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Lignins — Determination of inorganics content in kraft lignin, soda lignin and hydrolysis lignin

Lignines — Détermination de la teneur en matières inorganiques dans la lignine kraft, la lignine soude et la lignine d'hydrolyse

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Contents

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

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Introduction

This document describes methods for the determination of the total inorganics content of kraft lignin, soda lignin and lignin obtained from hydrolysis of biomass.

The inorganics content of lignins is of high significance in several applications of lignin as a replacement of fossil-based raw materials, in products such as solid fuels, phenolic resins, polyurethane foams, thermoplastics, carbon fibre and many others. For example, when lignin is used as a fuel in the lime kiln, the ash content must be very low since it can cause bridging and ringing problems in the lime kiln[15]. Similarly, when lignin is used as a feedstock to make carbon fibersfibres, it is recommended that the ash content be less than a mass fraction of 0,1 %[26]. In the case of resole-type phenolic resins, the lignin should be in the base form (i.e. have a high inorganics content) since the process of making such resins is conducted at an alkaline pH[37].

For kraft lignin in the acid form, soda lignin, and hydrolysis lignin, the ash content determined at 525 °C is a good approximation of the total inorganics content of the samples. However, for kraft lignin in the base form, the ash content significantly overestimates - by a factor of 2 to 3 - the inorganics content of lignin. This is largely due to the fact that, upon combustion, sodium and other metals associated with the phenolic and carboxylic acid groups in lignin are converted to sodium/metal sulfate, nitrate and especially carbonate, depending on the relative ratio of sulfur, nitrogen, and carbon in the lignin. In other words, the ashing process leads to the formation of chemical species (e.g. sulfsuate, nitrate, carbonate) that were not present in the lignin itself, thereby contributing to an overestimation of the inorganics content of the lignin since essentially all organic matter is destroyed at that temperature.

This phenomenon was demonstrated by establishing a sodium mass balance for kraft lignin in the base form. The amount of sodium ions needed to balance the phenolic and carboxylic acid groups was calculated, based on their respective pKa values[48]. Good agreement was found between the total sodium and the sodium needed to balance the phenolic and carboxylic acid groups. This shows that most of the sodium in kraft lignin in the base form is present as the salt of the phenolic and carboxylic acid groups.

Thus, for kraft lignin in the base form, the total inorganics content is best determined from an analysis of sodium, along with other major inorganic elements, including calcium, potassium, magnesium, iron, manganese, and copper. The level of trace elements such as zinc, cadmium, and chromium is considered to be too low to have a significant impact on the total inorganics content.

For kraft lignin in the acid form, soda lignin, and hydrolysis lignin, the method used for determining ash content is largely based on ISO 1762[51]. For kraft lignin in the base form, the method used for determining major inorganic elements is based on ISO 12830[62].

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Lignins — Determination of inorganics content in kraft lignin, soda lignin and hydrolysis lignin

1 Scope

This method describes procedures for the determination of inorganics content in kraft, soda, and hydrolysis lignin. The method is applicable to lignin isolated from a kraft pulping process, a soda pulping process, or lignin obtained by hydrolysis of biomass.

For kraft lignin in the acid form, soda lignin, and hydrolysis lignin, the inorganics content is determined from the ash content of the sample. For kraft lignin in the base form, the inorganics content is determined from the sum of the contents of calcium, magnesium, manganese, iron, copper, sodium and potassium.

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.

~~<std>ISO 6350, *Lignins – Determination of dry matter content – Oven-drying and freeze-drying methods*</std>~~

~~<std>ISO 3696, *Water for analytical laboratory use — Specification and test methods*</std>~~

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 6350, *Lignins – Determination of dry matter content – Oven-drying and freeze-drying methods*

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~~https://www.iso.org/obp

— IEC Electropedia: available at ~~https://www.electropedia.org/~~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
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

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

3.6
residue on ignition
ratio of the mass of the residue remaining after a test specimen of lignin is ignited at 525 °C ± 25 °C to the oven-dry mass of the test specimen before ignition

3.7
inorganics content
content of chemical elements or compounds that lack carbon–hydrogen bonds

4 Principle

For kraft lignin in the acid form, soda lignin, and hydrolysis lignin, the test specimen is weighed in a heat-resistant crucible and ignited in a muffle furnace at 525 °C ± 25 °C. The dry matter content of a separate test specimen is also measured. The percentage ash is then determined, on a dry (moisture-free) basis, from the mass of residue after ignition and the dry matter content of the sample. The ash content represents the total inorganics content of the sample.

For kraft lignin in the base form, the test specimen is ashed at 525 °C ± 25 °C, as described for kraft lignin in the acid form. The residue after ashing is then dissolved in 6 mol/l hydrochloric acid, and the sodium, calcium, potassium, magnesium, iron, manganese, and copper in the resulting solution are determined by Inductively Coupled Plasma Emission Spectrometry (ICP/ES). The inorganics content is estimated from the sum of the content of these seven elements. Trace elements, such as zinc, cadmium and chromium, are not included, since their levels are considered to be too low to have a significant impact on the total inorganics content.

NOTE 1 Other techniques or instrumentation other than ICP/ES, such as ICP-mass spectrometry (ICP/MS) or atomic absorption spectrometry (AAS), can also be used provided that they have been properly validated.

NOTE 2 Only the acid-soluble form of metals is determined by this method. If acid-insoluble metals are also present, as would be the case if combined with silicates, they can be determined after digestion or fusion as described in ISO 17812[~~7~~3]. However, in most cases, the level of silicates is considered to be too low to have a significant impact on the total inorganics content.

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NOTE 3 For some applications of kraft lignin in the acid form, soda lignin, or hydrolysis lignin, analysis of individual elements can also be required. In such cases the ash is dissolved in hydrochloric or nitric acid and the concentration of each element in the resulting solution is determined as specified for kraft lignin in the base form.

5 Reagents

5.1 General

All chemicals shall be of reagent grade or better unless otherwise indicated. Water shall be distilled or deionized, of grade 2 or better in accordance with ISO 3696.

5.2 Hydrochloric acid (HCl), about 6 mol/l, trace metal grade. Dilute 500 ml of concentrated hydrochloric acid (specific gravity 1,19 g/ml) to 1 000 ml with water.

5.3 Nitric acid (HNO_3), concentrated (specific ~~gravity1~~gravity 1,4 g/ml), trace metal grade.

5.4 Standard stock solutions of each element, commercially available certified atomic emission standard solutions can be used. Standard stock solutions can also be prepared as follows:

5.4.1 Magnesium, 1 000 mg/l standard solution. Dissolve 1,000 g of magnesium metal ribbon in 100 ml of a volume fraction of 25 % nitric acid (5.3) by volume and dilute to 1 000 ml with water.

5.4.2 Calcium, 1 000 mg/l standard solution. Dissolve 2,497 g of primary standard calcium carbonate ($CaCO_3$) in a minimum volume fraction of ~~1:4 (v/v)~~25 % nitric acid (5.3) and dilute to 1 000 ml with water.

5.4.3 Manganese, 1 000 mg/l standard solution. Dissolve 1,000 g of manganese metal strip or wire in a minimum volume fraction of ~~1:1 (v/v)~~100 % nitric acid (5.3) and dilute to 1 000 ml with water.

5.4.4 Iron, 1 000 mg/l standard solution. Dissolve 1,000 g or iron metal strip or wire in 20 ml of hydrochloric acid (5.2) and dilute to 1 000 ml with water.

5.4.5 Copper, 1 000 mg/l standard solution. Dissolve 1,000 g of copper metal strip or wire in a minimum volume fraction of ~~1:1 (v/v)~~100 % nitric acid (5.3) and dilute to 1 000 ml with water.

5.4.6 Sodium, 1 000 mg/l standard solution. Ignite a portion of anhydrous sodium sulfate (Na_2SO_4) at 550 °C in a crucible of platinum or porcelain. Allow to cool to room temperature in a desiccator. Dissolve 3,089 g of dried sodium sulfate in water and dilute to 1 000 ml with water. Store in a polyethylene bottle.

5.4.7 Potassium, 1 000 mg/l standard solution. Ignite a portion of anhydrous potassium sulfate (K_2SO_4) at 550 °C in a crucible of platinum or porcelain. Allow to cool to room temperature in a desiccator. Dissolve 2,228 g of dried potassium sulfate in water and dilute to 1 000 ml with water. Store in a polyethylene bottle.

5.5 Carrier gas, appropriate for the inductively coupled plasma spectrometer. Argon is usually recommended as a carrier gas.

6 Apparatus

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

6.2 Heat-resistant crucibles, made of platinum, porcelain or silica, with a capacity of 50 ml to 100 ml.

Larger-capacity crucibles may also be used for low-density materials to accommodate sufficient sample.

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A lid of an appropriate material, placed slightly ajar to allow entry of air for combustion, may also be used with the crucible to help prevent low-density or flyaway material from escaping during the ash ignition process.

Platinum crucibles are recommended if a small amount of residue is expected.

6.3 Muffle furnace, capable of maintaining a temperature of 525 °C ± 25 °C. It is recommended that the furnace be placed in a hood or that means be provided for evacuating smoke and fumes.

6.4 Analytical balance, with a scale division (readability) of 0,1 mg or better in order to obtain a measurement precision of 0,01 % or better.

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

6.6 Inductively coupled plasma/emission spectrometer (ICP/ES), for determination of inorganics content in kraft lignin in the base form only and if determination of individual elements is performed on kraft lignin in the acid form, soda lignin, or hydrolysis lignin

6.7 Freeze-dryer, (only if freeze-drying is used for the determination of moisture content) typically available with condenser refrigeration of -−80 °C, and capable of maintaining a pressure (vacuum) of about 3,33 Pa (25 mtorr.).

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. 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 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.

NOTE Larger amounts of sample are recommended if the analysis of minor elements, such as manganese, iron, or copper, is required.

8 Procedure

8.1 Overview

Subclauses 8.2 to 8.4 applies to all types of lignin. For kraft lignin in the acid form, soda lignin, and hydrolysis lignin, the inorganics content is determined from the measurement of the residue on ignition, as described in 8.4.2 and 10.1. However, for kraft lignin in the base form, the inorganics content is determined from the analysis of individual elements, as described in 9.4 and 10.2.

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