Priorities for Development of Standard Test Methods to Support the Commercialization of Cellulose Nanomaterials

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TAPPI

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WHY ARE STANDARDS NEEDED FOR CELLULOSE NANOMATERIALS?

Quality Control

Materials Specifications

Environmental Health and Safety

Occupational Health and Safety

Science-based, technically relevant standards facilitate open access to global markets

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CELLULOSE NANOMATERIAL ISO STANDARDS – **PUBLISHED**

ISO/TC 6 Paper, board and pulps

- ❑ **ISO 21400:2018**, *Determination of cellulose nanocrystal sulfur and sulfate half-ester content*
  - ✓ First international standard test method dedicated to cellulose nanomaterials
  - ✓ Provides ICP-OES and conductometric titration procedures

ISO/TC 229 Nanotechnologies

- ❑ **ISO/TR 19716:2016**, *Characterization of cellulose nanocrystals*
  - ✓ Reviews commonly used methods, including sample prep, measurement methods and data analysis
- ❑ **ISO/TS 20477**, *Standard terms and their definition for cellulose nanomaterial*
  - ✓ Provides terms and definitions for different types of cellulose nanomaterials

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CELLULOSE NANOMATERIAL ISO STANDARDS – **IN PROGRESS**

ISO/TC 6 Paper, board and pulps

- ❑ **FDIS 1762 + 2144**, *Ash content at 525 and 900 °C*
  - ✓ Determination of the residue (ash) on ignition at 525 °C and 900 °C
- ❑ **FDIS 12830**, *Acid-soluble metals content*
  - ✓ Determination of acid-soluble Mg, Ca, Mn, Fe, Cu, Na and K by AA or Plasma Emission Spectrometry

ISO/TC 229 Nanotechnologies

- ❑ **ISO/DTS 21346**, *Characterization of individualized cellulose nanofibril samples*
  - ✓ Characterization techniques for CNFs produced by TEMPO oxidation or phosphorylation
- ❑ **PWI 23351**, *Particle size distribution for cellulose nanocrystals*
  - ✓ CNC particle size distributions by AFM and TEM
- ❑ **PWI 23361**, *Crystallinity of cellulose nanomaterials by powder X-ray diffraction*
  - ✓ Bulk crystallinity of cellulose nanomaterials by powder X-ray diffraction (Ruland-Rietveld analysis)

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SURVEY PROJECT

Goals:
Capture producer perspective
Identify focus for future standards development

- Recipient list assembled by members of ISO/TC 6/TG 1
- 49 producers
- 9 countries
- Producers classified by
  - ✓ Type of material produced: CNC, CNF, or both
  - ✓ Scale of production: ≤ 100 kg/day or > 100 kg/day

SURVEY DESIGN

Measurand
Purity
Dry matter content
Residual free sulfate content
Crystallinity
Color and brightness
Carbohydrate content and profile
Lignin content
Metals content
Solvent extractives content
Morphology
Particle size and particle size distribution
Degree of agglomeration

Measurand
Surface Charge and Electrostatic Properties
pH
Zeta potential
Total sulfur content
Sulfate half-ester content
Conductivity of suspensions
Carboxylate content
Physico-chemical Properties
Dispersibility in aqueous media
Degree of polymerization
Viscosity and rheology
Thermal stability
Transparency and other optical properties of films
Specific surface area

Ranking

1 – Essential

2 – Nice to have

3 – N/A

SURVEY OVERVIEW

3. Please rate how important it is to you to measure the following properties

Measurand	Priority	Do you currently use a Method	Standard	Type
Carbohydrate content and profile	✓	Y	Y	TAPPI
Lignin content				
Solvent extractives content	⊘	N		
Metal ion content (please specify in Q4 below)	✓	Y	Y	ISO
Crystallinity				
Residual free sulfate content				
Dry matter content	✓	Y	Y	TAPPI
Color and brightness				
Particle size and particle size distributior				
Degree of agglomeration				
pH	✓	Y	N	
Viscosity/rheology				
Total sulfur content	✓	Y	N	
Sulfate half-ester content				
Carboxylate content				
Zeta potential				
Distribution of degree of polymerization (DP)				
Specific surface area				
Thermal stability				

	Priority of measurement	Do you currently use a method to measure this?	If you use a method, is it a standard?	If you use a standard, what type is it?
Conductivity of suspensions				
Dispersibility in aqueous media				
Transparency and other optical properties of films				

* 4. Please identify the metals that are important to you. At what level are you measuring each metal content (please specify level or threshold, e.g., trace)? What type of metal content are you measuring for each metal (e.g., acid-soluble, total)?

Metal(s): Transition metals, Na, Ca

Level(s): Trace

Type(s): Total

5. What other properties, if any, are you interested in measuring? Please list all properties.

Suspension stability

6. Please indicate how important it is to you to measure each of these properties: urgent, essential, or nice to have.

Nice to have

7. Do you currently have or use a method to measure any of these properties? If so, what method(s) do you use?

No

* 8. Would you or someone in your organization be interested in participating in standards development?

● Yes
○ No

Of course! ☺

SURVEY RESPONSE

25/49 CNM producers responded

50% response rate = Excellent!

Cellulose nanocrystals (CNC)	
> 100 kg/day (large)	2
≤ 100 kg/day (small)	5
CNC only	*3*
CNC + CNF	*4*
Total	**7**

Cellulose nanofibrils (CNF)	
> 100 kg/day (large)	14
≤ 100 kg/day (small)	8
CNF only	*18*
CNF + CNC	*4*
Total	**22**

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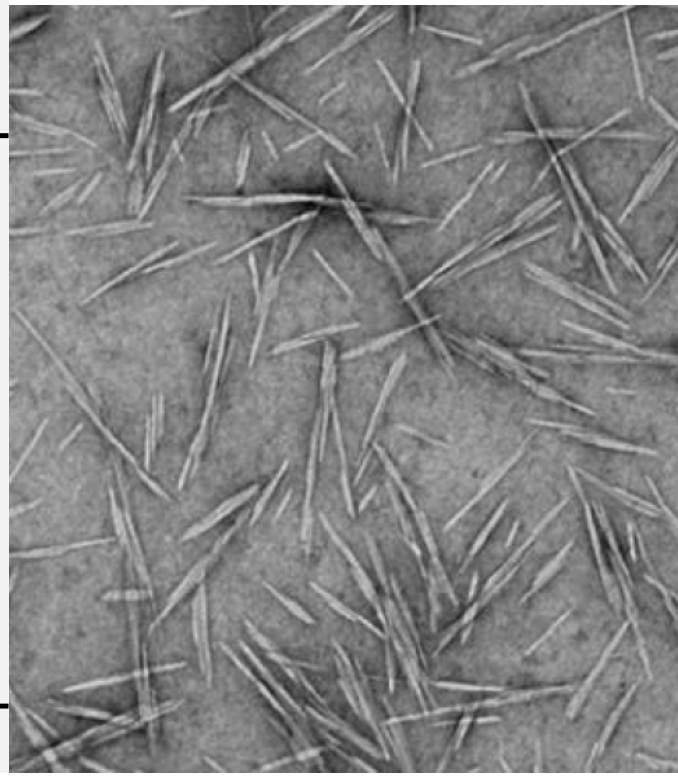
CNC MEASURAND RANKING

Tier 1 (> 50% producers = "Essential")	1 - **Particle size and particle size distribution**	(TAPPI)
	2 - pH	
	3 - **Dry matter content**	(TAPPI)
	4 - Residual free sulfate content	
	5 - Zeta potential	(TAPPI)
	6 - **Total sulfur content**	
	7 - **Sulfate half-ester content**	
	8 - Dispersibility in aqueous media	
	9 - Conductivity	
Tier 2 (< 50% producers = "Essential")	1 - Degree of polymerization	(TAPPI)
	2 - Viscosity and rheology	
	3 - **Crystallinity**	
	4 - Thermal stability	
	5 - Degree of agglomeration	
	6 - **Color and brightness**	(TAPPI)
	7 - Carbohydrate content/profile	(TAPPI, NREL)
	8 - Carboxylate content	
	9 - Film transparency	
	10 - Specific surface area	
	11 – Lignin content	
	12 - **Metals content**	(ISO)
Not needed	Solvent extractives content	



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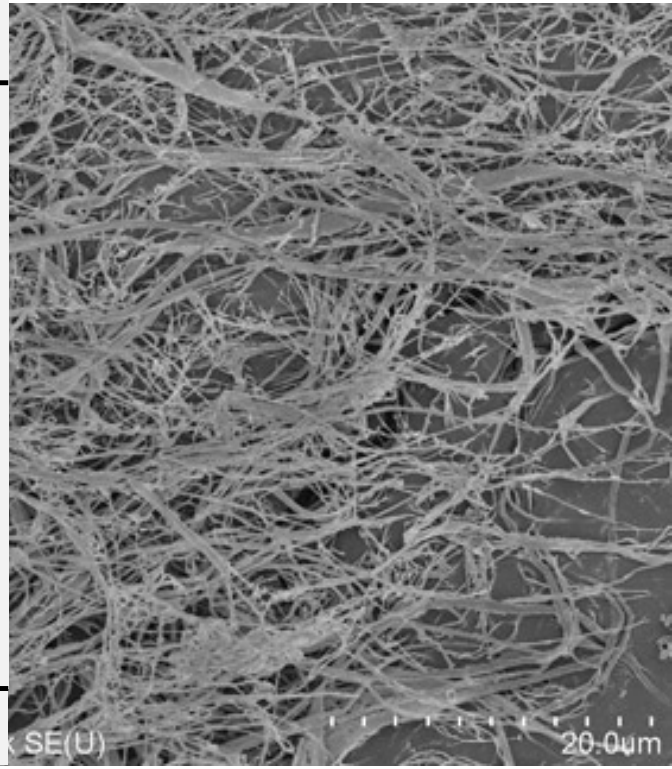
CNF MEASURAND RANKING

Tier 1 (> 50% producers = "Essential")	1 - **Dry matter content**	(TAPPI, ISO)
	2 - Viscosity and rheology	(TAPPI, ISO)
	3 - Particle size and particle size distribution	(ISO)
	4 - pH	(TAPPI)
	5 - Dispersibility in aqueous media	(TAPPI)
	6 - Specific surface area	(TAPPI, ISO)
	7 - Degree of agglomeration	
Tier 2 (< 50% producers = "Essential")	1 - Thermal stability	(TAPPI)
	2 - Zeta potential	(TAPPI, ISO)
	3 - **Color and brightness**	(TAPPI, ISO)
	4 - Conductivity	(TAPPI)
	5 - Lignin content	(TAPPI, ISO, JIS)
	6 - **Crystallinity**	(ISO)
	7 - Degree of polymerization	(TAPPI)
	8 - **Metals content**	(ISO)
	9 - Carbohydrate content/profile	(TAPPI, NREL)
	10 - Carboxylate content	(TAPPI)
	11 - Film transparency and optical props	(ISO)
Not needed	Solvent extractives content	



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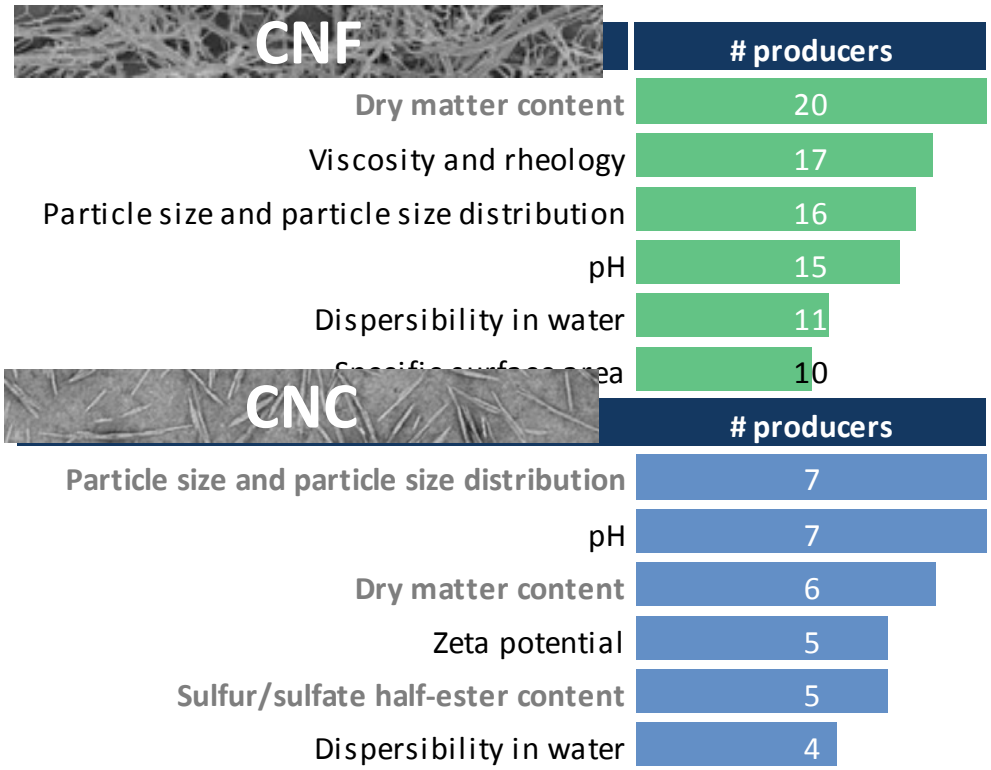
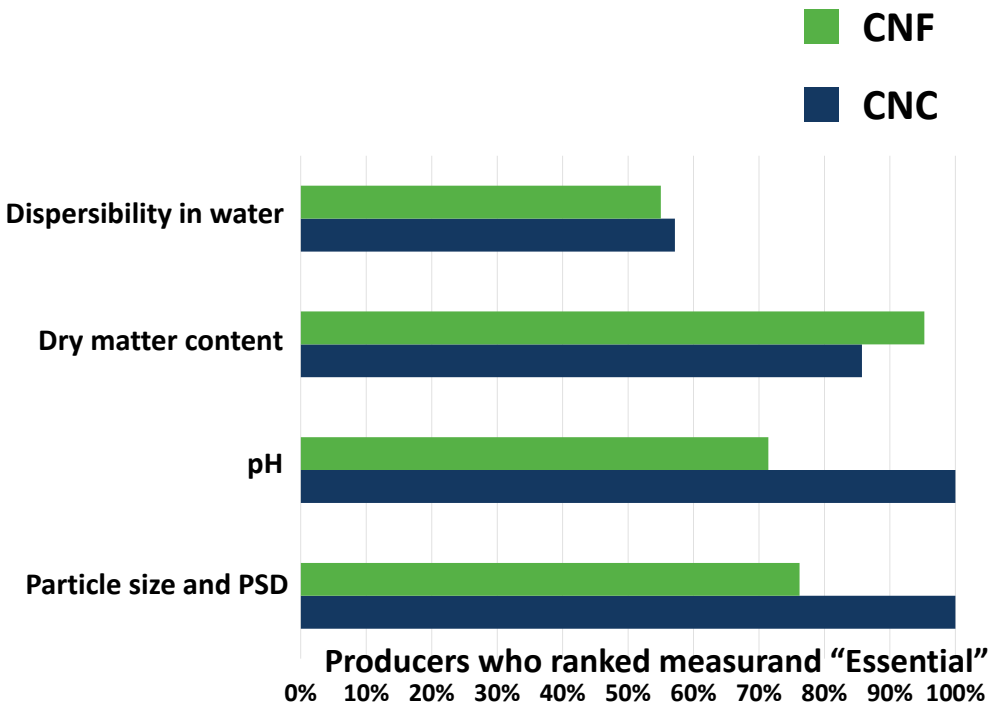
PRIORITY MEASURANDS: CNC vs. CNF





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KEY CHALLENGES IN DEVELOPING STANDARD TEST METHODS FOR HIGH PRIORITY CNM MEASURANDS

CNC

Measurand	Challenges
pH	High viscosity of concentrated suspension
Dispersibility in water	Complex: speed? final particle size? fraction of agglomerates?
Degree of polymerization	Dissolved (DPv) vs. derivatized (DPw) do not agree; short cellulose chains
Viscosity	Depends on many variables such as shear rate, geometry, oscillation frequency, and thixotropy
Crystallinity	Definition (e.g. bulk vs. high SSA); choice of method (XRD, ^{13}C NMR)

CNF

Measurand	Challenges
Viscosity	Settling (sampling and measurement); oxidized CNFs (gel-like) vs. non-oxidized CNFs
Particle size and PSD	Polydisperse, high aspect ratio samples; DLS assumes spherical particles; microscopy is time-consuming and expensive; long CNFs entangle; *L* and *w* cannot be measured simultaneously
Thermal stability	Complex/many variables to consider
Zeta potential	Method may need to be adapted for fibrous/polyelectroytic CNFs
Optical properties	Sample preparation: homogeneity

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OTHER MEASURANDS OF INTEREST

CNC

- Dispersibility in solvents and polymers
- Suspension stability

CNF

- Water retention
- Microbiology
- Film/mechanical properties
- Suspension stability

Metals content:

- Low priority for both CNC and CNF
- Will be needed for certain regulatory requirements (food, cosmetics)
- Transition metals (total, trace levels)

NEXT STEPS

- Relevant test methods depend on where in the value chain the measurement is performed
  - Quality control
  - Storage stability
  - Processing
  - Application
- More detailed surveys for each priority measurand
- End-users' perspective is also needed
- Collaboration among CNM community is essential

Thank you
Merci

ありがとうございました

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Acknowledgments

ISO TC6 / TG1 experts

Survey Participants

NRCan

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