TECHNICAL SPECIFICATION

ISO/TS 21236-1

First edition
2019-10

Nanotechnologies — Clay nanomaterials —

Part 1:
Specification of characteristics and measurement methods for layered clay nanomaterials

Nanotechnologies — Nano argiles —

Partie 1: Spécification des caractéristiques et des méthodes de mesure des nano argiles en couches

Reference number
ISO/TS 21236-1:2019(E)

Contents

Page

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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 229, *Nanotechnologies*.

A list of all parts in the ISO/TS 21236 series can be found on the ISO website.

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

Layered clay nanomaterials are a subgroup of clay materials with the external dimension (thickness) or the internal structural dimension (interlayer distance) in the nanoscale. Clay itself, as most important group of layered nanostructured silicates, refers to naturally occurring or synthetic material composed primarily of fine-grained minerals, which show plasticity through a variable range of water content and will harden when fired or dried. The minerals found in clay are generally silicates of less than 2 micrometres in lateral size. Clays are very abundant at the earth's surface; they form rocks known as shales and are a major component in nearly all sedimentary rocks. The small size of the particles and their unique crystal structures give clay materials special properties, including cation exchange capabilities, plastic behaviour when wet, catalytic abilities, swelling behaviour, and low permeability[1].

Other than the structure and composition, there are several additional factors which are important in determining the properties and applications of clays and clay nanomaterials (see Annex A). These are the mineral impurities, the presence of organic materials, the type and amount of exchangeable ions and soluble salts, and the morphological aspects[2].

Natural and modified clays as layered structured minerals are very important industrial materials. In pristine form, clay materials are normally subnano spaced layers, structured in bundles and in exfoliated state; they are nano-objects with thickness in the nanoscale while in intercalated form they are structured nanomaterials with interlayer space in nanoscale.

Modification of clay with change in its characteristic such as its hydrophobicity, interlayer distance, exchangeable ion, and surface connected groups leads to the extension of its applications e.g. for high performance nanocomposites, effective rheological modifier, or biomedical applications. A small quantity of well dispersed intercalated or exfoliated organo-modified layered clay nanomaterials in polymeric composites (see Annex B) is proved to show superior impacts on properties such as barrier, tensile modulus, mechanical strength, and flame retardancy.

There are numerous industrial applications for layered clay nanomaterials. Purified and modified clays are used as; coatings on paper to enhance whiteness and to allow the proper absorption of ink, the life time extender of rubber in tires, in concrete, as catalysts in many industries. Moreover, they can also be used in oil purification, pharmaceuticals, ceramic industry, soil stabilization, porcelains and barriers for nuclear and chemical wastes because of their cation-exchange capabilities, low permeability, and long-term structural stability. In addition, layered clay nanomaterials are utilized in purification industries, in agricultural and food engineering applications, polymeric nanocomposites, deodorizer, insecticide carrier, pesticides carrier, drilling fluids, desiccant, detergents, plasticizer, emulsion stabilizer, food additives, cosmetic applications, environmental remediation and many other miscellaneous applications[1][2].

For such a wide range of clay nanomaterial applications, various fundamental characteristics (as shown in Table 1) play undeniable roles. These characteristics are measured and reported by the provider of the layered clay nanomaterials. In fact, the determinations of these fundamental and basic characteristics will facilitate the communication between sellers and buyers of these nanomaterials for different applications. These characteristics are considered for all industrial layered clay nanomaterial applications such as nanocomposites, paper, ink, purification, and catalysts. In addition to fundamental characteristics, presented in Table 1, some other optional characteristics of layered clay nanomaterials as shown in Table 2 are measured and reported subject to the agreement between sellers and buyers.

Nanotechnologies — Clay nanomaterials —

Part 1:
Specification of characteristics and measurement methods for layered clay nanomaterials

1 Scope

This document specifies characteristics to be measured of layered clay nanomaterials in powder form and chemically modified ones, and describes their relevant measurement methods.

This document does not deal with health, safety and environmental issues.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain 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
aspect ratio
ratio of the sheet length to the sheet width

[SOURCE: ISO 8336:2017,3.13]

3.2
bulk density
ratio of the mass of an untapped powder sample and its volume including the contribution of the interparticulate void volume

3.3
cation exchange capacity
amount of exchangeable cations per defined mass of clay nanomaterial sample

3.4
clay
naturally occurring or synthetically manufactured material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired

Note 1 to entry: Taken from Reference [3].

Note 2 to entry: Although clay usually contains phyllosilicates, it may contain other materials that impart plasticity and harden when dried or fired. Associated phases in clay may include materials that do not impart plasticity and organic matter. Different disciplines have uniquely defined the size of clay particles, and it is for this reason that “fine grained” is used in the definition rather than a precise value. However, because of these size variations from discipline to discipline, it is important that the particle size be specified in the context of the application.

3.5
clay nanomaterials
material composed predominately of clay with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale

3.6
exchangeable ion
ions bearing in clays which can be exchanged with other ions

Note 1 to entry: See Reference [4].

3.7
exfoliated clay
state of separating clay layers and distributing individual layers

Note 1 to entry: Usually exfoliation of layered clay nanomaterials is conducted in liquid suspension by giving shear forces.

Note 2 to entry: See Reference [5].

3.8
film formability
ability of clay to form self-standing films (uniform and ordered lamination of clay layers)

Note 1 to entry: See Reference [6].

3.9
gallery thickness
distance between clay layers

3.10
intercalated clay
clay in which heterogeneous material (atoms, molecules and nanoparticles) is inserted into a host structure (crystal lattice or other macromolecular structure)

3.11
interlayer distance
distance between identical adjacent layers of clay which is sum of gallery thickness (height) and thickness of a single sheet of clay (d_s)

3.12
layer
discrete material restricted in one dimension, within or at the surface of a condensed phase

[SOURCE: ISO/TS 80004-11:2017, 3.1.2]

3.13
layered clay nanomaterial
clay nanomaterial composed of one or more structural layer

3.14
loss on ignition
dried sample’s weight loss during a heat treatment up to 1 000 °C

3.15
moisture content
ratio of the mass of water contained in a sample to that of the sample

3.16
nanocomposite
solid comprising a mixture of two or more phase-separated materials, one or more being nanophase

[SOURCE: ISO/TS 80004-4:2011, 3.2]

3.17
nanostructured
having internal or surface structure in the nanoscale

[SOURCE: ISO/TS 80004-11:2017, 3.1.8]

3.18
organoclay
modified clay by exchanging the original interlayer cations for organic cations

3.19
phyllosilicate
silicate mineral, such as mica, the tetrahedral silicate groups of which are linked in sheets

Note 1 to entry: See Reference [7].

3.20
smectite
clay mineral (e.g. bentonite) which undergoes reversible expansion on absorbing water

3.21
specific surface area
absolute surface area of the sample divided by sample mass

[SOURCE: ISO 9277:2010, 3.15]

3.22
tap density
mass of the powder divided by its volume after tapping the sample in powder form

3.23
total surface area
sum of external and internal surface area

4 Abbreviated terms

AFM	Atomic force microscopy
BET	Brunauer-Emmett-Teller
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectrometry
ICP-MS	Inductively coupled plasma - mass spectrometry
ICP-OES	Inductively coupled plasma - optical emission spectrometry
LOI	Loss on ignition

SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
UV-Vis	Ultraviolet-visible spectrophotometry
XPS	X-ray photoelectron spectrometry
XRD	X-ray diffraction
XRF	X-ray fluorescence

5 Characteristics and measurement methods

5.1 General

This clause provides both fundamental and optional characteristics of layered clay nanomaterials and their relevant measurement methods. Relevant standards describing measurement protocols for individual characteristics are also listed in this clause. However, it should be noted that these standards have not yet been fully validated for application to layered clay nanomaterials.

5.2 Fundamental characteristics

Table 1 lists the fundamental characteristics that are commonly used for material specifications of layered clay nanomaterials. The characteristics for measurements shall be selected from Table 1 based on the agreement between sellers and buyers. Table 1 additionally provides information on units suggested to be used for expressing the measurement results of individual characteristics, measurement methods recommended to be used, and other measurement method suggested to use when the recommended measurement methods are not available and existing standards for measurement protocols.

Table 1 — Fundamental characteristics and the relevant measurement methods

Characteristic		Units	Recommended measurement method(s)	Other measurement methods	Relevant measurement protocols
1–1	Chemical composition content	kg/kg	ICP-MS	ICP-OES or XRF	—
1–2	Mineral composition content	kg/kg	XRD	—	—
1–3	Interlayer distance	Nm	XRD	TEM or FESEM	—
1–4	Thickness	Nm	AFM	XRD, TEM or FESEM	—
1–5	Aspect ratio	—	AFM	SEM, FESEM or TEM	—
1–6	Bulk density	kg/m^3	Gravimetry and volumetry	—	Japanese Pharmacopoeia: 3.01[14]
1–7	Cation exchange capacity	cmol+/kg	Schollenberger method	—	ISO 23470:2018
1–8	Loss on ignition	kg/kg	Thermogravimetry	Heating and weighing method	ISO/TR 18230:2015
1–9	Water absorption capacity	kg/kg	Water absorption method	Enslin-Neff method	ISO 10769:2011
1–10	Moisture content	kg/kg	Thermogravimetry	Oven-drying method	ISO 10769:2011

5.3 Optional characteristics

In addition to the fundamental characteristics which shall be measured (Table 1), there are some other important characteristics which could be related to specific applications. The optional characteristics listed in Table 2 should be measured subject to the agreement between buyers and sellers. Table 2 additionally provides information on units suggested to be used for expressing the measurement results of individual characteristics, measurement methods recommended to be used, other measurement method suggested to use when the recommended measurement methods are not available and existing standards for measurement protocols.

Table 2 — Optional characteristics of layered clay nanomaterials and relevant measurement methods

Characteristic		Units	Recommended measurement method(s)	Other measurement methods	Relevant measurement protocols
2–1	Brightness	—	Reflectometry	—	TAPPI T646
2–2	Colour	—	Colorimetry	—	—
2–3	Methylene blue adsorption capacity	mmol/100g	Filter paper method	UV-Vis spectrophotometry	ASTM C837 – 09 (2014)
2–4	Cohesion coefficient	kPa	Direct Shear test	—	ISO 17892-7:2017/ ASTM D3080/D3080M
2–5	Tap density	kg/m^3	Gravimetry and volumetry	—	Japanese Pharmacopoeia: 3.01[14] and European Pharmacopoeia[15]

Table 2 *(continued)*

Characteristic		Units	Recommended measurement method(s)	Other measurement methods	Relevant measurement protocols
2–6	Specific surface area	m^2/g	Gas adsorption method	Ethylene glycol monomethyl ether absorption method	ISO 9277: 2010
2–7	Film formability	—	Film casting and visual inspection	—	—
2–8	Electrical Resistivity	Ω·m	Four-point probe method	—	—
2–9	Modifier Type	—	IR or FTIR	Raman spectrometry, XPS or UV-Vis	—

5.4 Descriptions on characteristics and measurement methods

Below, descriptions of the characteristics as well as of the measurement methods listed in Tables 1 and 2 are presented.

5.4.1 Chemical composition content

Chemical composition content is defined as the ratio of the mass of a constituent element included in a layered clay nanomaterial sample to that of the dried sample. The chemical composition content of a layered clay nanomaterial sample shall be measured using an appropriate measurement method. The measurement results are usually expressed as wt%.

Wet chemical analysis using ICP-MS can be applied to chemical composition content measurements for elements even at an impurity level. The method is such that ions are generated at a high temperature under the atmospheric pressure in argon plasma and detected using a mass spectrometer.

Layered clay nanomaterial samples can be decomposed using various dissolving agents, including mixtures of strong acids and or hydrogen fluoride. Lithium metaborate (LiBO2) fusion is one of the main options to decompose silicate material, because it is effective even in dissolving the most refractory minerals. A plasma source could be also used to dissociate the sample into its constituent atoms or ions, and the analysis of the atoms is done either with mass spectrometry or by detecting the optical emission from the excited atoms (ICP-OES). In chemical composition report in addition to report of major elements, it is required to report impurities, too.

The XRF spectrometry is also a method for the qualitative and quantitative determination of the elemental composition content of a layered clay nanomaterial sample in both laboratory and industrial environments. This method is less time consuming but it has some limitation on minimum content detection and so it cannot be recommended for chemical composition content measurements at an impurity level.

5.4.2 Mineral composition content

The mineral composition content is the ratio of the mass of a mineral composition included in a layered clay nanomaterial sample to that of the dried sample. The mineral composition content shall be measured using an appropriate measurement method. The measurement results are usually expressed as wt%.

The contents of major mineral composition of a layered clay nanomaterial sample can be determined using XRD spectra of the dried sample. This technique could provide crystallographic information about a sample by observing the diffraction pattern due to an X-ray beam hitting the sample[8][9].

Although many quantification methods based on the XRD technique are highly accurate, sample preparation, data processing and the selection of standards are essential for the XRD quantification of layered clay nanomaterial samples[10].