

Priorities for development of standard test methods to support the commercialization of cellulose nanomaterials

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ABSTRACT: With the growing number of producers and users of cellulose nanomaterials (CNMs), there is an increasing need to develop standard test methods to control production and quality of CNMs. In 2014, a Task Group was formed within the ISO Technical Committee 6 *Paper, board and pulps* to begin addressing the need for standards. This Task Group, TG 1, was tasked with reviewing existing standards and identifying the need for additional standards to characterize CNMs.

In March 2018, TG 1 launched a survey to ask CNM producers around the world about the importance of having standard procedures to measure and quantify a variety of CNM properties, both physical and chemical. Producers were asked to identify the type(s) of CNM they produced and their scale of production, and to rank the properties for which they felt standard test methods were most important.

In this paper, we summarize the survey responses and identify those properties of highest interest for producers of both cellulose nanocrystals (CNCs) and cellulose nano- and microfibril-based materials (CNFs/CMFs). Properties of importance can be divided into three broad groups: i) a standard has either been developed or is under development, ii) a currently used standard could be adapted for use with CNMs, or iii) no standard is currently available and further R&D and consultation with industry is needed before a suitable and well-validated standard can be developed. The paper also examines the challenges of developing new standard methods for some of the key properties—as well as the feasibility and limitations of adapting existing standards—to CNMs.

Application: The information in this paper will serve to guide the development of practical and industry-relevant measurement techniques and standard test methods to support the global commercialization of cellulose nanomaterials.

Cellulose nanomaterials (CNMs) encompass a wide range of materials that are not always quickly characterized with readily available and inexpensive laboratory equipment and protocols. As more producers and end-users of CNMs emerge, there is a growing need to accurately characterize these materials during the production process and for manipulation by end-users to produce CNM-enhanced products and materials. Several workshops have been conducted to bring experts together on this topic, for example at the 2016 and 2018 International Conferences on Nanotechnology for Renewable Materials.

ISO, the International Organization for Standardization, develops and publishes standards which are used by many countries to “help companies to access new markets, [...] facilitate free and fair global trade, and ensure that products [...] are safe, reliable and of good quality” [1]. Standard test methods ensure consistency in testing, quality control and materials specifications through the use of validated protocols. Standards will provide essential support for the commercialization of cellulose nanomaterials by facilitating inter-

national trade, harmonizing the implementation of regulations and allowing differentiation among competitive products.

ISO Technical Committee 6 (TC 6) *Paper, board and pulps* develops and maintains standard test methods for the production and use of paper, board, pulps, CNMs, and lignins. Within TC 6, a Task Group (TG 1 Cellulosic Nanomaterials) reviews existing standard test methods to evaluate whether they need to be revised to include CNMs and identifies additional standard test methods needed to characterize CNMs. ISO Task Groups provide guidance by identifying standards to be developed or revised and notifying the appropriate Working Group (WG) within the TC, which undertakes the activity. Within ISO/TC 6, several WGs are currently developing standard test methods for CNMs. TC 6 published the first international standard test method dedicated to cellulose nanomaterials, ISO 21400:2018 “Pulps – Determination of cellulose nanocrystal sulfur and sulfate half-ester content” in December 2018.

Another ISO TC, TC 229 *Nanotechnologies*, is also developing standards applicable to CNMs. ISO/TR 19716:2016 “Nano-

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technologies – Characterization of cellulose nanocrystals” and ISO/TS 20477:2017 “Nanotechnologies – Standard terms and their definition for cellulose nanomaterial” are of particular relevance to the goal of the survey discussed in this paper.

To assist in prioritizing future efforts to develop relevant and effective standard CNM test methods, TG 1 reached out to CNM producers worldwide seeking to understand their needs firsthand by conducting a voluntary and anonymous web-based survey in March 2018. The scope of the survey was limited to unmodified cellulose nanocrystals (CNCs) and cellulose nano- and microfibril-based materials (CNFs/CMFs). It was not intended to address solutions to industrial issues or to characterize CNM-enhanced materials or products. The survey was designed to consider producers of all types of CNMs, including sulfated and carboxylated CNCs, mechanically produced CNFs/CMFs, and CNFs/CMFs produced with pretreatments such as TEMPO-mediated oxidation, phosphorylation, and enzymatic treatment. This paper summarizes and discusses the survey responses, the findings of which have been posted on the public information area of the ISO/TC 6/TG 1 online workspace [2].

METHODOLOGY

Participants and production scale

The list of CNM producer survey participants was compiled by 43 expert TG 1 members representing 11 countries. Initial information was taken from the ISO/TC 6/TG 1 “Summary of International Activities on Cellulose Nanomaterials” (2017) [3]. TG 1 members also contributed CNM producer contacts within their countries who were eligible to complete the survey. To maintain as much confidentiality as possible, only the TG 1 Convenor and Secretary had access to the complete contacts list.

Eligible recipients were those companies or organizations that produced significant quantities of CNMs. As the efforts of TG 1 are directed towards supporting commercial CNM production, lab or bench scale production, and hence most universities, were excluded. To better understand and assess the responses, participants were asked to qualify their production capacity as i) large-scale, > 100 kg/day or ii) pilot scale, ≤ 100 kg/day.

Eligible participants included 49 producers representing nine countries. Contacts were encouraged to work together with colleagues within their company and only submit one response to the survey.

Selection of properties

The survey was developed to ask producers what properties were important to them in producing CNMs, both CNCs and CNFs/CMFs. The list of properties for this survey (see Appendix) was based on a survey conducted by the CSA (Canadian Standards Association) in 2016 and on the properties covered in the CSA standard Z5100-17 “Cellulose nanocrystals—Test methods for characterization”. Permission was obtained from CSA to use their list of properties and their description or significance.

Priorities

Respondents were asked to assign a priority level to each property based on their need for a standard test method to quantify or characterize it, designating it as 1) Urgent, 2) Essential, 3) Nice to have, or 4) Not needed. If the property did not apply to their material, respondents were asked to indicate “Not applicable”.

Respondents were requested to consider only the need for measuring the property itself, and not the accessibility of equipment/instrumentation or the complexity of the method used to measure the property when assigning a priority. However, it should be remembered that standard test methods must be accessible (available instrumentation; ease and speed of use) as well as relevant. Although having the highest priority does not guarantee that a given property will be the first standard developed, it does ensure that it will be given more immediate consideration.

Respondents were also requested to think about the following when assigning priorities to each measurand:

- Which properties distinguish your product from the others?
- Which properties are your customers asking for on data sheets or materials specifications?
- Which properties are required to ensure your products meet your customers’ needs?
- Which properties will regulations require to be monitored or controlled?

As the focus of the survey was to identify priorities for standards development, TG 1 wanted producers to identify priorities based on their customers’ needs and not purely on parameters for control of production and product quality.

Current measurements

The survey also asked respondents to indicate if they were measuring each property, and if so what type of standard they were using (in-house, ISO, TAPPI, etc.). Respondents were also asked if they were measuring any properties that were not listed in the survey, and if so, to indicate the degree of urgency with which they felt a standard test method was needed for these.

RESULTS

Of the 49 producers surveyed, 25 responded to at least a portion of the questions, a 50% response rate, which is excellent considering the length and detail of the survey. In particular, two large-scale CNC producers and 14 large-scale CNF producers responded, suggesting a high level of interest among commercial or industrial-scale CNM producers.

To assist with simplifying the data for discussion, the top 2 categories of “Urgent” and “Essential” were also combined into one “Essential” category. It was also clear from the responses that “Not needed” and “Not applicable” were often selected indiscriminately, so these responses were combined into one “Not applicable” category. The production capacity

Total number of CNC producers	7
CNC-only producers	3
CNC+CNF producers	4
> 100 kg/day CNC producers	2
≤ 100 kg/day CNC producers	5

I. Cellulose nanocrystal (CNC) producers who responded to the survey.

of the producers was taken into account when assigning priority levels to the measurands.

Priorities for producers of cellulose nanocrystals

Seven CNC producers responded to the survey; there are significantly fewer CNC producers than CNF producers. **Table I** shows the breakdown of the CNC producers who responded.

Table II summarizes the responses received from all the CNC producers. The top priority measurands for CNCs, which

CNC Measurand	Essential	Nice to Have	N/A
<i>Purity</i>			
Dry matter content	6	0	
Residual free sulfate content	5	0	2
Crystallinity	3	4	0
Color and brightness	2	4	1
Carbohydrate content and profile	3	2	2
Lignin content	2	3	2
Metals content	1	5	1
Solvent extractives content	0	2	5
<i>Morphology</i>			
Particle size and particle size distribution (PSD)	7	0	0
Degree of agglomeration	3	2	2
<i>Surface Charge and Electrostatic Properties</i>			
pH	7	0	0
Zeta potential	5	2	0
Total sulfur content	5	1	1
Sulfate half-ester content	3 ^a	1	1
Conductivity of suspensions	4	2	1
Carboxylate content	2	3	2
<i>Physico-chemical Properties</i>			
Dispersibility in aqueous media	4	2	1
Distribution of degree of polymerization (DP)	3	4	0
Viscosity and rheology	3	4	0
Thermal stability	2	5	0
Transparency and other optical properties of films	2	4	1
Specific surface area	2	4	1
^a Only 5 of the 7 CNC producers ranked the <i>sulfate half-ester content</i> measurand; both the large-scale (> 100 kg/day capacity) CNC producers ranked it as “Essential”.			

II. CNC measurand priority levels—distribution of responses from all CNC producers.

Priority Level	Measurands in Decreasing Order of Priority ^b
Tier 1	Particle size and particle size distribution (1)^c
	pH (0)
	Dry matter content (3)
	Residual free sulfate content (0)
	Zeta potential (1)
	Total sulfur content (0)
	Sulfate half-ester content (1)
	Dispersibility in aqueous media (0)
	Conductivity (0)
Tier 2	Degree of polymerization (2)
	Viscosity and rheology (1)
	Crystallinity (1)
	Thermal stability (0)
	Degree of agglomeration (0)
	Color and brightness (1)
	Carbohydrate content/profile (3)
	Carboxylate content (0)
	Film transparency (0)
	Specific surface area (0)
	Lignin (2)
	Metals content (2)
Not needed	Solvent extractives content (0)
^a Bold font indicates that a standard method is currently being developed for that measurand (see Table IV). ^b Within each tier, the measurands are listed in order of decreasing priority based on the sum of “Essential” and “Nice to have” responses. ^c Numbers in parentheses indicate the number of producers who measure the property using a published international, national, or industry standard method.	

III. Classification of CNC measurand priority levels for standards development according to international CNC producers.^a

were all ranked as “Essential” by both large-scale CNC producers, are (i) *particle size and particle size distribution*; (ii) pH; (iii) *dispersibility in aqueous media*; and (iv) *sulfate half-ester content*, with their order taking into account the overall responses to those measurands. Measurands ranked as “Essential” by one large-scale producer are *residual free sulfate content*, *dry matter content*, *degree of agglomeration*, *conductivity of suspensions*, *total sulfur content*, *viscosity and rheology*, and *distribution of degree of polymerization (DP)*.

Measurands were sorted into priority categories, or tiers, as shown in **Table III**: Tier 1 (highest priority) measurands were categorized as “Essential” by more than 50% of the CNC producers, and Tier 2 measurands were categorized as “Essential” by fewer than 50% of the CNC producers. Only one measurand (*solvent extractives content*) has been classed as

“Not needed”, as it received “N/A” responses from the majority (> 50%) of the CNC producers, including one large-scale producer.

Standard test methods are currently being developed or have been published for several of the measurands in Tier 1. The development work is being carried out in ISO/TC 6 and TC 229 (see **Table IV**). Existing ISO standards ISO 1762:2015 “Paper, board and pulps – Determination of residue (ash) on ignition at 525 degrees C” and ISO 2144:2015 “Paper, board and pulps – Determination of residue (ash) on ignition at 900 degrees C”) are also being revised to cover CNCs and CNFs. Of the remaining measurands, *pH* and *zeta potential* are the top priorities. These measurands, along with *suspension conductivity*, should only involve fairly straightforward adaptations of existing measurement methods, at least for “dilute” CNC suspensions with viscosity close to that of water. *Dispersibility in aqueous media* is more complex to define and therefore measure; further details are required to understand the producers’ exact needs prior to initiating the development of a standard method to assess CNC dispersibility. The top priority measurands based on the large-scale CNC producer responses mentioned previously are in agreement with the ranking in Table III.

Many of the Tier 2 measurands are quite complex to measure and can be measured with several commonly used measurement methods, which often yield different values or measurands. More detail from producers is needed regarding the specific sample format, measurement conditions, and the target production/handling conditions or applications that will determine the most appropriate protocol for each measurand, as described below:

- The majority of investigators determine CNC *degree of polymerization (DP)* by measuring the intrinsic viscosity of CNCs dissolved in a solvent such as CED or LiCl/DMAc and calculating the DP_v of the cellulose chains composing the nanocrystals [4-8]. A few also derivatize the cellulose by carbanilation to solubilize it in solvents such as THF and measure the DP_w using SEC-MALS [9,10]. However, the viscosity and weight average DP values do not coincide, and the lower DP cellulose chains found in CNCs present specific challenges to each method.
- Various aspects of CNC *crystallinity* can be elucidated using various methods. X-ray diffraction is used to determine the bulk crystallinity and the average crystallite size of CNMs. Solid-state ¹³C CP-MAS nuclear magnetic resonance (NMR) can also be used but gives lower values [11]. CNMs have a significantly higher specific surface area (SSA) than pulp fibers, for example, so care must be taken when selecting an analysis method to ensure that the correct property is quantified. A project is currently underway in ISO/TC 229 to develop a powder X-ray diffraction method for the determination of bulk crystallinity of CNCs.
- Measuring the *viscosity and rheology* of complex systems such as CNC suspensions and gels is also challeng-

CNM	Measurand	Standard/Method	SDO/TC	Development Stage
CNC, CNF	Ash content	ISO 1762:2015 ^b ISO 2144:2015 ^b	ISO/TC 6	FDIS
CNC, CNF	Metals content	ISO 12830:2011 ^b ICP-OES	ISO/TC 6	FDIS
CNC, CNF	Crystallinity	Powder XRD	ISO/TC 229	PWI
CNC, CNF	Dry matter content	ISO 638:2008 ^b Oven-drying	ISO/TC 6	WD
CNC	Color and brightness	–	ISO/TC 6	Method development
CNC	Particle size and PSD	TEM and AFM	ISO/TC 229	PWI
CNC	Total S content/ Sulfate half-ester content	ISO 21400:2018 ICP-OES/ Conductometric titration	ISO/TC 6	IS
CNF	Film optical properties: transparency and haze	–	ISO/TC 6	Method development

^a Abbreviations: CNC = cellulose nanocrystal; CNF = cellulose nanofibril; SDO = standards development organization; TC = technical committee; PWI = preliminary work item; WD = working draft; IS = international standard; FDIS = final draft international standard.
^b These standards are currently being adapted for use with cellulose nanomaterials.

IV. CNM measurands for which international standards are currently under development or have been published.^a

Measurand	Standard(s) Used ^a
Carbohydrate content and profile	TAPPI NREL/TP-51042618:2012
Metals content	ISO
Crystallinity	TAPPI ^c Segal et al., 1959 [17]
Dry matter content	TAPPI T 412 om-16^b
Color and brightness	TAPPI T 562 om-10 ^d
Particle size and PSD	TAPPI T 649 wd-98 (withdrawn)
Zeta potential	TAPPI ^c
Viscosity and rheology	PAPTAC ^e
Degree of polymerization (DP)	TAPPI

^a Some producers did not indicate the particular standard number they use.
^b Text in bold indicates that the standard is used by a large-scale (> 100 kg/day capacity) CNC producer.
^c Even though the producer reported using a TAPPI standard, there does not appear to be a TAPPI standard for the determination of this measurand.
^d The use of this standard test method for CNM analysis is mentioned and/or described in CSA standard Z5100-17.
^e Even though the producer reported using a PAPTAC standard, there does not appear to be a PAPTAC standard for the determination of this measurand. Furthermore, PAPTAC standards are now archival documents.

V. Standard characterization methods currently used by CNC producers to measure properties of their products.

ing, as the results depend on many variables, such as shear rate, geometry, oscillation frequency, and thixotropy effects. Methods to be developed will therefore be informed by the intended application or production phase for which the property is needed.

- **Thermal stability** encompasses the ability of a material to maintain its physical and chemical integrity until a change in a property during heating [12]. Thermogravi-

metric analysis (TGA) is typically used to evaluate thermal stability. Analytical conditions used in TGA vary widely in the literature, even for similar samples [13], which can strongly affect the results [14].

Thermal stability is a very important parameter to consider in CNM processing; for example, in polymer nanocomposite production. Different analytical methods yield different facets of thermal stability, such as the

Metals	Type	Detection Level
Transition metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Pt, Au, Hg)	Total	Trace
Na	Total	1%
Ca, Na	–	Trace
“All ICP metals”	–	mg/kg (ppm)
Fe, Cu	Total	mg/kg (ppm)
Ca, Na	Total	
Silica	Acid-soluble	Trace

^a Text in bold indicates responses from large-scale (> 100 kg/day capacity) CNC producers.

VI. Other metals of interest according to CNC producers.^a

onset temperature (tangent method and ASTM E2550-17 “Standard test method for thermal stability by thermogravimetry”), maximum loss rate, and the constant mass loss method. See ISO/TR 19716:2016 and CSA Z5100-17 for additional information.

- *Degree of agglomeration* indicates the extent to which the particles in a sample of CNM suspension are weakly bound to each other due to electrostatic or physical interactions and forces. Suspension matrix, CNM concentration, and surface chemistry all play a role and can determine the appropriate method for detection and quantification of agglomeration. Methods currently in use include turbidity, light scattering, and light absorbance/transmission. The appropriate method will depend greatly on the system and property or behavior of interest.
- Conductometric titration has been used to measure *carboxylate content* of around 600 mmol/kg in TEMPO-oxidized CNCs [15]. Above this degree of substitution, carboxylate content is difficult to measure accurately; carboxylate groups can also interfere with the quantification of CNC sulfate half-ester content (see ISO 21400:2018). ¹³C NMR spectroscopy, cationic demand/polyelectrolyte titration, Fourier transform infrared (FTIR) spectroscopy and combinations thereof are suggested in CSA Z5100-17; these methods are typically used to characterize the carboxylate content of colloidal particles or pulp fibers and require further research to develop well-understood and reliable protocols for application to CNMs.
- Measuring the *specific surface area* of CNCs also poses a challenge, as the methods currently used have not been thoroughly evaluated and validated for use with CNMs. Spray-dried CNC powder consists of tightly packed agglomerates, such that Brunauer–Emmett–Teller (BET) gas adsorption isotherms yield much lower SSA values than would be expected based on average particle dimensions. Larger SSA values for never-dried, well-dispersed CNCs in suspension have been measured using CP-MAS NMR [16]; however, NMR is expensive, and the instrumentation is not widely available.

Total number of CNF producers	22
CNF-only producers	18
CNC+CNF producers	4
> 100 kg/day CNF producers	14
≤ 100 kg/day CNF producers	8

VII. Cellulose nanofibril (CNF) producers who responded to the survey.

Among the Tier 2 measurands, measurement methods for *color and brightness* of spray-dried CNC powder are being investigated in ISO/TC 6. An existing ISO international standard (ISO 12830:2011 “Paper, board and pulps – Determination of acid-soluble magnesium, calcium, manganese, iron, copper, sodium and potassium”) for acid-soluble *metals content* determination is also being adapted for use with CNCs and CNFs. It may be challenging to develop accessible, accurate protocols for use as standard methods for many of the Tier 2 measurands; some are complex and difficult to accurately measure (e.g., *carboxylate content*, *specific surface area*), and some require further definition of what specifically is to be quantified, and how it is to be measured (e.g., *degree of agglomeration*).

Despite the uncertainty discussed here, several projects are already underway in ISO to develop standard test methods for CNC characterization (**Table IV**). *Color and brightness* measurement methods for CNC powder are being investigated in ISO/TC 6. The methods being developed in ISO/TC 229 will be validated by international round robin interlaboratory testing. ISO 638:2008 “Paper, board and pulps – Determination of dry matter content – Oven-drying method” and ISO 12830:2011 are existing TC 6 methods for *dry matter content* and *acid-soluble metals content*, respectively, of paper, board and pulps which are undergoing revision and adaptation to ensure they can be used for CNC samples. ISO 21400:2018 is a standard test method for CNC *total sulfur content and sulfate half-ester content* measurement by ICP-OES and conductometric titration. *Residual free sulfate content* may also be measured using ISO 21400:2018 in conjunc-

CNF Measurand	Essential	Nice to Have	N/A
Purity			
Dry matter content	20	1	0
Color and brightness	8	9	2
Lignin content	5	11	4
Crystallinity	9	7	5
Metals content	9	6	5
Carbohydrate content and profile	6	9	5
Solvent extractives content	2	6	12
Residual free sulfate content	1	2	17
Morphology			
Particle size and particle size distribution (PSD)	16	4	1
Degree of agglomeration	10	3	7
Surface Charge and Electrostatic Properties			
pH	15	5	1
Zeta potential	5	13	2
Conductivity of suspensions	7	10	3
Carboxylate content	6	9	5
Total sulfur content	1	1	18
Sulfate half-ester content	0	2	18
Physico-chemical Properties			
Viscosity and rheology	17	3	1
Dispersibility in aqueous media	11	6	3
Specific surface area	10	6	4
Thermal stability	8	10	1
Distribution of degree of polymerization (DP)	8	8	5
Transparency and other optical properties of films	6	8	6

VIII. CNF measurand priority levels—distribution of responses from all CNF producers.

tion with appropriate purification of the sample.

Several CNC producers indicated that they use published international, national or industry standard test methods to measure some of the survey measurands; these are shown in **Table V** [17]. Some of these methods may not be applicable or relevant to CNCs. The following comments highlight the need for adapted and/or targeted standard test methods for CNC characterization:

- TAPPI T 249 cm-09 “Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography” for *carbohydrate content and profile* measurement is listed in CSA Z5100-17 as applicable to CNCs; another method listed in CSA Z5100-17, the anion-exchange chromatography method by Sullivan and Douek

[18], is considered to be more sensitive, precise, and reliable. National Renewable Energy Laboratory (NREL) Technical Report NREL/TP-51042618:2012 “Determination of structural carbohydrates and lignin in biomass” is similar to TAPPI T 249 cm-09.

- TAPPI T 562 om-10 “CIE whiteness and tint of paper and paperboard (45/0 geometry, C/2 illuminant/observer)” and similar methods for measuring whiteness and tint indices of paper samples may require adaptation for use with CNCs, particularly for spray-dried CNC powders (the form in which CNCs are typically commercially produced). Sample preparation is key to the outcome and is not yet fully developed.
- TAPPI T 649 wd-98 “Particle-size distribution of coating

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clay” (withdrawn) is intended for measurement of *particle size and particle size distribution* for coating clays, which are very different from CNCs in terms of particle size and morphology.

- DPv values from CED intrinsic viscosity, such as those obtained using TAPPI Standards T 230 om-13 “Viscosity of pulp (capillary viscometer method)” (the use of which for CNM analysis is mentioned and/or described in CSA Z5100-17) and T 254 cm-10 “Cupriethylenediamine disperse viscosity of pulp (falling ball method)”, are always smaller than DPw. At low *degrees of polymerization* (i.e., for most CNCs), this can lead to very low or negative calculated DPv values and a loss of resolution in viscosity differences [19]). One must also use caution when derivatizing CNCs, as precipitation [20] can lead to a loss of low-DP components and erroneously high DPw values.

The survey responses also indicated that each of the measurands is measured by at least one producer using an in-house developed method, the majority being measured by two or three producers, each potentially using a distinct protocol, highlighting the need for standard characterization methods.

Despite survey responses indicating that *metals content* is a relatively low priority for CNC producers, many producers indicated metals of interest other than those covered by ISO 12830:2011. These are shown in **Table VI**. Total metal contents at trace levels are the priority for all CNC producers, including total sodium (Na), calcium (Ca), iron (Fe), and copper (Cu), as well as transition metals. For each metal of interest, “trace” levels must be defined and quantified. Metals of interest, as well as their required detection levels, will depend heavily on the intended application; CNCs for use in cosmetics or food contact applications, for example, are likely to have much more stringent requirements for toxic metals.

CNC producers were asked if they found a need for standard methods to quantify any measurands not listed in the survey. A large-scale CNC producer indicated that *CNC dispersibility in other solvents or polymers* was “Essential”, and that they currently use an in-house turbidity and transparency determination method. CNC dispersibility is more than likely heavily application dependent. Two pilot-scale CNC producers listed *CNC suspension stability* and *Reducing compounds content*, respectively, as being “Nice to have”. It is worth noting that “suspension stability” was suggested by both CNC and CNF producers. Collaboration with CNC producers will be critical to developing standards that meet their specific needs with respect to these measurands.

Priorities for producers of cellulose nanofibrils

Twenty-two CNF producers responded to the survey, over half of which are large-scale (**Table VII**). The challenge when analyzing the responses from CNF producers lies in the fact that there are many distinct types of CNMs being produced which fall in the “CNF” category. It is therefore important to

Priority Level	Measurands in Decreasing Order of Priority ^b
Tier 1	Dry matter content (4) ^c
	Viscosity and rheology (?) ^d
	Particle size and particle size distribution (2)
	pH (1)
	Dispersibility in aqueous media (0)
	Specific surface area (0)
	Degree of agglomeration (0)
Tier 2	Thermal stability (0)
	Zeta potential (1)
	Color and brightness (1)
	Conductivity (1)
	Lignin content (4)
	Crystallinity (1)
	Degree of polymerization (2)
	Metals content (1)
	Carbohydrate content/profile (3)
	Carboxylate content (1)
	Film transparency and optical properties (1)
Not needed	Solvent extractives content (0)
	Sulfur content (0)
	Sulfate half-ester content (0)
	Residual free sulfate content (0)

^a Bold font indicates that a standard method is currently being developed for that measurand (see Table IV).

^b Within each tier, the measurands are listed in order of decreasing priority based on the sum of “Essential” and “Nice to have” responses.

^c Numbers in parentheses indicate the number of producers who measure the property using a published international, national, or industry standard method.

^d At least one CNF producer indicated that they use ISO 5351:2010 “Pulps – Determination of limiting viscosity number in cupri-ethylenediamine (CED) solution,” which determines the limiting viscosity number in CED solution (an indication of DP); others simply indicated “ISO” or “TAPPI”. To the best of our knowledge, ISO and TAPPI standard test methods are not available for the determination of rheological properties of pulp fiber or CNF suspensions. It is possible that viscosity or rheology standard methods developed for other materials are being used.

IX. Classification of CNF measurand priority levels for standards development according to international CNF producers.^a

keep in mind that a measurand may be a top priority for one type of CNF, but less important or irrelevant for another.

Table VIII summarizes the responses from the CNF producers. The trends in aggregate responses parallel the responses of the large-scale producers. Measurands classified as “Essential” by more than 50% of the CNF producers are *dry matter content*, *viscosity and rheology*, *particle size distribution*, *pH*, *dispersibility in aqueous media*, *specific surface area*, *degree of agglomeration*, and *metals content*. *Solvent extractives content* and *sulfur/sulfate half-ester content* were classified as “N/A” by over 50% of the CNF pro-

Metals	Type	Detection Level
Pb, As	Acid-soluble	0.01 ppm
Na, K, Ca^b	Acid-soluble	Trace
Fe, Ni, Cr	Total	Trace
Ca, K, Na, Mg, Fe, As, Cd, Hg, Pb, Ag, Bi, Cr, Co, Cu, Mo, Mn, Ni, Sb, Sn	Total	Heavy metals: Trace
Heavy Metals	Total	Trace
Na	Total	1000 ppm
Na, Ag, Cu, Ca, Al	Total	ppm
Heavy Metals		
Al, As, Ba, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, P, K, Si, Na, Sr, Ti, V, Zn	Acid-soluble	Trace
Fe	Acid-soluble	
Ca, Na	Total	Trace
Silica	Acid-soluble	Trace

^a Text in bold indicates responses from large-scale (> 100 kg/day capacity) CNF producers.
^b Text in bold grey indicates that a method for acid-soluble Na, K and Ca determination is under development in ISO/TC 6.

X. Other metals of interest according to CNF producers.^a

ducers. Table VIII suggests that the top priority measurands for CNFs are (i) *dry matter content*; (ii) *viscosity and rheology*; (iii) *particle size and particle size distribution*; and (iv) *pH*.

Table IX classifies the CNF measurands by priority level. Tier 1 CNF measurands were categorized as “Essential” by more than 50% of the CNF producers; Tier 2 CNF measurands were categorized as “Essential” by fewer than 50% of the CNF producers. Measurands classed as “Not needed” received over 50% “N/A” responses. The top priority CNF measurands based on the large-scale CNF producer responses agree with the ranking in Table IX.

Two of the four measurands within Tier 1 will be challenging to develop as standard test methods: Methods for *dry matter content* determination of CNFs in both high consistency and dilute suspension form are currently being developed in ISO/TC 6.

- *Viscosity and rheology* appear to be the top priority; however, there do not appear to be any (e.g., TAPPI or ISO) standard test methods for measurement of these properties for suspensions of pulp fibers or fibrous material. Viscosity and rheology are very complex and much more specific information will be required before a standard(s) can be developed. Along with the many variables and measurement conditions, CNF-specific issues to be considered include settling (both in sampling and during measurement) and differences between oxidized CNFs (gel-like behavior) and non-oxidized CNFs.

- *Particle size and PSD* are problematic for polydisperse, fibrous, high aspect ratio CNFs. Many methods (e.g., dynamic light scattering [DLS]) assume the particles are close to spherical. Microscopy techniques are more accurate, but simultaneously much more time-consuming and much less accessible. Long nanofibers tend to become tangled, making it difficult to identify the ends of the fibers and therefore to determine their length. It is also difficult to measure both length and width in single images. Gel-point measurement has been used to estimate CNF aspect ratio but requires measurements at a range of solids concentrations [21].
- As for CNCs, the *pH* of aqueous CNF dispersions is straightforward to measure for dilute suspensions.

The highest priority Tier 2 measurands all present more or less of a challenge to standardize:

- *Thermal stability* of CNFs is complex, as for CNC, many variables must be considered and more detail is needed from producers as to which specific parameters are of interest.
- Although an ISO method for *zeta potential* determination has been published, it is intended for colloidal systems, and may require adaptation for fibrous, possibly polyelectrolytic (surface charged) CNFs.
- A variety of published TAPPI and ISO standard test methods exist for the determination of paper *optical properties*, including tint, blue reflectance, whiteness, and

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color. As for CNCs, more information is needed regarding the exact CNF optical properties required by industry. Many existing ISO/TC 6 standard test methods will likely apply to certain types of CNFs or CMFs with minimal or no adaptation.

Several Tier 2 CNF measurands are already being developed within ISO (Table IV). Despite their relatively low priority, a variety of other metals contents have also been suggested for future standards development (see suggestions in **Table X**). Some considerations for other Tier 2 measurands are detailed below:

- Many types of methods for *lignin content* determination exist, including kappa number (e.g., TAPPI T 236 om-13 “Kappa number of pulp”), Klason lignin, and acid-insoluble lignin. Mechanical CNFs are similar to pulp and therefore these methods should be applicable, but validation of the methods is required.
- Methods for cellulose *degree of polymerization* determination by CED viscosity and derivatization/SEC-MALS should be applicable to CNFs, although caution may be required for shorter, narrower CNFs such as TEMPO/phosphorylated-CNFs when using derivatization and precipitation.

Measurand	Standard(s) Used
Carbohydrate content and profile	TAPPI NREL/TP-51042618:2012
Lignin content	TAPPI ISO JIS (Japan Industrial Standard)
Metals content	ISO
Crystallinity	ISO Segal et al., 1959 [17]
Dry matter content	TAPPI ISO
Color and brightness	TAPPI T 562 om-10 ISO
Particle size and PSD	ISO
pH	TAPPI
Conductivity	TAPPI
Carboxylate content	TAPPI
Zeta potential	TAPPI^a ISO
Viscosity and rheology	TAPPI ISO 5351:2010^d
Degree of polymerization (DP)	TAPPI
Specific surface area	TAPPI ISO
Thermal stability	TAPPI^a ISO
Transparency and other film optical properties	ISO 2470

^a Some producers did not indicate the particular standard number they use.

^b Text in bold indicates that the standard is used by a large-scale (> 100 kg/day capacity) CNF producer.

^c Even though the producer reported using a TAPPI standard, there does not appear to be a TAPPI standard for the determination of this measurand.

^d ISO 5351:2010 “Pulps – Determination of limiting viscosity number in cupri-ethylenediamine (CED) solution” measures the intrinsic viscosity of cellulose dissolved in a CED solution, not the viscosity of the CNF suspension or gel itself.

XI. Standard characterization methods currently used by CNF producers to measure properties of their products.

Property	Priority Level Indicated	Method(s) Currently Used
Water retention value (WRV)	Urgent	Centrifugation plus gravimetry
Water holding properties (WRV)	Essential	Centrifugation of suspensions
Water holding capacity (WRV)	Essential or Nice to have	SCAN, TAPPI, ISO
Water retention capacity (WRV)	Urgent	Company-designed method
Charge distribution	Essential	
Charge^b	Essential or Nice to have	SCAN, TAPPI, ISO
Mechanical properties (tensile strength) including film preparation	Nice to have	
Separate standard for films needed^b	Essential or Nice to have	SCAN, TAPPI, ISO
Mechanical properties (of films?) ^b	Urgent	TAPPI, ASTM
Surface energy ^b	Nice to have to Essential	
Permeability	Urgent	TAPPI, ASTM
Enumeration of bacteria, yeast and mold on surface	Essential	ISO
Microbiology	Essential or Nice to have	SCAN, TAPPI, ISO
Transparency, other optical properties of dispersion/suspension	Urgent	
Degree of dispersion	Essential	Microscopy, visual observation and film testing
Suspension stability^b; properties in application-relevant systems (e.g., non-aqueous solvents)^b	Nice to have	
Purity^b	Essential or Nice to have	SCAN, TAPPI, ISO
Constituent sugars^b	Nice to have	HPLC
Nanofiber yield^b	Nice to have	
Real nanocellulose content to prevent fake nanocellulose materials^b	Urgent	
Degree of polymerization (DP_v)	Essential	ISO
Adhesion of fibers ^b	Nice to have to Essential	
^a Text in bold indicates responses from large-scale (> 100 kg/day capacity) CNF producers.		
^b More information from CNF producers is required to select the analysis protocol(s) of priority for development as standard test methods.		

XII. Other properties of interest for CNFs according to CNF producers.^a

- The *carboxylate content* of CNFs is complicated to measure, particularly for highly carboxylated TEMPO-CNFs. See CSA Z5100-17 for more details.
- To measure *film optical properties* such as *color and brightness, transparency and haze, reflectance*, etc., care must be taken to ensure that representative films or handsheets are prepared appropriately if the CNFs are very narrow with high fines content. Interestingly, CNF film transparency was not included in Tier 2 or even Tier 3, likely because there are relatively few producers of TEMPO-oxidized and phosphorylated CNFs, which are the only CNF products for which transparent films are obtained.

Several of the CNF producers surveyed indicated that they already use published standard methods to measure some of the measurands listed in the survey; these are shown in **Table XI**. The following comments highlight the need for adapted or targeted standard test methods for CNF characterization:

- ISO test methods for gravitational sedimentation (ISO 13317-1:2001 “Determination of particle size distribution by gravitational liquid sedimentation methods – Part 1: General principles and guidelines” and ISO 13318:2001 “Determination of particle size distribution by centrifugal liquid sedimentation methods – Part 1: General principles and guidelines”), laser diffraction (ISO 13320:2009

“Particle size analysis – Laser diffraction methods”) and DLS (ISO 22412:2017 “Particle size analysis – Dynamic light scattering [DLS]”) all estimate *particle size and PSD* of various types of materials, including powders, emulsions, or fine bubbles, but likely require adaptation for use with non-spherical, high aspect ratio CNFs, as they typically give a volume equivalent sphere diameter.

- TAPPI T 252 om-16 “pH and electrical conductivity of hot water extracts of pulp, paper, and paperboard” is intended for *pH* and *conductivity* measurements on hot water extracts of pulp and may not be appropriate for CNF dispersions or gels.
- TAPPI T 648 om-14 “Viscosity of coating clay slurry” is used to measure the viscosity of 70 wt% slurries of coating clays, which are a very different system from more dilute fibrous CNF dispersions. The high aspect ratio of CNFs typically restricts rheological measurements to CNF dispersions of concentration 5 wt% and under. It is also likely that different standards will be required for the measurement of the viscosity of the gel-like oxidized CNF dispersions and the conventional mechanically separated CNF suspensions, which are closer in behavior to conventional pulp suspensions.
- TAPPI T 237 cm-08 “Carboxyl content of pulp” measures the *carboxylate content* of pulp by reacting washed hydrochloric acid (HCl)-extracted pulp with sodium bicarbonate and titrating the filtrate with HCl. Investigation is required to determine which CNF forms and degrees of substitution may be analyzed using this method. CSA Z5100-17 also suggests conductometric titration for carboxylate content determination.
- CNF *specific surface area* determination, as for CNCs, has many challenges. TAPPI T 226 cm-11 “Specific external surface of pulp”, used to determine the external surface area of pulp, is only suitable for unbeaten, or only slightly beaten, chemical pulps and similar materials, since the silvering step causes some of the finest fibrils to collapse. The gas adsorption (BET) method (for example, ISO 9277:2010 “Determination of the specific surface area of solids by gas adsorption – BET method”) can also be used to measure the specific surface area of dried materials. For both methods, agglomeration or hornification is a problem when working with dried samples.
- General conditions for the analysis of *thermal stability* and decomposition rates of polymers using thermogravimetric techniques are given in an ISO standard method (ISO 11358-1:2014 “Plastics – Thermogravimetry (TG) of polymers – Part 1: General principles”), which is likely not suitable for CNMs without adaptation.
- A CNF producer indicated that they use ISO 2470 (e.g., ISO 2470-1:2016 “Paper, board and pulps – Measurement of diffuse blue reflectance factor – Part 1: Indoor daylight conditions [ISO brightness]”) to measure CNF *film optical properties*; this can also be considered a *color and*

brightness measurand for CNF. ISO methods for transparency of plastics may possibly be used or adapted for such CNFs, but this will depend on the requirements of the application.

Many CNF producers are also using “in-house” developed methods as opposed to published standard methods to measure a variety of CNF properties; again, the need for universally applied, comparable methods is evident.

Many CNF producers indicated metals of interest apart from those covered by ISO 12830:2011. The responses are very similar to those given by CNC producers (Table XI). Total metal contents are clearly the priority for CNF producers, including total Na, Ca, Fe, and Cu at ppm or trace levels, as well as transition metals at trace levels. Acid-soluble lead (Pb) and arsenic (As) at < ppm levels are also a priority for CNFs. As discussed for CNCs, “trace” levels must be defined and quantified for each metal, and the required detection levels will depend on the intended application.

When asked to indicate other measurands not given in the survey for which they felt standard test methods were needed, CNF producers gave a variety of responses, which are summarized in **Table XII**.

- *Water retention value (WRV)* is a clear priority for CNF producers, likely as a quality control parameter to monitor property development during production as well as a desirable property or functionality in itself. See, for example, recent work used to characterize the degree of fibrillation of cellulose micro- and nanofibrils using WRV in comparison with several other methods [22].
- *(Surface) charge and charge distribution* were mentioned by two large-scale CNF producers, but not listed as “Urgent”.
- *Film properties such as mechanical properties* are of interest to two large-scale CNF producers. Other film properties such as permeability were also mentioned. Thus, a standard method or methods for film preparation should also be of interest. A standard method for the preparation of CF handsheets for physical tests is under development by the CSA Group Technical Committee on Cellulose Nanomaterials.
- *Microbiology* is another interest, being mentioned by two large-scale CNF producers as “Essential”, presumably with respect to stability of the product to fungal or bacterial degradation during storage.
- *Properties of suspensions/dispersions* such as optical properties (related to degree of dispersion), and suspension stability were also mentioned (suspension stability was also mentioned by a CNC producer).
- *Purity and sugars* were also mentioned by two large-scale producers, but more details are needed. Carbohydrate content/profile and lignin content address this need already, but more information is needed from producers to understand what other properties are required.

Again, collaboration with producers will be required to determine their exact needs for many of the measurands.

CONCLUSIONS / NEXT STEPS

Perhaps unsurprisingly, there is significant overlap between CNC and CNF priorities for future standards development. *Dry matter content, particle size and PSD, pH and dispersibility* are all high priority measurands found in Tier 1 for both CNMs. While some standard test methods are already being developed, more R&D and method development will be necessary for other measurands if the currently used methods are not feasible for use in industry and/or not amenable to standardization.

More detailed surveys may be sent to producers to further establish ranked priority levels, and to obtain more details about the property to be measured (e.g., which specific metals are of primary interest? what exactly is meant by suspension stability?). Future surveys should focus on elucidating industry's needs with respect to specific, high priority measurands, including the level of precision required for a given application of the CNM of interest. For any measurand, research and/or testing must be done to ensure that the methods chosen are applicable to the CNM system being tested and

will provide relevant, accurate results, even for apparently straightforward measurands.

It is important to bear in mind that producers' priorities do not necessarily reflect the views of end-users. Producers likely based their responses in part on their customers' needs and requests, but they are also concerned with CNM properties during production, purification, and handling, whereas end-users must consider the systems into which the CNM is

ABOUT THE AUTHORS

Cellulose nanomaterials (CNMs) are anticipated to have significant commercial impact. As such, there is a critical need for the development of international standard methods for characterizing the CNMs in order to ensure harmonization of testing practices among CNM producers, and to facilitate the commercialization and trade of CNM-based products. Clearly, the needs and priorities of producers must inform the development process, so we and the members of ISO/TC 6/TG 1 developed the survey discussed in this paper.

This was a general survey covering many different CNM properties of interest, so it was difficult to make the survey comprehensive but not too long to answer. We addressed this mostly by having drop-down answers to select from, but also letting producers add information when they wished. We were surprised to get such a good response for such a long survey! It was also interesting to see that there are many points of agreement between CNC and CNF producers as to priority measurands. However, this doesn't mean that one standard test method will fit both materials for the same measurand!

The survey results confirm that some of the standards currently under development are of high priority to CNM producers. Some properties that were expected to be higher priority were lower priority and vice-versa. There were some measurands that were in high demand by the producers, for which we do not yet have good measurement methods. Also,



Beck



Walker



Batchelor

we learned that it is hard to make a good survey!

Mills utilizing CNMs in their products will benefit from materials that are well-defined using recognized standards. The next step is to reach a consensus on which standard method(s) should be developed next, based on the survey results and the availability of experts to work on them. More surveys may also be needed before the standards can be developed (must be targeted to a specific industry need). End-users of CNMs may also be surveyed about their more specific needs for the chosen measurands.

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to be incorporated. For example, the survey responses indicate that thermal stability is not among the top priorities for producers. However, thermal stability will be a very important issue in composite applications of CNMs. While this preliminary survey focuses on the needs of producers as the first links in the CNM value chain on whom the first regulatory restrictions will fall, future input from end-users will be valuable and essential for the development of standard test methods relevant to the application of cellulose nanomaterials in CNM-enhanced products.

Industry-wide participation and collaboration in all standards development activities, including document drafting as well as round robin testing, is vital to production of accessible, relevant, and truly useful CNM standard test methods that effectively respond to regulatory and market needs and have no adverse effects on fair competition in the global marketplace. If you are interested in participating as an expert on ISO/TC 6/TG 1, please contact your country's member body, or one of the authors, for guidance on how to join. **TJ**

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APPENDIX

Description and significance of measurands included in the survey to cellulose nanomaterial producers conducted by ISO/TC 6/TG 1 in March 2018.

CNM Measurand	Description/Significance
Purity	
Carbohydrate content and profile	Content of monosaccharides from hemicelluloses: glucose, mannose, arabinose, xylose, and galactose.
Lignin content	<i>Affects color, optical properties, hydrophobicity, dispersibility and product performance.</i>
Solvent extractives content	Terpenes and fatty acids present in the wood pulp from which the CNM was produced. <i>May affect product performance.</i>
Metals content	<i>Potential health and environmental risk.</i>
Crystallinity	Relative amount of crystalline material present in a CNM sample. <i>May be used for quality control, or to differentiate among CNM grades.</i>
Residual free sulfate content	Excess free SO_4^{2-} ions from either residual acid or salt. <i>Measure of purity, quality control parameter: ionic strength controls many important CNM suspension behaviors and properties.</i>
Dry matter content	Residue remaining after drying a sample to constant mass. <i>Affects product value and shipping quantity, shelf-life, and re-dispersibility of dried product.</i>
Color and brightness	Optical properties of, e.g., paper-like CNMs or CNM powders. <i>Can be used to uniquely characterize solid CNM samples' appearance, assess contamination, or monitor production.</i>
Morphology	
Particle size and particle size distribution (PSD)	<i>Batch and quality control: qualify the level of agglomeration or track changes in particle size with a modification reaction.</i>
Degree of agglomeration	Particle size of agglomerates formed; fraction of particles present in agglomerates or flocs; ratio of size of agglomerate to size of primary particle. <i>Indication of colloidal stability; affected by surface chemistry, fibrillation and entanglement, etc.</i>
Surface Charge and Electrostatic Properties	
pH	Indicates the degree of neutralization and the counter-ion associated with surface ionic groups. <i>Quality control parameter.</i>
Conductivity of suspensions	Conductivity of ionically charged CNMs can be used to quantify the charged surface groups. <i>Quality control parameter.</i>
Total sulfur content	Total amount of elemental sulfur present in the CNM sample, e.g., CNCs produced by sulfuric acid hydrolysis. <i>Can be converted to sulfate half-ester content and also be used to determine the purity of the sample.</i>
Sulfate half-ester content	Quantity of acidic sulfate half-ester groups located at the surface of CNCs produced by sulfuric acid hydrolysis. <i>Surface charge density controls many important suspension behaviors and properties; means of differentiating among CNC grades.</i>
Carboxylate content	Quantity of carboxylic acid groups located at the surface of oxidized CNCs, CNFs or CMFs. <i>Surface charge density controls many important suspension behaviors and properties; means of differentiating among CNM grades.</i>

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Zeta potential	Potential difference between the dispersed medium and the stationary layer of fluid attached to a colloidal CNM particle. <i>Used to quantify the magnitude and type (positive or negative) of electrical charge on the surface of dispersed CNM particles; provides a measure of the colloidal stability; can be used to semi-quantitatively detect charged species grafted to the CNM surface.</i>
Physico-chemical Properties	
Viscosity and rheology	Key properties for processing and many end-use applications, including gel and shear thinning behaviors.
Distribution of degree of polymerization (DP)	DP_n, DP_w, and DP_v are measures of the distribution of the degree of polymerization of the cellulose chains composing the CNM. <i>Provides an indication of the degradation of the cellulose chains during hydrolysis, oxidation, or mechanical processing; indication of the reaction or process homogeneity; DP information might also be requested for regulatory purposes.</i>
Specific surface area	Total surface area of a material per unit of mass. <i>Provides information on the dispersibility of the material and on the available surface area for modification, as well as interaction with a matrix (e.g., dispersion in a solvent or polymer).</i>
Thermal stability	Resistance of CNMs to degradation during heating. <i>Provides an indication of usability for high temperature processing and end use.</i>
Dispersibility in aqueous media	Recovery of individual nanoparticles when a dried CNM is dispersed in water or aqueous solutions. <i>Important for the expression of the unique material properties that are due to the nanoscale size of a CNM.</i>
Transparency and other optical properties of films	<i>Optical properties such as transparency and haze are key parameters for application of CNMs in, e.g., transparent packaging, opto-electronics, etc.; can be used to distinguish grades of a CNM.</i>