



Technical Specification

ISO/TS 23361

Nanotechnologies — Crystallinity of cellulose nanomaterials by powder X-ray diffraction (Rietveld analysis)

*Nanotechnologies — Cristallinité des nanomatériaux à base de
cellulose par diffraction aux rayons X sur poudre (analyse de
Ruland-Rietveld)*

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Contents

	Page
Foreword	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Terms and definitions	1
3.1 Core nanotechnology terms related to cellulose nanomaterials.....	1
3.2 Non-nanotechnology terms related to cellulose nanomaterials.....	2
3.3 Terms specific to cellulose nanomaterials.....	2
4 Principle	4
5 Sample preparation	5
5.1 General considerations.....	5
5.2 Preparation of samples from powders.....	5
6 Instrument and software requirements	6
6.1 Diffractometer.....	6
6.2 Software.....	6
6.3 Crystallographic information files.....	6
7 Data collection	6
8 Data processing and analysis	7
8.1 General considerations.....	7
8.2 Modelling procedure.....	8
9 Uncertainty	10
10 Test report	11
Annex A (informative) Results of interlaboratory comparison	12
Bibliography	21

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Foreword

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This document was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

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.

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Introduction

Cellulose nanomaterials (CNM) are a family of emerging bioproducts with significant commercial impact. Their production from abundant cellulose sources such as wood pulps makes them a candidate for use as a potentially non-toxic, biodegradable and sustainable nanomaterial for a wide range of applications, including those that currently use petroleum-based components. Several types of CNM are currently produced in a number of countries on pilot, pre-commercial or commercial scales. Realizing the full potential of these materials requires standard methods for characterization of a range of material properties, including crystallinity. Crystallinity is an indication of material quality, success of processing, and degradation of the material during processing, which can affect performance for various applications, particularly for use in nanocomposites. Crystallinity is also important for distinguishing between CNC grades and products and ensuring batch control and repeatability, and can provide information on the cellulose source and production method.

Crystallinity of CNM is defined as the fraction of the material composed of crystallites. There are several approaches for measuring crystallinity of materials, including powder X-ray diffraction, differential scanning calorimetry and solid-state nuclear magnetic resonance. Each of these techniques obviously has its merits and limitations. Use of crystallinity for quality control purposes for CNM production and further processing requires a measurement method that can be quickly, routinely and reproducibly implemented and that is easily accessible and can be run in most laboratories with the same level of proficiency. Powder X-ray diffraction addresses these criteria. This technical specification describes the measurement of CNM crystallinity by powder X-ray diffraction using deconvolution of the diffraction pattern based on Rietveld analysis. The Rietveld method allows a diffraction profile to be modelled based on known diffraction peaks for a specific crystallographic structure by attempting to minimize the difference between the calculated and observed patterns by the least-squares method.

The Rietveld method requires that the powder diffraction pattern be representative of the sample, which requires careful sample preparation and assumes a randomly oriented sample. The instrument configuration and detector sensitivity are also important. This document provides guidance on both sample preparation and instrument configuration and operating parameters. The method is applicable to all types of CNM, including cellulose nanocrystals, cellulose nanofibrils and cellulose filaments.

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Nanotechnologies — Crystallinity of cellulose nanomaterials by powder X-ray diffraction (Rietveld analysis)

1 Scope

This document specifies the determination of the bulk crystallinity (crystalline contribution relative to the total crystalline and amorphous contributions in the material) of cellulose nanomaterials using powder X-ray diffraction followed by deconvolution of the diffraction patterns based on Rietveld analysis. It is applicable to all types of cellulose nanomaterials, assuming a representative sample.

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 Core nanotechnology terms related to cellulose nanomaterials

3.1.1

nanoscale

length range approximately from 1 nm to 100 nm

[SOURCE: ISO 80004-1:2023, 3.1.1]

3.1.2

nanomaterial

material with any external dimension in the *nanoscale* (3.1.1) or having internal structure or surface structure in the nanoscale

Note 1 to entry: Certain types of nanomaterials include engineered, manufactured and incidental nanomaterials.

Note 2 to entry: The nanoform of a material is a nanomaterial.

[SOURCE: ISO 80004-1:2023, 3.14, modified — Note 1 to entry has been adapted to this document.]

3.1.3

nano-object

discrete piece of material with one, two or three external dimensions in the *nanoscale* (3.1.1)

[SOURCE: ISO 80004-1:2023, 3.1.5]

3.1.4

nanofibre

nano-object (3.1.3) with two similar external dimensions in the *nanoscale* (3.1.1) and the third dimension significantly larger

Note 1 to entry: The largest external dimension is not necessarily in the nanoscale.

[SOURCE: ISO 80004-1:2023, 3.3.5]

3.1.5

nanocrystal

nano-object (3.1.3) with a crystalline structure

[SOURCE: ISO 80004-1:2023, 3.1.15]

3.2 Non-nanotechnology terms related to cellulose nanomaterials

3.2.1

crystalline

having a solid structure with a three-dimensional arrangement of ions, molecules, or atoms with long range order

[SOURCE: ISO/TS 20477:2023, 3.2.1]

3.2.2

amorphous

regions within a polymeric material that, on the basis of X-ray diffraction or other suitable techniques, do not show any evidence of crystalline structure

[SOURCE: ISO 472:2013, 2.50]

3.2.3

paracrystalline

having short and medium range ordered lattice structure and lacking long range order in at least one direction; in the intermediate state between *crystalline* (3.2.1) and *amorphous* (3.2.2)

[SOURCE: ISO/TS 20477:2023, 3.2.2]

3.2.4

cellulose

linear polymeric chains of β (1 \rightarrow 4) linked D-glucopyranose units

[SOURCE: ISO/TS 20477:2023, 3.2.3]

3.2.5

elementary fibril

structure, originating from a single terminal enzyme complex, having a configuration of cellulose chains specific to each cellulose-producing plant, animal, algal and bacterial species

[SOURCE: ISO/TS 20477:2023, 3.2.4]

3.3 Terms specific to cellulose nanomaterials

3.3.1

cellulose nanomaterial

CNM

material composed predominantly of *cellulose* (3.2.4), with any external dimension in the *nanoscale* (3.1.1), or a material having internal structure or surface structure in the nanoscale, with the internal structure or surface structure composed predominantly of cellulose

Note 1 to entry: Some cellulose nanomaterials can be composed of chemically modified cellulose.

Note 2 to entry: This term is inclusive of cellulose nano-object and cellulose nanostructured material.

[SOURCE: ISO/TS 20477:2023, 3.3.1]

3.3.2

cellulose nanofibre

nanofibre (3.1.4) composed predominantly of *cellulose* (3.2.4)

Note 1 to entry: This definition is a description of the morphology and the size of an object. It should not be confused with wood fibres or wood pulp fibres which typically have diameters of tens of micrometres.

[SOURCE: ISO/TS 20477:2023, 3.3.4]

3.3.3

cellulose nanocrystal

CNC

nanocrystal (3.1.5) predominantly composed of *cellulose* (3.2.4) containing predominantly *crystalline* (3.2.1) and *paracrystalline* (3.2.3) regions, with at least one *elementary fibril* (3.2.5), not exhibiting longitudinal splits

Note 1 to entry: The aspect ratio of cellulose nanocrystals is usually smaller than 50 but usually greater than 5, where aspect ratio refers to the ratio of the longest to the shortest dimensions.

Note 2 to entry: Cellulose nanocrystals do not exhibit interparticle entanglement or network-like structures.

Note 3 to entry: Historically, cellulose nanocrystals have been called nanocrystalline cellulose (NCC) and whiskers such as cellulose nanowhiskers (CNW); they have also been called spheres, needles or nanowires based on their shape, dimensions and morphology; other names have included cellulose micelles, cellulose crystallites and cellulose microcrystals.

[SOURCE: ISO/TS 20477:2023, 3.3.5, modified — Note 4 to entry has been deleted.]

3.3.4

cellulose nanofibril

CNF

cellulose (3.2.4) *nanofibre* (3.1.4) composed of at least one *elementary fibril* (3.2.5) that can contain branches, a significant fraction of which are in the nanoscale

Note 1 to entry: The dimensions are typically 3 nm to 100 nm in cross-section and typically up to 100 µm in length.

Note 2 to entry: CNF can form entanglements between particles or network-like structure when the distance between CNF fibres is sufficiently close.

Note 3 to entry: Cellulose nanofibrils from plant sources, produced by mechanical processes, can be accompanied by hemicellulose, and in some cases lignin.

Note 4 to entry: Some cellulose nanofibrils can have functional groups on their surface as a result of the manufacturing process.

Note 5 to entry: The terms nanofibrillated cellulose (NFC), nanofibrillar cellulose (NFC), microfibrillated cellulose (MFC), microfibrillar cellulose (MFC), cellulose microfibril (CMF) and *cellulose nanofibre* (3.3.2) have been used interchangeably with cellulose nanofibril. The terms microfibrillated cellulose (MFC), microfibrillar cellulose (MFC), cellulose microfibril (CMF) have also been used incorrectly to describe cellulose nanofibrils.

Note 6 to entry: The term cellulose nanoribbon has been used to describe cellulose nanofibrils from bacterial sources.

[SOURCE: ISO/TS 20477:2023, 3.3.6, modified — Note 5 to entry has been adapted to this document and Note 7 to entry has been deleted.]

3.3.5

individualized cellulose nanofibril iCNF

discrete *cellulose nanofibril* (3.3.4) composed of one *elementary fibril* (3.2.5) with ionic functional groups on its surface

[SOURCE: ISO/TS 20477:2023, 3.3.7]

4 Principle

Crystallinity of cellulose nanomaterials (CNM) is defined as the mass fraction of the material composed of crystallites. This document describes the measurement of CNM crystallinity by powder X-ray diffraction using deconvolution of the diffraction pattern based on Rietveld analysis.^{[1],[2]} The scattering due to the crystalline peaks is separated from background scattering, including any amorphous component, and the background is fit over the entire angular range.^[3] The Rietveld method fits either known crystallographic structures or peaks, or both, to collected powder diffraction data, attempting to minimize the difference between the calculated and observed patterns by the least-squares method. As such, the method adopts the original diffraction pattern in its entirety, unlike the widely used Segal method which uses the intensity of the (200) peak as an indicator of crystalline content and the minimum between the (100) and (200) peaks as the indicator of amorphous content.^[4] The minimum, which is assumed to represent the maximum of amorphous scattering, has been reported to depend on crystallite size for small crystals.^[5]

A commonly overlooked and poorly understood requirement is that the powder diffraction pattern must be representative of the sample if the Rietveld method is to be employed. This is not a trivial matter and requires stringent sample preparation.^[6] In general, the sample must be in powder form, with particles between 1 µm to 5 µm in size, packed in random orientations (theory requires infinite depth). Proper instrument alignment and sample placement are also important. Selecting instrument components with higher spatial resolution or better resolved options can also improve the data quality. For example, using a silicon strip position sensitive detector on the X-ray diffractometer rather than a sodium iodide (NaI) scintillation point detector results in vastly improved signal to noise ratios within a given time and, consequently, improved data and models.

Once the sample is properly prepared and a representative data set is obtained, a large number of corrections can be applied to obtain a better fit during Rietveld modelling. These corrections range from instrumental parameters to finer crystallographic details of each particular sample. Since it is difficult to completely remove preferred orientation for samples with high aspect ratio particles, it is important that the modelling procedure be able to correct for preferred orientation and crystallite size anisotropy. The modelling process is involved and requires crystallographic understanding and is thus impacted by the subjectivity of the analyst. A fitting description of the Rietveld modelling process is given in Reference [7].

The availability of crystallographic information files (CIF) for cellulose I α and I β and Cellulose II and III allows the crystal structure to be input directly into the Rietveld modelling program.^{[8] - [10]} The space group, unit cell dimensions and atomic coordinates of a material are used to construct the CIF and are routinely output from single crystal diffraction software. The use of a CIF eliminates the need for a peak fitting method which would require that individual peaks representing cellulose peak positions be input into the modelling program. That is not a simple procedure because cellulose samples result in broad and overlapped peaks which are difficult to model. The availability of CIF files significantly simplifies the modelling procedure and provides higher crystallographic accuracy.

The raw powder X-ray diffraction patterns are deconvoluted based on the Rietveld approach using known diffraction patterns for cellulose from the appropriate CIF. When modelling percent crystallinity using the degree of crystallinity method, the crystalline and amorphous areas are defined, and their total area is used to calculate the percentage of crystallinity. In general, the crystalline peaks are the well-defined peaks (although there can be considerable peak overlap due to broadened peaks). Amorphous phase contributions normally appear as very broad humps in the same region as background signals from other sources. A number of factors can contribute to the background signal. Minimizing or eliminating these contributions is critical to avoid a situation where secondary background-related factors significantly contribute to the amorphous content. The following factors can affect the background contribution:

- air scatter, particularly at lower angles;
- an uneven sample surface;
- fluorescence;
- contributions from the sample holder, mount or mounting medium.

Refer to Reference [11] for a summary and examples of the relative merits and limitations of the Rietveld modelling approach as compared to the Segal method and an amorphous subtraction method. Reference [11] discusses the various approaches that have been used to model the amorphous component, specifically the use of a small cellulose crystallite or a user-input function.

5 Sample preparation

5.1 General considerations

The method described in this document has been tested with different types of wood-derived-CNM, including cellulose nanocrystals (CNC), cellulose nanofibrils (CNF), and individualized cellulose nanofibrils (iCNF) in an interlaboratory comparison (see [Annex A](#)) and may also be applicable to CNM derived from other sources. The CNM samples used in this study were received as dry powders that had been dried by either spray drying (CNC) or freeze-drying (CNF, iCNF). The CNF and iCNF samples were milled using a laboratory Wiley Mill with a 0,5 mm sieve opening to ensure uniform particle size. Using randomly packed dry powdered samples with uniform particle sizes in the range of 1 μm to 5 μm will average out orientational effects in individual crystals. Independent of the CNM source or the method used to prepare samples, the sub-sample(s) used for XRD analysis must be representative of the bulk sample.

A range of sample preparation methods have been used in literature studies, including preparation of thin films or sheets and pellets. Different sample preparation methods can lead to issues with orientational effects that require larger corrections than those in the interlaboratory comparison (ILC) study (see [Annex A](#)). Similarly, CNM generated from other sources can lead to larger degrees of orientation, depending on the particle morphology. Although it is desirable to ensure that the sample has a uniform particle size, unnecessary or excessive grinding of the sample should be avoided in order to minimize possible damage to the crystalline structure.

As for any hygroscopic material, care should be employed to ensure that the effects of moisture content in the sample are taken into account either by recording the environmental conditions during sample preparation and XRD measurements or by using sample holders specifically designed for environmentally sensitive samples. While studies that focus on the moisture content effects on the XRD data from cellulosic materials are limited, it is known that the moisture content in various types of lignocellulosic samples (including wood, cotton and even CNC) will directly influence the diffraction peak position^{[12],[13]} and, consequently, the apparent crystallinity can decrease if the water content is higher.^{[14],[15]} Thus, it is important to prepare the samples to be compared in the same environmental conditions; this can be accomplished by equilibrating the sample at a specific relative humidity and temperature for 24 h. Likewise, the room conditions during the XRD measurements should be recorded, which is particularly important if the sample holders used allow for any moisture to enter the samples.

5.2 Preparation of samples from powders

Mix the sample to ensure homogeneity prior to removing a specimen of powder for powder X-ray diffraction measurement. Pack the powdered CNM into the sample holder. A zero-background cell is preferred to minimize background signals, but other typical sample cells (e.g. 25 mm plastic, Al sample holder) can also be used. Level the surface that will be exposed to the X-ray beam with a blade. This is the normal sample preparation method for data collection in the Bragg-Brentano configuration for Rietveld modelling.

NOTE This sample preparation method works well for fine powdered samples (e.g. spray-dried CNC). Samples that have interconnected fibrous structures (e.g. freeze-dried CNC, CNF or iCNF) do not pack as well, leading to a rough surface that can increase background signals and peak broadening. It is recommended to pre-treat such samples by milling with a laboratory mill with an appropriately sized sieve opening to ensure a uniform particle size.