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Nanotechnologies — Specification for developing representative test materials consisting of nano-objects in dry powder form

Nanotechnologies — Spécifications relatives au développement de matériaux d'essai représentatifs constitués de nano-objets sous forme de poudre sèche

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Foreword

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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 229, *Nanotechnologies*.

This second edition cancels and replaces the first edition (ISO/TS 16195:2013), which has been technically revised.

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

As new manufactured nano-objects are developed and find a wider range of industrial applications, the roles of physico-chemical, performance, and safety testing of their powders (i.e. dry, unsuspended accumulations of such objects) have become more important than ever. However, many testing methods are still under development and have to be properly evaluated in terms of their reliability. Where possible, validation of new measurement methods is performed using certified reference materials, which have known and quantified properties. In the absence of certified reference materials, one often has to rely on non-certified reference materials, with assigned but not certified property values. However, in developing fields of measurement and testing, such as that of nanotechnology, even non-certified reference materials are scarce. In such cases, "test materials," which are evaluated for homogeneity and stability of one or several of their properties, will be helpful in efforts to improve the reproducibility of testing methods across testing laboratories and the comparability of test results across different test methods. This document specifies that for dry powders of nano-objects the following minimum information be gathered and provided in a verification report to qualify the material as a nanoscale representative test material:

— information describing the manufacturing process,

— information on the quality management of its manufacturing process,

— data from physico-chemical measurements representing the principal features of the representative test material, and

— data on the stability and homogeneity of the above parameters.

Conformity to this document, expressed in the form of a verification report, will provide a level of assurance that the representative test material is homogeneous, statistically representative of the manufacturing process, and has stability. This will increase the likelihood that measurements that are undertaken on the representative test material, whether for safety or function, are comparable across testing laboratories, even for properties for which methods are being developed and for which homogeneity and stability have not been quantitatively assessed.

Nanotechnologies — Specification for developing representative test materials consisting of nano-objects in dry powder form

1 Scope

This document specifies development of representative test materials consisting of nano-objects in dry powder form, to enable test method development and improve comparability of data for nanotechnology applications. It includes the physico-chemical properties (specifically, size and shape, specific surface area, crystal structure, and bulk chemical composition) that are required to be measured and reported with the representative test material.

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 Guide 31:2015, *Reference materials — Contents of certificates, labels and accompanying documentation*

ISO Guide 35, *Reference materials — Guidance for characterization and assessment of homogeneity and stability*

ISO 9276-1, *Representation of results of particle size analysis — Part 1: Graphical representation*

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

ISO/TS 80004-2:2015, *Nanotechnologies — Vocabulary — Part 2: Nano-objects*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004-1 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
representative test material
RTM
material, which is sufficiently homogenous and stable with respect to one or more specified properties, and is implicitly assumed to be fit for its intended use in the development of measurement and test methods that target properties other than those for which homogeneity and stability have been demonstrated

Note 1 to entry: An RTM may be a reference material for other properties (i.e. properties for which homogeneity and stability have been demonstrated), and a candidate reference material for the target property.

Note 2 to entry: An RTM can be a useful tool in inter- or intra-laboratory developments of test methods for which reference materials cannot (yet) be produced.

4 Specific physico-chemical characterization requirements for representative test materials consisting of nano-objects in dry powder form

4.1 General

Following physico-chemical properties shall be evaluated in order to represent the principal features of the representative test material consisting of nano-objects in dry powder form.

4.2 Properties and measurement methods

4.2.1 Size and shape of nano-objects

4.2.1.1 Size distribution of primary particles and of their aggregates

A particle counting-based method shall be performed for measurement of the size distribution of primary particles or of their aggregates. An example of such a measurement method is transmission electron microscopy (TEM). Scanning electron microscopy (SEM) can also be used if the SEM resolution is sufficient to measure the particle size of interest. The method or calibrant used to calibrate the sizing method should be given, as an indication of the metrological traceability [1] of the obtained data.

One critical issue is sample preparation, in particular the dispersion of agglomerated particles and deposition onto the substrate without overlapping of particles. A defined dispersion procedure shall be followed and details thereof reported.

Another critical issue is statistical representativeness of the particles selected for analysis. Depending on the width of the size distribution and on the particle shape, a large number of particles might need to be counted to obtain sufficient statistical reliability.

Typically two different types of particle size distributions may be determined. It shall be reported whether the size distribution is that of primary particles or that of their aggregates. Also, the resulting size distribution shall be reported in a table and/or a graphical representation (histograms, density distributions or cumulative distributions) in accordance with ISO 9276-1.

If traceability to SI units is not available, metrological traceability should be established by a traceability to appropriate measurement standards [1][2] such as:

— the use of certified reference materials provided by a competent supplier to give a reliable physical or chemical characterization of a material;

— the use of specified methods and/or consensus standards that are clearly described and agreed by all parties concerned.

Use of ISO 13322-1 is recommended as a comprehensive guide for image analysis[3]. It also provides information about the number of particles to be measured.

4.2.1.2 Representative size of primary particles and of their aggregates

Representative size of primary particles and of their aggregates shall be derived from the size distribution (4.2.1.1). It may be reported as, for example, mean and standard deviation, and/or 10, 50, and 90th percentiles of the cumulative size distribution.

ISO 9276-2 and ISO 9276-3 should be used for the expression of the representative size[4][5].

4.2.1.3 Shape of primary particles and of their aggregates

Shape of primary particles and of their aggregates shall be deduced from imaging techniques, such as TEM, SEM or atomic force microscopy (AFM). A brief, qualitative description shall be done using clearly-defined or widely-acknowledged vocabulary.

Attention should be paid to the fact that TEM and SEM provides 2D-images of the contours (TEM) or surface (SEM) of nano-objects, and that AFM provides a surface topographical image of the particles. Image acquisition with AFM requires special attention, because tip geometry can cause significant ambiguity of particle shape.

NOTE Examples of the description are: spherical, spheroidal, polygonal, ellipsoidal, spherical aggregates, fractal aggregates. Some useful guidance is given in ISO 3252 and ISO/TS 80004-3[6] [7]. More detailed, quantitative description can be made using shape factors defined, for example, in ISO 9276-6[8].

4.2.1.4 Images showing representative primary particles and their aggregates

Representative TEM, SEM or AFM images that illustrate both primary particles and their aggregates shall be acquired. To ensure representativeness, take several images of the specimen to show the size and shape of different nano-objects. Sample identification and scale bar shall be presented with each image. Instrumental settings and preparation method should be reported if they are different from those employed in 4.2.1.1.

4.2.2 Specific surface area

Specific surface area of the representative test material shall be determined, for example, by gas adsorption using the BET method as described in ISO 9277[12].

4.2.3 Bulk chemical composition

Bulk chemical composition of the representative test material shall be measured. Depending on the material, any suitable method(s) (e.g., titrimetry, gravimetry, X-ray fluorescence spectrometry, inductively coupled plasma-mass spectrometry, inductively coupled plasma-atomic emission spectrometry or atomic absorption spectrometry) can be used. The results shall be provided with a metrological traceability[1] statement, where appropriate.

4.2.4 Crystal structure

The structure of the nano-objects constituting the representative test material shall be characterized. In case that the nano-objects are crystalline, the crystalline phase (e.g. rutile and anatase in titanium dioxide) shall be identified by X-ray diffraction. In case that the nano-objects are not crystalline (i.e. "amorphous"), this shall be reported.

4.2.5 Evaluation of stability

Stability of the physico-chemical properties specified in 4.2.1.2, 4.2.2, 4.2.3 and 4.2.4 shall be assessed according to, e.g. ISO Guide 35 by measurements in classical or isochronous stability studies[9]. In the measurements, and depending on the material, the influence of environmental temperature, humidity and/or electromagnetic radiation, and the influence of vibration, are studied and a tolerable environment for storage should be deduced. Representative test materials described in this document should be supplied in an appropriately packaged form (e.g. bottles or vials) in order to minimize the potential for changes in environmental conditions that influence the physico-chemical properties.

NOTE Stability is a characteristic of a representative test material, when stored under specified conditions, to maintain a stated property value within specified limits for a specified period of time [SOURCE: ISO Guide 30:2015].

4.2.6 Evaluation of homogeneity

The homogeneity of the physico-chemical properties specified in 4.2.1.2, 4.2.2, 4.2.3 and 4.2.4 shall be evaluated between packages (e.g. bottles, vials or test pieces) as described in ISO Guide 35. Homogeneity within a single package ("Within-bottle homogeneity" in ISO Guide 35) should be evaluated if appropriate.

ISO 14488 may be consulted for guidance on sampling[11].

5 Information related to quality management

Information on the manufacturing process of the representative test material and on the level of its quality control are required to support claims of homogeneity and representativeness of the representative test materials. The document certifying conformity to the quality management system (QMS) of the manufacturing process, the technical description of the management system, the description of the management of the measurement system and the record of the implementation of the QMS can be included as an informative reference. It is recommended to apply a quality management system, such as ISO 9001, to the manufacture of the representative test material.

6 Contents of verification report

6.1 General

The following items shall be reported. Headings of the report shall be prepared as specified in Clause 5 of ISO Guide 31:2015. See Annex A for an example of verification report.

6.2 Description of the representative test material

a) Manufacturing process of the raw nano-objects used for the representative test material. A brief description specifying the manufacturing method and/or equipment shall be given as, for example, "Carbon nanotubes manufactured by CVD method" and "Titanium dioxide manufactured by sulfuric acid method". Post-manufacturing processes which would influence the physico-chemical properties shall also be described (e.g., purification using acids and alkalis, thermal oxidization, or intense pulverization).

b) Surface coating. If the surface of the representative test material is coated or modified by other substances, information about the surface (for example, materials and coating thickness) shall be given.

c) Impurities and additives in the representative test material. Impurities and additives, such as metal catalysts and stabilizers, shall be identified and quantified by a general statement (such as “99,2 % pure” or by listing all the impurities of a significant mass fraction, including a reference to the method(s) used to quantify the impurities).

6.3 Measurement result

The verification report shall contain the following items with respect to measurement conditions and results of the physico-chemical properties specified in 4.2 with statements about their homogeneity and stability. The measurement conditions shall also accompany the evaluation of homogeneity and stability.

6.3.1 Size and shape of nano-objects

a) Measurement methods including detailed sample preparation (e.g., sampling, dispersion, drying and degassing), calibration, and data analysis.

b) Graphical representation or tables showing size distribution of primary particles and their aggregates.

c) Measures and types of the particle size according to ISO 9276-1.

d) Representative size of primary particles and their aggregates.

e) Shape of primary particles and their aggregates.

f) Definition of the shape, if the shape is described on the basis of other documents (for example, those mentioned in the NOTE of 4.2.1.3).

g) Image showing representative primary particles and their aggregates with its sample identification and scale bar.

6.3.2 Specific surface area

a) Pre-treatment and degassing conditions.

b) Experimental procedure for adsorption isotherm determination, e.g. volumetric or gravimetric, static or continuous gas admission, calibration of dead volume or buoyancy.

c) Adsorptive (chemical nature, purity).

d) Specific surface area and calculation method (for example, single or multi-point analysis with BET method).

e) (Certified) reference material(s) used for performance testing of the instrument and validation of results.

6.3.3 Bulk chemical composition

a) Sample preparation including sampling method and number of samples.

b) Method of chemical analysis including measurement conditions and data reduction.

c) Chemical composition measured (mean and standard deviation if available).

d) (Certified) reference material(s) used for calibration.

6.3.4 Crystal structure

a) Sample preparation.

b) X-ray source and wavelength.

c) Position and intensity of major X-ray diffraction peaks for each of the coexisting phases.

d) Method of data analysis.

e) Type of crystal (or "amorphous").

Annex A
(informative)

Verification report (example)

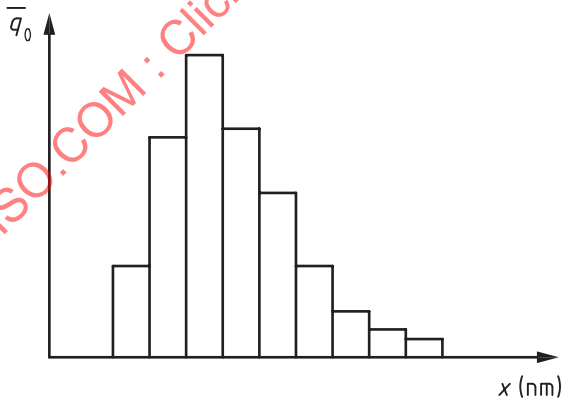
A.1 Representative test material

RTM code and batch number

Physico-chemical properties of the RTM is summarized in Table A.1.

Table A.1 — Physico-chemical properties

Property		Value	Homogeneity
Size and shape	Size distribution	See Figure A.1	—
	Mean particle size [nm]	30	5[a]
	Shape	Spheroidal to polygonal particles	—
Specific surface area [m^2g^{-1}]		120	10[b]
Bulk chemical composition		See Table A.2	—
Crystal structure / crystalline phase		Rutile	—
[a] 95 % confidence interval of the arithmetic mean diameter of 2 000 measured particles.			
[b] 95 % confidence interval of the mean of measurements performed in 10 bottles.			



Key

x particles size

$\overline{q}_0$ density distribution by number

Figure A.1 — Size distribution of *RTM code*