Pulp, August 16–19, 2010, Hamburg, Germany)