ISO/~~DIS~~FDIS 6350:~~2022~~2023(E)

Date: ~~2022-11-30~~2023-09-21

ISO TC 6/WG 16

Secretariat: SCC

~~Secretariat: CA~~

Lignins — Determination of dry matter content — Oven-drying and freeze-drying methods

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Published in Switzerland

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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

This document describes methods for the determination of dry matter content in lignins by oven-drying or freeze drying.

In general, freeze-drying is preferred over oven-drying at 105 °C, especially for kraft lignins in the sodium form, in order to preserve the integrity of the sample. In a study on the effect of drying on lignin solids~~,~~[1], kraft lignins – particularly hardwood lignins – in the sodium form were most affected by oven-drying. In some cases, the solids contents of oven-dried samples were over four percentage points lower than those of the corresponding freeze-dried samples.

When drying samples prior to the determination of other lignin properties, only the freeze-drying method is acceptable. Water interferes with certain lignin analyses~~,~~[2,3], and oven-drying might lead to changes in lignin structure as a result of, for example, decomposition or condensation reactions. Thus, any residual water is removed from the test specimen through lyophilization (freeze-drying). In addition, freeze-drying prevents the loss of volatile organic compounds (VOC's) which can be determined separately if required.

Several related procedures for the preparation of biomass for compositional analysis and for the determination of solids and extractives in biomass have been published by the National Renewable Energy Laboratory (NREL~~),~~[4-7]. However, the procedures described in this document are specifically applicable to lignins.

Lignins – Determination of dry matter content – Oven-drying and freeze-drying methods

1 Scope

This document describes methods for the determination of the dry matter content of lignins by oven-drying and freeze-drying. The methods are applicable to all types of lignins isolated from kraft, organosolv, soda, and sulfite pulping processes, and to lignin obtained by enzymatic or acid hydrolysis of biomass. However, the oven-drying method is not applicable to kraft lignins in the base form. Both methods apply only to lignins in the solid form.

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.

1TermsThere 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 plays 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
organosolv lignin
depolymerized and chemically modified lignin isolated from an organosolv pulping process, such as that originating from organosolv liquor

3.5
~~**lignosulfonates**~~
~~depolymerized, sulfonated, and chemically modified lignin generated from a sulfite pulping process, such as that originating from sulfite red liquor~~

~~**3.6**~~
hydrolysis lignin
lignin produced by conversion of biomass, through enzymatic or acid hydrolysis, into sugars and lignin streams, followed by separation of the lignin fraction

3.~~7~~6
biomass
biological material derived from living, or previously living organisms, such as wood, agricultural crops and other plant-based biodegradable material

3.~~8~~7
constant mass
mass of the test specimen determined at the equilibrium condition after drying until the difference between two successive drying and weighings, separated in time by at least half the initial drying period, does not exceed 0,1 % mass fraction of the test specimen before drying

4 Principle

The dry matter content is calculated from the difference in the mass of the specimen before and after drying.

5 Apparatus

5.1 Containers, appropriate for freeze-drying or oven-drying, as recommended by the manufacturer. Containers shall be water-vapour-proof with tightly fitting lids, and made from a material not affected by the conditions of the test, previously dried to constant mass and weighed.

5.2 Drying oven, capable of maintaining the air temperature at 105 °C ± 2 °C, and suitably ventilated.

5.3 Freeze-dryer, typically available with condenser refrigeration of -80 °C, and capable of maintaining a pressure (vacuum) of about 25 ~~mtorr~~mTorr.

5.4 Analytical balance, accurate to 0,1 mg.

5.5 Desiccator, using Drierite™[1] or equivalent desiccant.

[1] ~~[trade name(s) or trademark(s) of product(s)] ...~~Drierite™ is ~~(are)~~ an example~~(s)~~ of a suitable product(s) available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ~~... [~~ISO ~~or IEC] ...~~ of this ~~(these)~~ product~~(s).~~

6 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. For example, in the case of kraft lignin samples, it shall be reported whether they were collected in their base form, or after acid-washing; or as they come out of the press, partly dried, flash dried, or otherwise.

If the sample is not ~~analyzed~~analysed immediately after collection, it shall be stored in an airtight container or sealable polyethylene bag. If it is necessary to store the samples for longer than 2 days to 3 days, they shall be kept in a refrigerator or cold room at 5 °C ± 1 °C prior to use. Samples shall be brought back to room temperature before opening the container or bag.

All samples shall be air-dried to over 75 % solids prior to the determination of dry matter content or analysis of other properties. This is necessary to minimize the extent of lignin degradation reactions during the subsequent drying period.

7 Determination of dry matter content

7.1 General

The choice of method for the determination of dry matter content depends on the type of lignin sample being ~~analyzed~~analysed. Freeze-drying is preferred over oven-drying at 105 °C, especially for kraft lignins in the sodium form, in order to preserve the integrity of the sample.

In a study on the effect of drying on lignin solids,~~[11]~~[1], kraft lignins – particularly hardwood lignins – in the sodium form were most affected by drying. In some cases, the solids contents of oven-dried samples were over four percentage points lower than those of the corresponding freeze-dried samples. Thus, oven-drying is not recommended for kraft lignin samples in the sodium or base form.

The same study also showed that vacuum oven-drying at 60 °C was not an acceptable alternative to freeze-drying as the solids contents of vacuum oven-dried kraft lignin samples in the base form were lower than the corresponding freeze-dried samples.

NOTE Milder conditions of vacuum-drying can still affect the results, when the specimens are composed of extremely thermally-labile components and/or under some conditions susceptible to secondary reactions

~~7.1~~7.2 Oven-drying

7.~~1~~2.1 Weigh 1 g to 2 g of air-dried test specimen in a closed container (5.1) that has been previously dried to constant mass and weighed.

7.~~1~~2.2 Place the open container with the test piece and lid in an oven (5.2) at 105 °C ± 2 °C for 4 h.

7.~~1~~2.3 After drying, place the lid on the container and allow the test piece to cool in the desiccator (5.5).

7.~~1~~2.4 Weigh the closed container with the test piece.

7.~~1~~2.5 Repeat steps 7.~~1~~2.2 to 7.~~1~~2.4 with a drying period of 1 h until the test piece reaches constant mass, when the difference between two successive weighings does not exceed 0,1 % of the test piece mass before drying. The total drying period shall not exceed 7 h.

NOTE In a study on the effect of drying on lignin solids,~~[11]~~[1], oven-dried lignin samples reached constant weight after seven hours. Longer periods are unnecessary and are not recommended as they could result in lignin degradation. For example, it was reported that, when subjected to high temperature, lignin in the base form produces a significant quantity of monomers[9].

7.~~1~~2.6 Repeat this procedure on a new test specimen. The results of duplicate determinations shall not deviate by more than 0,5 % from their mean. Otherwise, repeat the determination with a larger test specimen.

7.~~1~~2.7 Calculate the dry matter content of the sample as described in Clause 8.

~~7.2~~7.3 Lyophilization (Freeze-drying)

7.3.1 General Lyophilization (freeze-drying) is preferred over oven-drying for the determination of dry matter content in order to preserve the integrity of the sample.

For drying samples prior to determination of lignin properties other than dry matter content, only the freeze-drying method is acceptable. Water interferes with certain lignin analyses~~,~~[~~1~~][2,3], and oven-drying might lead to changes in lignin structure as a result of, for example, decomposition or condensation reactions. Thus, any residual water shall be removed from the test specimen through lyophilization (freeze-drying). In addition, freeze-drying prevents the loss of volatile organic compounds (VOC's) which can be determined separately if required.

7.3.2.~~1~~ Weigh 1 g to 2 g of air-dried **test** specimen in a closed container (5.1) that has been previously dried to constant mass and weighed.

NOTE If lignin properties other than dry matter content are determined, a larger amount of sample is ~~required~~needed. An appropriate amount of test specimen can then be collected from the freeze-dried sample for use in other analyses. In such cases, grinding the sample with a mortar and pestle prior to freeze-drying ~~might~~can be needed in order to homogenize the sample to a uniform powder.

7.~~2.2~~3.3 Freeze the test specimen in a freezer overnight or for at least 4 h. If the sample is in slurry form, place a well-mixed sample in a container in a freezer overnight.

7.~~2.~~3.4 Dry the test specimen in a freeze-dryer (5.3) at -80 °C and at a pressure (vacuum) of about 25 ~~mtorr~~ mTorr for 24 h. Gradually increase the vacuum at the start of freeze-drying, and gradually release the vacuum to atmospheric pressure at the end of the freeze-drying period, in order to avoid scattering of the powder inside the container which can result in loss of test specimen material.

It is also recommended to attach a tissue paper to the adapter side of the vacuum dryer to avoid any scattered test specimen from entering the vacuum dryer

NOTE The use of higher freeze-drying temperatures and/or different vacuum levels ~~could require~~can necessitate longer drying times. However, these changes are acceptable provided the samples are dried to constant mass.

7.~~2.4~~3.5 Weigh the closed container with the test piece.

7.~~2.5~~3.6 Repeat steps 7.~~2.2~~3.3 to 7.~~2.4~~3.5 for a drying period of another 24 h or more, until the test piece reaches constant mass, when the difference between two successive weighings does not exceed 0,1 % of the test piece mass before drying.

7.~~2.6~~3.7 Repeat this procedure on a new test specimen. The results of duplicate determinations shall not deviate by more than 0,5 % mass fraction from their mean. Otherwise, repeat the determination with a larger test specimen.

7.~~2.7~~3.8 Calculate the dry matter content of the test specimen as described in Clause 8.