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Pulp — Determination of cellulose nanocrystal sulfur and sulfate half-ester content

Pâte — Détermination de la teneur en soufre et en demi-ester de sulfate des nanocristaux de cellulose

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Foreword

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

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document, which establishes testing methodologies for measuring the total elemental sulfur and sulfate half-ester group contents of cellulose nanocrystals (CNCs), was developed in response to a need for a simple and rapid method for indirect quantification of CNC surface charge.

The main purpose of the two methods covered (inductively coupled plasma-optical emission spectroscopy (ICP-OES) and conductometric titration) in this document is to measure the surface charge of sulfated CNCs. Sulfate half-ester groups ($R–OSO_3H$) covalently bound at the nanocrystal surface are introduced during concentrated sulfuric acid hydrolysis by partial esterification of the cellulose hydroxy groups[1]. The anionic sulfate half-ester groups are strong acids, such that at neutral and basic pH values, the protons dissociate and the CNC surface is negatively charged ($R–OSO_3^-$). The pKa of the sulfate half-ester groups on CNCs is approximately 2,5 (as determined by potentiometric titration), implying that at very low pH the surface groups are protonated and CNCs have a net neutral charge[2]. This surface charge controls many important properties of CNC suspensions, including the colloidal stability, self-assembly and rheological behaviour, both in the pure state and in the presence of salts and other additives. As such, the CNC surface charge is a very important factor in the processing and development of commercial products containing CNCs. The sulfate half-ester (sulfur) content will also be a key entry on material specifications sheets which will accompany the commercial product, enabling different product grades to be distinguished from each other and from other companies' products.

ICP-OES and conductometric titration are both included in this document as they provide different but complementary ways of measuring the surface charge. ICP-OES measures elemental sulfur which is present in a 1:1 ratio with the charged sulfate half-ester groups, and does not depend on the nature of the counterion. Conductometric titration, on the other hand, measures only protons associated with the anionic $R–OSO_3^-$, but is much less complicated to carry out. The two analysis methods should yield equivalent results (see 5.1 and 6.1), or within 5 % to 10 % owing to sources of uncertainty/error such as transfer losses and slight differences in the purification and protonation steps. CNCs derived from different cellulose sources have shown different levels of agreement between the results from the two methods[3]. The objective of this document is to use this information in quantifying the CNC surface charge arising from the easily ionized sulfate half-ester moieties introduced during hydrolysis or post-sulfation.

The tests contained herein are based on literature methods and were developed over several years by a group of industry experts, and were identified as being those which can yield reproducible and accurate results. The tests are anticipated to be performed in a laboratory setting.

As with any laboratory procedure requiring the use of potentially hazardous chemicals, the user is expected to have received proper knowledge and training in the use and disposal of these chemicals.

This document contains footnotes giving examples of apparatus, reagents and sometimes the supplier(s) of those materials that are available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the products named. Equivalent products may be used if they can be shown to lead to the same results.

Annex A provides an alternative method of sample digestion for ICP-OES by wet ashing. Annex B provides an alternative method of sample protonation for conductometric titration by treatment with batches of ion exchange resin.

Pulp — Determination of cellulose nanocrystal sulfur and sulfate half-ester content

1 Scope

This document specifies procedures for the laboratory determination of the total elemental sulfur and the sulfate half-ester content of cellulose nanocrystals (CNCs) by inductively coupled plasma-optical emission spectroscopy and conductometric titration, respectively, including sample preparation, measurement methods and data analysis.

This document is applicable to the characterization of CNCs:

a) with all monovalent counterions (particularly hydronium and sodium cations);

b) which are either in the never-dried state in aqueous suspension, or have been redispersed from a dried form; and

c) which have been extracted from any naturally occurring cellulose source using a range of sulfuric acid hydrolysis conditions, or have been sulfated post-hydrolysis using sulfuric acid.

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.

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

ISO 14644-1, *Cleanrooms and associated controlled environments — Part 1: Classification of air cleanliness by particle concentration*

ISO/TS 80004-1, *Nanotechnologies — Vocabulary — Part 1: Core terms*

ISO/TS 80004-2, *Nanotechnologies — Vocabulary — Part 2: Nano-objects*

ISO/TS 80004-6, *Nanotechnologies — Vocabulary — Part 6: Nano-object characterization*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004-1, ISO/TS 80004-2, ISO/TS 80004-6 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
nanoscale
length range approximately from 1 nm to 100 nm

Note 1 to entry: Properties that are not extrapolations from larger sizes are predominantly exhibited in this length range.

[SOURCE: ISO/TS 80004-1:2015, 2.1]

3.2
nano-object
discrete piece of material with one, two or three external dimensions in the *nanoscale* (3.1)

Note 1 to entry: The second and third external dimensions are orthogonal to the first dimension and to each other.

[SOURCE: ISO/TS 80004-1:2015, 2.5]

3.3
nanocrystal
nano-object (3.2) with a crystalline structure

[SOURCE: ISO/TS 80004-2:2015, 4.15]

3.4
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 20477:2017, 3.2.5]

3.5
cellulose nanocrystal
CNC
nanocrystal (3.3) predominantly composed of cellulose with at least one *elementary fibril* (3.4), containing predominantly crystalline and paracrystalline regions, with aspect ratio of usually less than 50 but usually greater than 5, not exhibiting longitudinal splits, inter-particle entanglement, or network-like structures

Note 1 to entry: The dimensions are typically 3 nm to 50 nm in cross-section and 100 nm to several µm in length, depending on the source of the cellulose nanocrystal.

Note 2 to entry: The aspect ratio refers to the ratio of the longest to the shortest dimension.

Note 3 to entry: Historically, cellulose nanocrystals have been called nanocrystalline cellulose (NCC), cellulose whiskers or cellulose nanowhiskers (CNW), and cellulose microfibrils; 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 20477:2017, 3.3.5, modified — Note 3 to entry has been revised.]

3.6
agglomerate
collection of weakly or medium-strongly bound particles where the resulting external surface area is similar to the sum of the surface areas of the individual components

Note 1 to entry: The forces holding an agglomerate together are weak forces, for example van der Waals forces or simple physical entanglement.

Note 2 to entry: Agglomerates are also termed secondary particles and the original source particles are termed primary particles.

[SOURCE: ISO/TS 80004-2:2015, 3.4]

3.7
analyte
element to be determined

3.8
calibration blank solution
solution prepared in the same way as the *calibration solution* (3.9) but leaving out the *analyte* (3.7)

3.9
calibration solution
solution used to calibrate the instrument, prepared from a *stock solution* (3.11) or a certified standard by adding acids, buffer, reference element and salts as needed

3.10
matrix blank solution
solution prepared in the same way as the *test sample solution* (3.14) but omitting the *test sample* (3.13)

3.11
stock solution
solution with accurately known *analyte* (3.7) concentration(s), prepared from pure chemicals such as a primary standard

3.12
quality control sample solution
solution of known composition within the range of the *calibration solutions* (3.8), but prepared independently

3.13
test sample
portion taken from the laboratory sample after, for example, homogenizing or dividing

3.14
test sample solution
solution prepared after extraction, dispersion, purification or other preparation of the *test sample* (3.13), such that it can be used for the envisaged measurement

4 Symbols and abbreviated terms

a	slope of the standard addition plot, in mg/kg
b	intercept of the standard addition plot, in mg/kg
c	concentration (titre) of sodium hydroxide, in mol/l
CAS	Chemical Abstracts Service, a division of American Chemical Society
CNC	cellulose nanocrystal
cps	counts per second
ICP-OES	inductively coupled plasma-optical emission spectroscopy
κ	conductivity corrected for dilution, in S/cm
m_{d}	mass of dry sample, expressed in g
$m_{\mathrm{int},\,i}$	mass of the internal standard added to sample aliquot number i, in g
m_{KHP}	mass of potassium hydrogen phthalate standard, in g
m_{o}	mass of original sample, in g
$m_{\mathrm{S},\,i}$	mass of the CNC sample present in sample aliquot number i, in g
$m_{\mathrm{std},\,i}$	mass of the sulfur standard added to sample aliquot number i, in g
m_{t}	oven-dry mass of resin-treated CNCs in the suspension being titrated, in kg

meq	milliequivalent
MWCO	molecular weight cut-off
NIST	National Institute of Standards and Technology
o.d.	oven-dry
ppm	parts per million
R_i	ratio of ICP-OES signals corresponding to the analyte and the internal standard
σ	CNC surface charge content, in meq/kg
S_{blk}	concentration of sulfur in the undiluted matrix blank solution, in mg/kg or mg/l
S_{std}	mass fraction of analyte (sulfur) in the sulfur standard added to each sample aliquot, in mg/kg
SAC	strong acid cation
v	added volume of titrant, in l
V_e	volume of sodium hydroxide solution required to reach the equivalence point, in l
V_t	initial volume of test sample solution being titrated, in l
w	mass fraction solids content, in percent
[R–OSO_3H]	quantity of protonated sulfate half-ester groups [R–OSO_3H] present on the CNC surface, in moles per kg of dry CNCs
[S]	blank corrected concentration of sulfur in the CNC test sample, in mg/kg

5 Total elemental sulfur content — ICP-OES method

5.1 Principle

5.1.1 This method covers the determination of total elemental sulfur (S) content of cellulose nanocrystals (CNCs). Inductively coupled plasma-optical emission spectroscopy (ICP-OES) is used for analysis, following sample purification by dialysis to remove any sulfur-containing contaminants found in the water matrix of the aqueous CNC suspension, and sample digestion to ensure that most (all) of the S in the CNC sample is dissolved in the aqueous medium used for analysis.

5.1.2 Dialysis is typically used to purify CNC suspensions by removing dissolved ions, including residual sulfur-containing contaminants such as sulfuric acid or sodium sulfate, from the aqueous phase[4]. The final dialysed samples are freeze-dried prior to analysis by ICP-OES. Samples can also be digested and analysed beginning directly from aqueous CNC suspensions, but this method is less precise owing to the variations in solids content.

5.1.3 The aqueous sample containing the dissolved sulfur-containing ions is delivered by a peristaltic pump into an analytical nebulizer where it is atomized and introduced into a plasma flame. The sample is broken down into ions, which break up into their respective atoms, which then lose electrons and recombine repeatedly in the plasma, giving off radiation at the characteristic wavelengths of the elements involved. During analysis, light of wavelength around 180 nm to 182 nm (atom and ion lines) is emitted from the sulfur and onto a detector that measures the amount of light emitted. The emission intensity is a measure of the concentration of sulfur in the sample. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by a detector. The signals from the detector(s) are then

processed and controlled by a computer system. A suitable background correction technique is used to compensate for variable background contributions.

5.1.4 ICP-OES is used to measure the total elemental sulfur content in a CNC sample. Sulfur is not typically present in cellulose derived from native sources; the sulfur in the CNCs can therefore be assumed to originate only from the surface sulfate half-ester groups imparted during CNC production by sulfuric acid hydrolysis. However, if sulfur is known to be present in the original cellulose sample[5] [6], comparing the total S content of the CNCs with that of the original material and with CNCs produced from the same source by HCl hydrolysis (which do not contain sulfate half-ester groups) should give the concentration of sulfur derived from sulfate half-ester groups.

5.2 Reagents and apparatus

5.2.1 **Water**, ultrapure (deionized or distilled), conforming to Grade 2 of ISO 3696 or better[1)].

5.2.2 **Nitric acid (HNO_3) solution**, concentrated, trace metal grade (60 % – 70 % assay) (CAS number 7697-37-2).

5.2.3 **Hydrochloric acid (HCl) solution**, concentrated, reagent grade (36 %) (CAS number 7647-01-0).

5.2.4 **Calibration blank**, solution of acid used to digest samples (see 5.5.3).

5.2.5 **Standard sulfur reference material**, for quality control sample solution[2)].

5.2.6 **Primary sulfur standard stock calibration solution**, containing 1 000 ppm to 10 000 ppm S, and other elements[3)].

5.2.7 **Solution of yttrium (Y) for internal standard**, or other appropriate internal standard such as europium (Eu) which will not interfere with measurement of the sulfur wavelengths[4)].

5.2.8 **Probe-type sonicator**, with variable power output control, fitted with a probe of appropriate processing capability for the volume of sample to be treated[5)].

5.2.9 **Plastic centrifuge tubes**, 50 ml capacity.

1) Millipore Milli-Q® water purification systems are examples of suitable systems available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

2) CNCD-1 certified CNC reference material (National Research Council Canada) containing 8 720 mg/kg ± 140 mg/kg S in a matrix similar to the samples intended for analysis, and NIST bovine liver standard reference material 1577c containing 7 490 ± 340 mg S/kg are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

3) Pre-mixed calibration stock solution composed of 27 elements including 1 000 ppm S (Delta Scientific) or NIST stock sulfur solution (10 300 mg/kg ± 30 mg/kg) are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

4) A 10 000 ppm Y solution from SCP Science is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

5) A Sonics vibra-cell™ 130 watt ultrasonic processor with a 6 mm diameter probe is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.