
**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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Published in Switzerland

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

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 ($\text{R-OSO}_3\text{H}$) 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 pK_a 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]