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Nanomaterials — Quantification of nano-object release from powders by generation of aerosols

Nanomatériaux — Quantification de la libération de nano-objets par les poudres par production d'aérosols

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Foreword

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ISO/TS 12025 was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

Introduction

The emissions or release of nano-objects into the surrounding air from powdered nanostructured materials resulting from handling is an important consideration in the design and operation of many industrial processes. Released nano-objects may affect human health and the environment, depending on the nature and quanitity of the nanomaterial. It is therefore important to obtain data about the propensity of nanomaterials to release nano-objects, thereby allowing exposure to be evaluated, controlled and minimised.

Three main target groups of experts for the evaluation of the release of nano-objects from powdered nanostructured materials are:

— material scientists and engineers, who design safe nanomaterials and safe nanomaterial handling processes;

— occupational, health and safety specialists;

— environmental specialists, who need exposure data in addition to toxicity data for risk assessment of manufactured nanomaterials (see A.2) and who collect dustiness data (gravimetric as well as particle concentration and particle size information).

The propensity of nanomaterials to release nano-objects into the air is determined by test methods devised to apply energy to a sample to stress the intra-particle bonds. This stressing induces abrasion, erosion or comminution, which causes dissemination of the particles into the gaseous phase, i.e. generation of aerosols allowing quantification with aerosol instrumentation.

Methods to measure the release of nano-objects from nanomaterials may include dustiness testing methods but basic differences from conventional dustiness methods should be considered. The high variability of the flow properties of powders and the influence of the test setup should also be considered. Conventional dustiness methods for micrometre size particles estimate the amount of dust generated in terms of dust mass fraction or dustiness indices. The methods of aerosol generation for the determination of the dustiness of powders containing primary particles of less than 10 µm in diameter have been found to produce very dissimilar results.

There are a large number of possible combinations of different approaches for the design of dustiness methods[1]. The only current standard, EN 15051:2006[2], selected two methods: the rotating drum method and continuous drop method. The measured values are the inhalable, thoracic or respirable mass fractions, expressed in mg/kg.

Definitions of the inhalable, thoracic and respirable fractions can be found in EN 481[3]. Aerodynamic diameters of 100 µm, 10 µm and 4 µm are the upper limits of the corresponding size fractions. These mass fractions, which are relevant for inhalation, can be added as measurands in measurement of aerosolised nano-objects to characterize the complete particle release scenario.

Schneider and Jensen[4] described approaches using particle size distributions by number to relate exposure from nano-objects in the indoor environment to source strengths resulting from the release of nano-objects during the handling of nanostructured powders. They concluded that dustiness testing combined with online size distribution measurements provides insight into the state of agglomeration of particles released during handling of bulk powder materials.

Furthermore, the evaluation of the release of nano-objects from powdered nanostructured materials requires additional methods and measurands compared to the methods assessing the dustiness of powders. Particle number concentration and size distribution are other measurands necessary for quantifying the release of nano-objects.

Aerosols of nano-objects are more dynamic than micrometre sized particles because of greater sensitivity to physical effects such as Brownian diffusion. Porosity and cohesion of the powder can be much higher than those containing larger particles with more resistance to flow and lower volume-specific surface area. Nano-objects in powdered materials can dominate relevant properties of the bulk material by particle-particle interactions that form clusters like agglomerates. There is still a lack of understanding in the characterization of these secondary nanostructured particles, consisting of primary nano-objects. It has been shown for fumed silica, as an example, that the resulting aerosol particle size distribution depends strongly upon the conditions involved in the different measuring methods[5][6].

Aerosols and powders are also generated by tribological abrasive tests[7] of nano-composites and paints containing nanoparticles[8][9]. Such abrasion tests are not addressed by this Technical Specification. However, the measurement methodology of these publications has been proven for the quantification of nano-object release from wear powders by generation of aerosols.

TECHNICAL SPECIFICATION **ISO/TS 12025:2012(E)**

Nanomaterials — Quantification of nano-object release from powders by generation of aerosols

WARNING — The execution of the provisions of this document should be entrusted only to appropriately qualified and experienced people, for whose use it has been produced.

1 Scope

This Technical Specification provides methodology for the quantification of nano-object release from powders as a result of treatment, ranging from handling to high energy dispersion, by measuring aerosols liberated after a defined aerosolization procedure. In addition to information in terms of mass, the aerosol is characterized for particle concentrations and size distributions. This Technical Specification provides information on factors to be considered when selecting from the available methods for powder sampling and treatment procedures and specifies minimum requirements for test sample preparation, test protocol development, measuring particle release and reporting data. In order to characterize the full size range of particles generated, the measurement of nano-objects as well as agglomerates and aggregates is recommended in this Technical Specification.

This Technical Specification does not include the characterization of particle sizes within the powder. Tribological methods are excluded where direct mechanical friction is applied to grind or abrade the material.

2 Normative references

The following referenced documents are indispensable for the application of this document. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/TS 27687:2008, *Nanotechnologies — Terminology and definitions for nano-objects — nanoparticle, nanofibre and nanoplate*

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

3 Terms, definitions and abbreviated terms

For the purposes of this document, the terms and definitions given in ISO/TS 27687 and ISO/TS 80004-1 and the following apply.

3.1 General terms

3.1.1
release from powder
transfer of material from a powder to a liquid or gas as a consequence of a disturbance

3.1.2
nano-object number release
n
total number of nano-objects, released from a sample as a consequence of a disturbance

3.1.3
nano-object release rate
n_{t}
total number of nano-objects, released per second as a consequence of a disturbance

3.1.4

mass-specific nano-object number release

n_{m}

nano-object number release, divided by the mass of the sample before the disturbance

3.1.5

mass loss-specific nano-object number release

$n_{\Delta\mathrm{m}}$

nano-object number release, divided by the mass difference of the sample before and after the disturbance

3.1.6

nano-object aerosol number concentration

c_{n}

number of nano-objects per aerosol volume unit in the sample treatment zone

3.1.7

aerosol volume flow rate

V_{t}

volume flow rate through the sample treatment zone

3.2 Terms related to particle properties and measurement

3.2.1

aerosol

system of solid or liquid particles suspended in gas

[ISO 15900:2009, definition 2.1]

3.2.2

intraparticle porosity

ratio of the volume of open pores internal to the particle to the total volume occupied by the solid

[ISO 15901-1:2005, definition 3.9]

3.2.3

interparticle porosity

ratio of the volume of space between particles in a powder to the apparent volume of the particles or powder

[ISO 15901-1:2005, definition 3.10]

3.2.4

equivalent spherical diameter

diameter of a sphere that produces a response by a given particle-sizing instrument, that is equivalent to the response produced by the particle being measured

NOTE 1 The physical property to which the equivalent diameter refers is indicated using a suitable subscript (ISO 9276-1:1998).

NOTE 2 For discrete-particle-counting, light-scattering instruments, the equivalent optical diameter is used.

NOTE 3 For inertial instruments, the aerodynamic diameter is used. Aerodynamic diameter is the diameter of a sphere of density 1 000 kg m^{-3} that has the same settling velocity as the irregular particle.

NOTE 4 [ISO/TS 27687:2008, definition A.3.3]

3.2.5
particle size distribution
PSD
cumulative distribution or distribution density of a quantity of particle sizes, represented by equivalent spherical diameters or other linear dimensions

NOTE Quantity measures and types of distributions are defined in ISO 9276-1:1998.

3.2.6
particulate matter smaller 2,5 µm
PM2,5
mass concentration of fine particulate matter having an aerodynamic diameter less than or equal to a nominal 2.5 micrometres ($PM_{2,5}$)

NOTE See Reference [10].

3.2.7
particulate matter smaller 10 µm
PM10
mass concentration of fine particulate matter having an aerodynamic diameter less than or equal to a nominal 10 micrometres (PM_{10})

NOTE 1 See Reference [11].

NOTE 2 PM10 is used for the thoracic fraction as explained in EN 481:1993.

3.2.8
condensation particle counter
CPC
instrument that measures the particle number concentration of an aerosol using a condensation effect to increase the size of the aerosolised particles

NOTE 1 The sizes of particles detected are usually smaller than several hundred nanometres and larger than a few nanometres.

NOTE 2 A CPC is one possible detector for use with a DEMC.

NOTE 3 In some cases, a condensation particle counter may be called a condensation nucleus counter (CNC).

NOTE 4 Adapted from ISO 15900:2009, definition 2.5.

3.2.9
differential electrical mobility classifier
DEMC
classifier that is able to select aerosol particles according to their electrical mobility and pass them to its exit

NOTE A DEMC classifies aerosol particles by balancing the electrical force on each particle with its aerodynamic drag force in an electrical field. Classified particles are in a narrow range of electrical mobility determined by the operating conditions and physical dimensions of the DEMC, while they can have different sizes due to difference in the number of charges that they have.

3.2.10
differential mobility analysing system
DMAS
system to measure the size distribution of sub-micrometre aerosol particles consisting of a DEMC, flow meters, a particle detector, interconnecting plumbing, a computer and suitable software

NOTE [ISO 15900:2009, definition 2.8]

3.2.11
nano-object
material with one, two or three external dimensions in the nanoscale

NOTE 1 Generic term for all discrete nanoscale objects.

NOTE 2 [ISO/TS 27687:2008, definition 2.2]

3.2.12
nanoscale
size range from approximately 1 nm to 100 nm

NOTE 1 Properties that are not extrapolations from a larger size will typically, but not exclusively, be exhibited in this size range. For such properties the size limits are considered approximate.

NOTE 2 The lower limit in this definition (approximately 1 nm) is introduced to avoid single and small groups of atoms from being designated as nano-objects or elements of nanostructures, which might be implied by the absence of a lower limit.

NOTE 3 [ISO/TS 27687:2008, definition 2.1]

3.2.13
agglomerate
collection of loosely bound particles or aggregates or mixtures of the two held together by weak forces where the resulting external surface area is similar to the sum of the surface areas of the individual components

NOTE 1 The weak forces, for example, are van der Waals forces or simple physical entanglement.

NOTE 2 Agglomerates are secondary particles and the original source particles are primary particles.

NOTE 3 Adapted from ISO/TS 27687:2008, definition 3.2.

3.2.14
aggregate
particle comprising strongly bonded or fused particles held together by strong forces where the resulting external surface area is significantly smaller than the sum of calculated surface areas of the individual components

NOTE 1 The strong forces, for example, are covalent bonds, or those resulting from sintering or complex physical entanglement.

NOTE 2 Aggregates are secondary particles and the original source particles are primary particles.

NOTE 3 Adapted from ISO/TS 27687:2008, definition 3.3.

3.2.15
dustiness
propensity of materials to produce airborne dust during handling

NOTE 1 For the purposes of this document, dustiness is derived from the amount of dust emitted during a standard test procedure.

NOTE 2 [EN 15051:2006, definition 3.4]

4 Symbols

For the purposes of this document, the following symbols apply:

Symbol	**Quantity**	**SI unit**
n	nano-object number release	dimensionless
n_t	nano-object release rate	s^{-1}
c_n	nano-object aerosol number concentration	m^{-3}
n_m	mass specific nano-object number release	kg^{-1}
$n_{\Delta m}$	mass loss specific nano-object number release from a treated sample with a mass loss Δm	kg^{-1}
V_t	aerosol volume flow rate	$m^3 s^{-1}$

5 Factors influencing results of nano-object release from powders

5.1 Test method selection

The purpose of the planned test or experimental program should be carefully defined during selection.

Selection of the test method depends on the following considerations:

a) powder properties listed in Table 1;

b) applicability of standardized dustiness test methods[2] or of other powder treatment methods to simulate the typical powder handling process in practice as well as selection of the appropriate treatment parameters.

The outcome of the planned test will be dependent on the experimental conditions selected.

EXAMPLE 1 Determination of the nano-object release and of the dustiness of a powder to predict release of particles during handling in typical industrial processes.

EXAMPLE 2 Estimation of nano-object and agglomerate/aggregate release from powder during very high energy testing.

5.2 Material properties influencing nano-object release from powder

Properties influencing generation and measurements of aerosolized powders containing nano-objects are summarized in Table 1. Presently, many of these properties might not be easily measured, however, they should be considered.

Table 1 — Representative properties influencing nano-object release from powders

Property	Description
Particle size	Fundamental property. The value of the particle size depends on the sizing method and the corresponding equivalent diameter (e.g. aerodynamic diameter, electrical mobility diameter, equivalent area diameter). The particle size of primary particles or aggregates will not change during the handling of nanostructured powders. Particle size of agglomerates will change under certain process and handling conditions. Therefore it may behave like a process parameter. The measured size distribution of particles will depend on the type of instrument. The instrument might measure aerodynamic or mobility diameters, specific surface areas or other parameters. The exact shape of primary particles will depend on the manufacturing process. Nano-objects may be a small fraction of the total mass for some materials.
Particle shape	Particle shapes are found in a wide range of geometries depending on the material and the process. Agglomerates and aggregates of nano-objects may have a fractal shape. Adhesion forces depend on the particle shape because of the contact geometry.
Crystallinity	Some powdered materials can exist in various crystalline states or in amorphous form. The fraction of the crystalline phase may vary depending on the particle size.
Hygroscopicity	Interaction of the particle with moisture in the air characterized by the relative humidity will affect the cohesion of the particles. Thus, the history of the relative humidity of the environmental conditions used to store the powder may be important. The hydrophobic versus hydrophilic characteristics affect dustiness because, as time goes on, a hydrophilic nanomaterial such as magnesium oxide will become less dusty as it absorbs water from the air. Some synthetic amorphous silica, on the other hand, for example, can be easily electrostatically charged and is readily aerosolized.
Cohesion	The magnitude of adhesion forces between particles will affect the detachment of particles as force is introduced into the system. Cohesion will affect the porosity between the particles and flow ability of the powder. The tendency of the nanopowders to sinter or agglomerate is also a consideration.
Material density	The material density will affect aerosolization. For example some tungsten oxide has a high density and is not very dusty.
Porosity	Porosity is a measure of the void spaces in a material. This includes the porosity of primary nano-objects, agglomerates and generally the packing density of the bulk powder.
Electrical resistivity	The electrical resistance of the powder affects the ability of the system to dissipate electrical charge.
Triboelectrics	The ability of the material to generate static electricity will affect the forces within the powder.

These material-specific properties of powder are considered in the test design in Clause 6 or in the data reporting in Clause 8, respectively.

5.3 Test stages

A schematic overview of the test stages necessary for the quantification of nano-object release from powders is shown in Figure 1. Based on the multitude of factors that influence sample preparation and sample treatment, and the current lack of understanding of sample treatment, this Technical Specification provides normative content on basic conditions for the aerosol measurement stage.

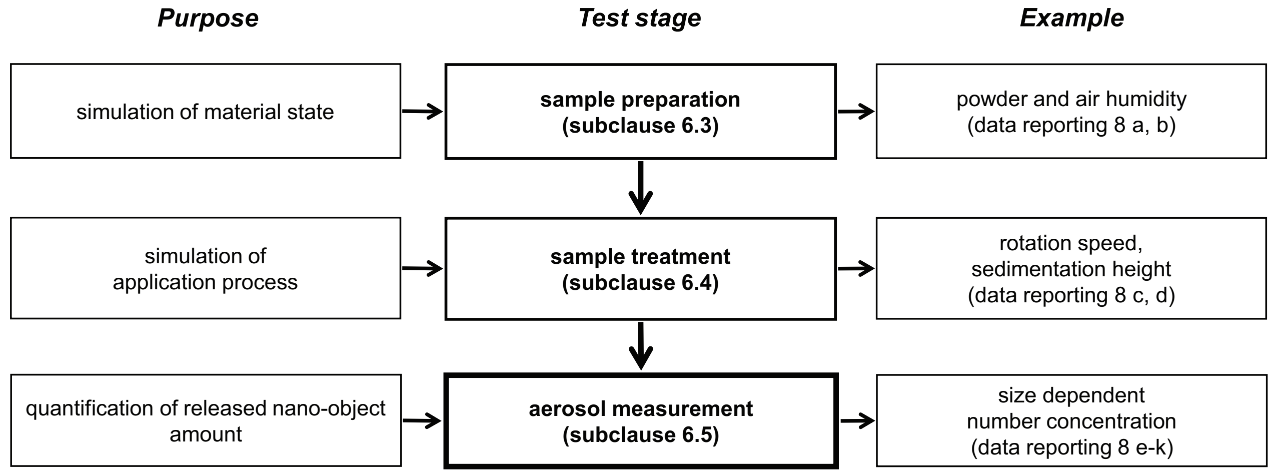

Figure 1 — Schematic overview of test stages for the quantification of nano-object release from powders

Currently, for sample treatment no one general method can be normatively standardized. Nearly all powder studies suffer from incomplete determination of the energy input during sample treatment[12]. For repeatable powder treatment, two devices have been standardized for dustiness measurement (see Annex B) and further devices are tested and recommended in literature (see Annexes C and D). Annex E adds continuous treatment in technical disagglomeration principles.

6 Test requirements

6.1 General

6.1.1 Process parameters of the sampling procedure and of the measurement procedure shall be selected with regard to the purpose of the test and to relevant material properties from Table 1.

6.1.2 The test protocol shall contain these considerations: the purpose, the procedure parameters and the relevant material properties.

6.1.3 Agreements between buyer and seller should include considerations of the process conditions simulated, ability to relate to standard methods and the objectives of the study.

6.2 Safety assessment

6.2.1 A safety assessment shall be conducted for the materials before beginning the tests. Guidance is given in ISO/TR 13121[47] and ISO/TR 27628[13].

NOTE 1 Some nanomaterials might be toxic. The severity of the toxicity might depend on particle composition, size, morphology and other physico-chemical properties of the material.

NOTE 2 A nanomaterial that is potentially explosive, pyrophoric or sensitive to ignition might present a fire or explosive hazard.

6.2.2 Electrical earthing shall be considered to prevent electrostatic charge build-up.

6.2.3 The tests should be tailored according to the hazard. The following examples are not exhaustive but rather are representative: