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Nanotechnologies — Guidance on measurands for characterising nano-objects and materials that contain them

National foreword

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Nanotechnologies - Guide sur les mesurandes pour la caractérisation de nano-objects et des matériaux les contenant

Nanotechnologien - Leitfaden über Messgrößen zur Charakterisierung von Nanoobjekten und von Werkstoffen, die welche enthalten

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European foreword

This document (CEN/TS 17010:2016) has been prepared by Technical Committee CEN/TC 352 “Nanotechnologies”, the secretariat of which is held by AFNOR.

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Introduction

The term “nano-object” applies to materials having one, two or three external dimensions in the nanoscale (therefore in the range of approximately 1 to 100 nanometres). Specific properties of nano-objects are usually exhibited in this size range, even if they do not disappear abruptly beyond these limits. Nano-objects, either natural or manufactured, can then be found in the form of nanoplates (one dimension in the nanoscale), nanofibres (two dimensions, or the diameter, in the nanoscale), and nanoparticles (three dimensions in the nanoscale). Nano-objects exhibit higher specific surface areas than larger objects. They are particularly prone to aggregation and agglomeration phenomena due to attractive interactions during their life cycle.

There is increasing use of nano-objects in research and development, industry and commercial applications. Characterization of nano-objects, and their agglomerates and aggregates (sometimes referred to as NOAA) plays an essential role in basic and applied research, through process and product quality control and commercialization to health and environmental protection. Characterization of nano-objects is key to determine their properties, performance and life-time. The methods available for characterization of larger scale materials are often difficult to apply to nano-objects, sometimes due to restrictions of the test systems (e.g. low sensitivity, inadequate resolution of equipment). This has resulted in new techniques and adapting old methods.

One definition of “measurand” used in many ISO standards is the “quantity intended to be measured”. In nanotechnologies measurement and characterization this “intended quantity” could be size, shape, chemical composition, surface charge, etc. However, in reality, an instrument does not always directly measure this fundamental characteristic but measures something else, which is ultimately related to the intended quantity.

This Technical Specification (TS) describes and defines the measurands, both the overarching intended measurands and those actually measured by the instruments, in order to elucidate which measurements can be compared with each other and under which conditions and assumptions. The Technical Specification is split into ten main clauses covering:

- Size and shape (see Clause 6);
- Chemical analysis (see Clause 7);
- Mass and density (see Clause 8);
- Charge (see Clause 9);
- Crystallinity (see Clause 10);
- Optical (see Clause 11);
- Electrical and electronic (see Clause 12);
- Magnetic (see Clause 13);
- Thermal (see Clause 14);
- Other performance related measurands (see Clause 15).

1 Scope

This Technical Specification provides guidelines for the identification of measurands to characterize nano-objects, and their agglomerates and aggregates and to assess specific properties relevant to the performance of materials that contain them. It provides guidance for relevant and reliable measurement.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 481:1993, *Workplace atmospheres - Size fraction definitions for measurement of airborne particles*

EN ISO 3219:1994, *Plastics - Polymers/resins in the liquid state or as emulsions or dispersions - Determination of viscosity using a rotational viscometer with defined shear rate (ISO 3219:1993)*

EN ISO 6892-1:2016, *Metallic materials - Tensile testing - Part 1: Method of test at room temperature (ISO 6892-1:2016)*

CEN ISO/TS 12025:2015, *Nanomaterials - Quantification of nano-object release from powders by generation of aerosols (ISO/TS 12025:2012)*

EN ISO 14577-1:2015, *Metallic materials - Instrumented indentation test for hardness and materials parameters - Part 1: Test method (ISO 14577-1:2015)*

EN ISO 14577-2:2015, *Metallic materials - Instrumented indentation test for hardness and materials parameters - Part 2: Verification and calibration of testing machines (ISO 14577-2:2015)*

EN ISO 14577-3:2015, *Metallic materials - Instrumented indentation test for hardness and materials parameters - Part 3: Calibration of reference blocks (ISO 14577-3:2015)*

EN ISO 14577-4:2007, *Metallic materials - Instrumented indentation test for hardness and materials parameters - Part 4: Test method for metallic and non-metallic coatings (ISO 14577-4:2007)*

EN 15051-1:2013, *Workplace exposure - Measurement of the dustiness of bulk materials - Part 1: Requirements and choice of test methods*

EN 15051-2:2013, *Workplace exposure - Measurement of the dustiness of bulk materials - Part 2: Rotating drum method*

EN 15051-3:2013, *Workplace exposure - Measurement of the dustiness of bulk materials - Part 3: Continuous drop method*

CEN ISO/TS 80004-1:2015, *Nanotechnologies - Vocabulary - Part 1: Core terms (ISO/TS 80004-1:2015)*

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

CEN ISO/TS 80004-6:2015, *Nanotechnologies - Vocabulary - Part 6: Nano-object characterization (ISO/TS 80004-6:2013)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in CEN ISO/TS 80004-1:2015, ISO/TS 80004-2:2015 and CEN ISO/TS 80004-6:2015 and the following apply.

3.1 General core terms

3.1.1

nanoscale

size range from approximately 1 nm to 100 nm

Note 1 to entry: 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 to entry: 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* (3.1.2) or elements of nanostructures, which might be implied by the absence of a lower limit.

[SOURCE: CEN ISO/TS 80004-6:2015, 2.1]

3.1.2

nano-object

material with one, two or three external dimensions in the *nanoscale* (3.1.1)

Note 1 to entry: Generic term for all discrete nanoscale objects.

[SOURCE: CEN ISO/TS 80004-6:2015, 2.2]

3.1.3

agglomerate

collection of weakly bound *particles* (CEN ISO/TS 80004-6:2015, 2.9) or *aggregates* (3.1.4) or mixtures of the two 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: CEN ISO/TS 80004-6:2015, 2.10]

3.1.4

aggregate

particle (CEN ISO/TS 80004-6:2015, 2.9) comprising strongly bonded or fused particles where the resulting external surface area may be significantly smaller than the sum of calculated surface areas of the individual components

Note 1 to entry: The forces holding an aggregate together are strong forces, for example covalent bonds, or those resulting from sintering or complex physical entanglement.

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

[SOURCE: CEN ISO/TS 80004-6:2015, 2.11]

3.2 Measurand terms

3.2.1

measurand

quantity intended to be measured

Note 1 to entry: The specification of a measurand requires knowledge of the kind of quantity, description of the state of the phenomenon, body, or substance carrying the quantity, including any relevant component, and the chemical entities involved.

Note 2 to entry: In the second edition of the VIM and in IEC 60050–300:2001, the measurand is defined as the "particular quantity subject to measurement".

Note 3 to entry: The measurement, including the measuring system and the conditions under which the measurement is carried out, might change the phenomenon, body, or substance such that the quantity being measured may differ from the measurand as defined. In this case, adequate correction is necessary.

EXAMPLE 1 The potential difference between the terminals of a battery may decrease when using a voltmeter with a significant internal conductance to perform the measurement. The open-circuit potential difference can be calculated from the internal resistances of the battery and the voltmeter.

EXAMPLE 2 The length of a steel rod in equilibrium with the ambient Celsius temperature of 23 °C will be different from the length at the specified temperature of 20 °C, which is the measurand. In this case, a correction is necessary.

Note 4 to entry: In chemistry, "analyte", or the name of a substance or compound, are terms sometimes used for "measurand". This usage is erroneous because these terms do not refer to quantities.

[SOURCE: ISO/IEC GUIDE 99:2007, 2.3]

3.2.2
particle size

linear dimension of a *particle* (CEN ISO/TS 80004-6:2015, 2.9) determined by a specified measurement method and under specified measurement conditions

Note 1 to entry: Different methods of analysis are based on the measurement of different physical properties. Independent of the particle property actually measured, the particle size can be reported as a linear dimension, e.g. as the equivalent spherical diameter.

[SOURCE: CEN ISO/TS 80004-6:2015, 3.1.1]

3.2.3
particle size distribution

distribution of *particles* (CEN ISO/TS 80004-6:2015, 2.9) as a function of *particle size* (3.2.2)

Note 1 to entry: Particle size distribution may be expressed as cumulative distribution or a distribution density (distribution of the fraction of material in a size class, divided by the width of that class).

[SOURCE: CEN ISO/TS 80004-6:2015, 3.1.2]

3.2.4
particle shape

external geometric form of a *particle* (CEN ISO/TS 80004-6:2015, 2.9)

[SOURCE: CEN ISO/TS 80004-6:2015, 3.1.3]

3.2.5
aspect ratio

ratio of length of a *particle* (CEN ISO/TS 80004-6:2015, 2.9) to its width

[SOURCE: CEN ISO/TS 80004-6:2015, 3.1.4]

3.2.6
equivalent diameter

diameter of a sphere that produces a response by a given particle-sizing method, that is equivalent to the response produced by the particle (see CEN ISO/TS 80004-6:2015, 2.9) being measured

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

Note 2 to entry: For discrete-particle-counting, light-scattering instruments, an equivalent optical diameter is used.

Note 3 to entry: Other material constants like density of the particle are used for the calculation of the equivalent diameter like Stokes diameter or sedimentation equivalent diameter. The material constants, used for the calculation, should be reported additionally.

Note 4 to entry: 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.

[SOURCE: CEN ISO/TS 80004-6:2015, 3.1.5]

3.2.7
light scattering

change in propagation of light at the interface of two media having different optical properties

[SOURCE: CEN ISO/TS 80004-6:2015, 3.2.5]

3.2.8
hydrodynamic diameter

equivalent diameter (3.2.6) of a *particle* (CEN ISO/TS 80004-6:2015, 2.9) in a liquid having the same diffusion coefficient as the real particle in that liquid

[SOURCE: CEN ISO/TS 80004-6:2015, 3.2.6]

3.2.9
aerodynamic diameter

diameter of a sphere of density 1 g/cm^3 with the same terminal velocity due to gravitational force in calm air as the particle, under prevailing conditions of temperature, pressure and relative humidity

Note 1 to entry: Adapted from ISO 7708:1995, 2.2.

[SOURCE: EN ISO 23210:2009, 3.1.1]

3.2.10
thermodynamic diameter

diameter of a sphere with the same diffusion coefficient as the particle under prevailing condition of temperature and pressure

Note 1 to entry: The thermodynamic diameter of a particle depends on its size and shape, but not its density.

[SOURCE: EN ISO 13138:2012, 3.2, modified]

3.2.11
(electrical) mobility (equivalent) diameter

diameter of a sphere carrying a single elementary charge with the same drift speed in an electric field as the particle under prevailing condition of temperature and pressure

Note 1 to entry: The mobility diameter of a particle depends on its size, shape and electric charge level (which depends on the charging process involved its capacitance, i.e. its capacity to become electrically charged by bipolar air ions), but not of its density.

[SOURCE: prEN 16966:2016]

3.2.12
mass specific surface area

absolute surface area of the sample divided by sample mass

Note 1 to entry: Mass specific surface area has units of m^2/kg.

[SOURCE: CEN ISO/TS 80004-6:2015, 3.6.1]

3.2.13
volume specific surface area

absolute surface area of the sample divided by sample volume

Note 1 to entry: Volume specific surface area has units of m^{-1}.

[SOURCE: CEN ISO/TS 80004-6:2015, 3.6.2]

3.2.14
photoluminescence

luminescence (see CEN ISO/TS 80004-6:2015, 4.2) caused by absorption of optical radiation

[SOURCE: CEN ISO/TS 80004-6:2015, 4.3]

3.2.15
Raman effect

emitted radiation, associated with molecules illuminated with monochromatic radiation, characterized by an energy loss or gain arising from rotational or vibrational excitations

[SOURCE: CEN ISO/TS 80004-6:2015, 4.9]

3.2.16
lattice parameters

linear and angular dimensions of the crystallographic unit cell

Note 1 to entry: Most engineering materials have either cubic or hexagonal crystal structures. Hence the lattice parameters usually only refer to the lengths of the unit cell edges.

[SOURCE: CEN ISO/TS 21432:2005, definition 3.18]

3.2.17
scattering angle

angle between the direction of the incident particle or photon and the direction that the particle or photon is travelling after scattering

[SOURCE: ISO 18115-1:2013, definition 4.18]

3.2.18
electrokinetic potential
zeta potential

difference in electric potential between that at the slipping plane and that of the bulk liquid

Note 1 to entry: Electrokinetic potential is expressed in volts

[SOURCE: CEN ISO/TS 80004-6:2015, 5.3.4]

3.2.19
fluorescence

phenomenon in which absorption of light of a given wavelength by a substance is followed by the emission of light at a longer wavelength

[SOURCE: CEN ISO/TS 80004-6:2015, 3.5.12]

3.2.20
Curie temperature

temperature at which a ferromagnetic material passes from the ferromagnetic state to the paramagnetic state or vice versa

[SOURCE: EN ISO 11358-1:2014, 3.3]

3.2.21
thermal diffusivity

ratio of thermal conductivity to specific heat capacity per unit mass, which describes the rate at which heat flows through a material, expressed in m^2/s

[SOURCE: ISO 13826:2013, 2.1]

3.2.22
solubility

maximum mass of a nanomaterial that is soluble in a given volume of a particular solvent under specified conditions

Note 1 to entry: Solubility is expressed in grams per litre of solvent.

[SOURCE: ISO/TS 12901-2:2014, 3.17]

3.2.23
dispersibility

extent to which nano-objects can be distributed homogeneously in a medium under defined conditions

[SOURCE: ISO 23900-1:2015, 3.1, modified]

4 Symbols and abbreviations

For the purposes of this document, the following symbols and abbreviations apply.

In the list of abbreviated terms below, note that the final “M”, given as “Microscopy”, may be taken equally as “Microscope” and “S”, given as “Spectroscopy”, may be taken equally as “Spectrometer” depending on the context.

1D	one dimensional
2D	two dimensional
3D	three dimensional
AES	Auger electron spectroscopy
AFM	atomic force microscopy
AGFM	alternating gradient-field magnetometer
APM	aerosol particle mass analyser
APS	aerodynamic particle sizing
ARPES	angle-resolved ultraviolet photoemission spectroscopy
ATR	attenuated total reflectance
BET	Brunauer, Emmet and Teller (BET) method
CLS	centrifugal liquid sedimentation
CPC	condensation particle counter
DC	direct current
DCS	differential centrifugal sedimentation
DEMC	differential electrical mobility classifier
DLS	dynamic light scattering
DMAS	differential mobility analysing system
DRIFT	diffuse reflectance infrared Fourier transform spectroscopy
DSC	differential scanning calorimetry
EBSD	electron backscatter diffraction
EDS or EDX	energy dispersive X-ray spectroscopy
EELS	electron energy loss spectroscopy
EGA	evolved gas analyser
EL	electroluminescence
ELPI	electrical low pressure impaction
EPR	electron paramagnetic resonance
ESR	electron spin resonance
FIB	focused ion beam
FTIR	Fourier transform infrared spectroscopy
HRTEM	high-resolution transmission electron microscopy

LD	laser diffraction
ICP-AES	inductively coupled plasma atomic emission spectroscopy
ICP-OES	inductively coupled plasma optical emission spectroscopy
ICP-MS	inductively coupled plasma mass spectroscopy
IR	infrared
LALS	low angle light scattering
LEED	low-energy electron diffraction
MALS	multi-angle light scattering
MFM	magnetic force microscopy
MOKE	magneto-optical Kerr effect
NIR	near infrared
NMR	nuclear magnetic resonance
NOAA	nano-objects, and their agglomerates and aggregates
OPC	optical particulate counters
PAS	photoacoustic spectroscopy
PFM	piezoforce microscopy
PL	photoluminescence
PSD	particle size distribution
PTA	particle tracking analysis
QMS	quadrupole mass spectrometer
RALS	right angle light scattering
RF	radio frequency
RBM	radial breathing mode
RHEED-	reflection high-energy electron diffraction
RLC	resistor, inductor and capacitor
RMM	resonant mass measurement
SAXS	small angle X-ray scattering
SEM	scanning electron microscopy
SIMS	secondary ion mass spectroscopy
SLS	static light scattering
SMLS	static multiple light scattering
SMPS	scanning mobility particle sizing
SP-ICP-MS	single particle ICP-MS
SPR	surface plasmon resonance
SP-STM	spin polarized scanning tunnelling microscopy
SThM	scanning thermal microscopy

STM	scanning tunnelling microscopy
STS	scanning tunnelling spectroscopy
SQUID	superconducting quantum interference device
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
TOF	time of flight
TXRF	total reflection X-ray fluorescence
UHV	Ultra-high vacuum
UV-Vis	ultraviolet-visible
USAXS	Ultra-small angle X-ray scattering
VSM	vibrating sample magnetometer
WAXS	wide angle X-ray scattering
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy
XPS	X-ray photoelectron spectroscopy

5 Approaches to identify measurands to characterize nano-objects and their agglomerates and aggregates, and materials containing nano-objects

5.1 Method

There are many measurands that are used to characterize nano-objects and their agglomerates and aggregates, each providing different information about the nano-objects. The sample under test can be a material that partly contains nano-objects, for example to obtain a performance enhancement over the same material that does not contain the nano-objects. In this Technical Specification, we describe measurands from different categories. Use one of more of the measurands to characterize nano-objects and their agglomerates and aggregates. The measurands that shall be used depend on the information that the user requires.

5.2 Types of measurands

This Technical Specification describes the measurands for characterizing nano-objects based on popular current techniques for characterizing nano-objects. Tables and texts in each section are provided that describe:

a) Overarching measurand. This is the measurand intended to be measured, typically as the final output.

b) Measurands specific to the method. These are the measurands measured by the instrument and are related to the overarching measurand.

c) Range and resolution of particular techniques. These are given in units that depend on the particular measurand.

d) Limitations and references. References to EN or ISO standards are stated where they are available. Limitations refer to limitations of the technique.

5.3 State of nano-objects

Nano-objects exist in a number of different states and different techniques require the nano-objects to be in different phases, a summary of this is shown in Table 1.

The material under test may be composed entirely of nano-objects or it may contain a percentage of nano-objects where the percentage can be measured via different measurands for example number or mass. The degree and nature of the dispersion of the nano-objects is also important and is considered in Clause 14.

Table 1 —Different states of Nano-objects

Continuous phase	**Dispersed phase**		
	Solid	**Liquid**	**Gas**
Solid	Nano-composite, nano-(structured) powder mixture	Nanoporous material	Nanoporous material. Solid Nanofoam
Liquid	Nano-suspension / colloid	Nano-emulsion	Liquid Nanofoam
Gas	Nano-aerosol (solid)	Nano-aerosol (liquid)	(does not apply)

6 Measurands related to size and shape measurement of nano-objects and their agglomerates and aggregates

6.1 Introduction

The shape, mean size, and particle size distribution of nano-objects and their agglomerates and aggregates (NOAA) have a strong influence on their intrinsic properties or the properties of composite materials that contain them. Polymers and elastomers reinforced by nano-sized fillers are telling examples of such influence. The morphology of the fillers in addition to the nature of the interface between the fillers and the matrix are among the parameters that make the mechanical properties of the composite.

During their life cycle, nano-objects and the materials that contain them need to be characterized. After the synthesis, this characterization allows checking whether they will exhibit the properties they are designed for, even if, in some instances, the relationship between intrinsic characteristics of nano-objects and the desired application property (optical, electrical, and mechanical) is not fully understood. Regarding size and shape, their characterization may be made in dry form or in liquid dispersion, depending on the analytical technique used.

Due to the possibility of toxicological effects of some nano-objects, measurement methods in the air matrix, either at the workplace (in the immediate vicinity of a production or transformation process), or in ambient air in the immediate vicinity of a production plant can be useful. In this case, *in situ* and real-time measurements are favoured since they allow monitoring emission fluctuations whereas classical laboratory techniques are used after sampling on suitable supports.

During the use of a material containing nano-objects, some of them may be released from the material, as a consequence of a mechanical or atmospheric wear for instance (cutting or drilling of building materials, wear of paints or varnishes). Measurements in air are also needed in this case. Nano-objects may be coated on surfaces, to give (for example) antibacterial, optical or self-washing properties. Specific measurements of size and shape parameters on the surface of materials are then needed.

Overarching and specific measurands differ according to the techniques used and the continuous phase the nano-objects are in. These measurands and the techniques used to assess them are presented below.

6.2 Measurands related to size and shape measurement

Particle size distribution (PSD) is a list of numerical values that represent the relative or in rare cases the absolute amount of particles present in different size classes or bins ranging from the smallest particle size to the largest particle size. There are a number of different amount evaluators, the most relevant of which are:

a) the number of particles in a size class;

b) the total surface area of particles in a size class;

c) the total volume of the particles in a size class and;

d) the mass of the particles in a size class.

Evaluators like scattered light intensity are used to obtain PSD’s in techniques using the scattering of light (e.g. dynamic light scattering, DLS or small-angle X-ray scattering, SAXS). These PSD’s can be transformed into number or volume PSD’s using specific mathematical models, often requiring assumptions on the spherical shape of particles, uniform particle density or the knowledge of other physical parameters like refractive index. Here, the term “particle” refers to nano-objects, and their agglomerates and aggregates since many techniques used for size measurement are not able to differentiate between them and obtain separate PSD’s for individual nano-objects and their agglomerates and aggregates.

Shape is the external geometric form of a particle. When direct observational techniques are used like microscopy, more specific measurands can be defined in image analysis software to describe the shape of an object. Commonly used measurands are Feret diameter (which is the distance between two parallel tangential lines in a specific direction), elongation (the ratio between maximum Feret diameter and minimum Feret diameter) and convexity (the ratio between the projected area of the object and the area of its convex hull).

Particle shape distributions containing the amount of particles in different shape classes can be obtained by means of image analysis. The distribution amount is classified by particle number, surface area or volume.

6.3 Measurands related to size and shape measurement in aerosols

6.3.1 Overview

Nano-objects are prone to aggregation and agglomeration in all the matrices they are distributed in. It is especially the case with aerosols where aggregates and agglomerates are present in most circumstances. As a consequence, measurement techniques have to be applicable not only in the nanoscale range but also for particles above 100 nm.

Table 2 provides a summary of the measurands and methods used to determine size and shape of nano-objects in aerosols. In this table and the other tables that follow in this Technical Specification the term “overarching measurand” refers to the physical parameter that the technique intends to measure. The term “measurand(s) specific to method” refers to the physical parameter actually measured by the technique. For example, in electrical impaction, the inertia of particles is the specific measurand since it determines their trajectory in the device – therefore the plate which collects them. This plate corresponds to a particular equivalent aerodynamic diameter size class (the amount of particles on this plate – and on all others – will give a particle size distribution which is the overarching measurand). The term “resolution” does not refer to the minimum size achievable by the technique (this is indicated by the “typical size range”) but to the ability to distinguish two different sizes: it is therefore mainly linked to the number of measuring channels typically offered by the devices.

“Limitation” refers to the main drawback of the technique. It can be a concentration range, a measurement time or a minimum achievable size. Even if a particular technique gives number-weighted PSD, the concentration range is given in mass concentrations since it is easily known prior to measurement, e.g. by sampling on filters.

Table 2 contains techniques that measure in real-time with the exception of cascade impaction that detect the two microscopy techniques at the end of the table.

Table 2 — Measurands related to the size and shape measurement in aerosols

Overarching measurand	**Measurand specific to the method**	**Method**	**Size range**	**Resolution**	**Limitations**	**Reference (see Bibliography)**
Number-weighted size distribution, where "size" is the particle equivalent aerodynamic diameter	Electrical mobility	Electrical low-pressure impaction (ELPI)	Medium equivalent aerodynamic diameter between 6 nm and 10 µm	typically 13 to 500 size classes or bins split over the whole size range	Concentration range: 10 µg/m³ to 100 mg/m³ Particle density shall be known. Particle bounce and charge transfer problems.	[1]
Mass-weighted size distribution	Inertia	Cascade impaction	10 nm to 18 µm (depending on specific design)	typically 3 to 14 size classes or bins split over the size range		
Number-mass electrical mobility size distribution	Electrical mobility	Scanning mobility particle sizing (SMPS)	3 nm to 1 000 nm	A few nanometres	Measuring takes at least one minute – not adapted for fast phenomena.	[2]
Number-weighted size distribution, "size" being the equivalent optical diameter of particles.	Scattering cross section	Optical particle counters (OPC)	0,5 µm to 20 µm	0,1 µm	For NOAA, only usable for aggregates and agglomerates > 0,5 µm (nanoplate issue). The refractive index shall be known.	[3]
Mass-weighed aerodynamic size distribution	Velocity	aerodynamic particle sampler (APS)	0,5 µm to 20 µm	0,1 µm	The resolution is lower for non-spherical particles.	[4]
3D Size and shape of NOAA	2D-projected size and shape	Particle sampler with	1 nm to 10 µm	0,2 nm	Typical sampling	[5, 6]

	of NOAA. Number-weighted geometric size and shape distributions	TEM and image analysis			efficiency has a minimum (10 %) at 20 nm to 30 nm. TEM is not a real time technique.	
3D Size and shape of NOAA	2D-projected size and shape of NOAA. Number-weighted geometric size and shape distributions	Scanning electron microscopy (SEM) on filters	1 nm to 1 000 µm	1 nm to 5 nm	Needs sample preparation onto a substrate. Slow, individual particle measurement. SEM is not a real time technique.	[7]

6.3.2 General relevant standard

ISO 9276-1:1998, *Representation of results of particle size analysis – Part 1: Graphical representation*

ISO 9276-1:1/Cor 1:2004, *Representation of results of particle size analysis – Part 1: Graphical representation – Technical corrigendum 1*

ISO 9276-2:2014, *Representation of results of particle size analysis – Part 2: Calculation of average particle sizes/diameters and moments from particle size distributions*

ISO 9276-3:2008, *Representation of results of particle size analysis – Part 3: Adjustment of an experimental model to a reference model*

ISO 9276-4:2001, *Representation of results of particle size analysis – Part 4: Characterization of a classification process*

ISO 9276-5:2005, *Representation of results of particle size analysis – Part 5: Methods of calculation relating to particle size analysis using logarithmic normal probability distribution*

ISO 9276-6:2008, *Representation of results of particle size analysis – Part 6: Descriptive and quantitative representation of particle shape and morphology*

ISO 26824:2013, *Particle characterization of particulate systems – Vocabulary*

CEN ISO/TS 80004-6:2015, *Nanotechnologies – Vocabulary – Part 6: Nano-object characterization*

ISO/TR 27628:2007, *Workplace atmospheres – Ultrafine, nanoparticle and nano-structured aerosols – Inhalation exposure characterization and assessment*

6.3.3 Electrical low-pressure impaction (ELPI)

In this technique, the aerosol particles are first electrically charged by a corona effect, and fed into a low-pressure impactor fitted with several plates. Due to their inertial motion, the largest particles (or aggregates and agglomerates) accumulate on the upper plates whereas the smallest accumulate on lower plates. Each plate is equipped with an electrical counting system delivering a signal proportional to the electric charge received by the plate. A number PSD containing a number of size classes equal to the number of plates in the impactor is thus obtained.

The specific measurand involved in this technique is the inertia of objects. This measurand is directly linked to density and aerodynamic diameter for a given gas flow. Therefore, each plate collects particles in a given aerodynamic diameter range, for a given density.

At each plate, the total number of collected particles in the corresponding mass/diameter range is derived from the measured electrical current signal. This is possible after the experimental determination of the charger efficiency function. For each aerodynamic diameter, this function takes into account particle losses inside the charger, the fraction of particles charged and their average charge. The density of particles shall be known. Number-weighted size distributions can be obtained by this technique.

Recent enhanced designs (high resolution electrical low-pressure impactors) can provide size distribution with up to 500 size classes. Their specific impactor technology enables post-measurement chemical analysis of size classified particles.

As the technique assumes the particles to be spherical, it is not able to give direct information about the shape of nano-objects. However, it is possible to examine individual particles on the plates using Scanning Electron Microscopy (SEM) to obtain information on the shape versus size and operate as a cascade impactor.

6.3.4 Cascade impactors

Other designs are 13- and 14-stage cascade impactors that classify particles according to their inertia into 13 or 14 size fractions in the range of 16 nm to 10 µm. Each stage is weighed before and after measurement: therefore a mass-weighted particle size distribution is obtained.

Micro-orifice uniform deposit impactors are cascade impactors used to fractionate aerosol particles according to their aerodynamic size. They differ from other conventional cascade impactors, in the use of a large number of micro-orifice nozzles to reduce jet velocity and pressure drop, minimize particle bounce and re-entrainment, and enhance collection efficiency. This results in sharper cut-size characteristics and more accurate mass-weighted size distributions.

NOTE Typical electrical impactors determine size range in the order of 16 nm to 10 µm. The measurable mass concentration range depends on the size for example for an aerodynamic diameter of 100 nm, it is about 10 µg/m^3 to 100 mg/m^3.

6.3.5 Differential mobility analysing system (DMAS)

A differential mobility analysing system is a combination of differential electrical mobility classifier (DEMC) and a condensation particle counter (CPC). Here, particles are first electrically charged by means of a radioactive source, according to the Fuchs equilibrium charge distribution law. An adjustable electric field is applied between two electrodes in order to deflect the path of charged objects. Since this deflection is proportional to mass, each value of the electric field is able to extract a specific size class of objects from the system. A CPC placed at the outlet records the number concentration of each class. A number-mass mobility size distribution is thus obtained in a typical size range 3 nm to 1 000 nm, although novel instruments are improving the size range down to particles from 0,5 nm. The specific measurand involved in this technique is the electrical mobility, directly linked to mass and aerodynamic diameter of objects since their charge law is known. No information can be obtained on the shape. For very anisotropic objects like nanofibres, the charging law may become unpredictable, resulting in large uncertainties in the results.

Some alternate DEMC designs exist, where one of the electrodes is divided in a number of segments, each connected to highly sensitive electrometers. This allows the extension of the size range of the technique, typically to 10 nm to 10 µm. The fast mobility particle sizer spectrometer is an example of such design and can measure particles in the range 5,6 nm to 560 nm with a total of 32 channels. These designs are much faster than classical DMAS since they can perform measurements at more than 1 Hz.

NOTE A differential mobility analysing system (DMAS) is also sometimes called a scanning mobility particle sizer (SMPS)

6.3.6 Relevant standards

ISO 15900:2009, *Determination of particle size distribution – Differential electrical mobility analysis for aerosol particles*

EN ISO 28439:2011, *Workplace atmospheres - Characterization of ultrafine aerosols/nanoaerosols – Determination of the size distribution and number concentration using differential electrical mobility analysing systems*

6.3.7 Optical Particulate Counters (OPC)

The aerosol containing the nano-objects flows into a cell illuminated by a laser beam. Objects crossing the beam scatter light according to their particle size and shape. This phenomenon is due to the physical effects of diffraction, reflection and refraction. A photodetector converts light flashes received at given angles into electrical pulses. Using the height and count rate of the pulses, the number concentration and the equivalent sphere aerodynamic diameter can be derived from Mie theory. The refractive index of particles shall be known. Number-weighed aerodynamic size distribution ranging from 0,5 µm to 20 µm may be measured using such counters. This size range may seem irrelevant for the nanoscale but is complementary e.g. to SMPS measurements since nanoparticles are often found in aerosols under the form of aggregates and agglomerates.

No information can be obtained on the shape of the objects.

6.3.8 Relevant standards

ISO 13320:2009, *Particle size analysis - Laser diffraction methods*

ISO 21501-1:2009, *Determination of particle size distribution – Single particle light interaction methods – Part1: Light scattering aerosol spectrometer*

6.3.9 Aerodynamic Particle Sizing (APS)

The aerosol is pumped and accelerated through a nozzle. Particles exiting the jet have a velocity which depends on their surface area and mass. They cross two laser beams separated by a known distance, which produces two pulses of scattered light. Measuring the time delay between the two pulses allows the determination of the velocity. Aerodynamic diameter of particles (overarching measurand) is derived from the measured velocity, assuming spherical shape and unity density. A mass PSD is obtained in the size range 0,5 µm to 20 µm so this technique is only suitable for measuring aggregates and agglomerates of nano-objects and not the nano-objects themselves.

6.3.10 Transmission electron microscopy (TEM) combined with TEM grid samplers

Number-weighted geometric size and shape distributions can be obtained by means of image analysis of Transmission Electron Microscopy (TEM) micrographs, with some limits and restrictions. It is usually not possible to obtain separate PSD’s for nano-objects and their agglomerates and aggregates since elemental particles are very difficult to isolate in an aggregate or agglomerate with automatic criteria used by the software. Very long nanofibres, like carbon nanotubes, may be difficult to separate as individual particles since they are often entangled inside complex agglomerates. When using sampling devices, the flow rate and sampling duration should be carefully set for the amount of collected particles to be optimized. Indeed, low concentrations could limit the counting statistics whereas high concentrations could hinder the counting, overlapping objects being seen as a single particle by the software. Preliminary calibration of the pixel size shall be done by using reference materials.

Image analysis software gives access to number-weighted geometric size or shape distributions (expressed in equivalent sphere diameter or various dimensional parameters like length, width, Feret diameters, perimeter, and projected area). It usually requires object identification and separation from background using intensity thresholds applied to a grey-level image. Shape distributions can also be obtained, for instance by measuring individual aspect ratio of NOAA (length divided by width). TEM allows the differentiation between primary particles and those that are aggregates and agglomerates.

Sampling devices enable collection of aerosol particles on TEM grids with subsequent analysis in the instrument to obtain size and shape information.

There are different methods of sample collecting available. One method uses holey TEM grids to collect particles by filtration, using a pumping device. The grid is then examined in a transmission electron microscope. The collection efficiency – percentage of particles retained on the grid for a given size class – depends on the size of particles.

NOTE For example, for one instrument at a pumping rate of 0,3 l/min, the collection efficiency has a minimum value of about 15 % at 20 nm to 30 nm and is higher at lower and upper sizes [5].

Another method uses an electric field generated by an electrode to precipitate aerosol charged particles onto a TEM grid. The collection efficiency depends of several parameters (electric tension and electrode diameter). Concentration measurement by CPC before and after the sampler gives a global collection efficiency of 50 %. But the actual collection efficiency on TEM grids, as measured by TEM, is less than 1 % which means severe losses somewhere inside the device. The disadvantage of this method is that the particles shall be charged.

6.3.11 Relevant standards

ISO/TR 27628:2007, *Workplace atmospheres — Ultrafine, nanoparticle and nano-structured aerosols — Inhalation exposure characterization and assessment*

ISO/TS 10797:2012, *Nanotechnologies - Characterization of single-wall carbon nanotubes using transmission electron microscopy*

ISO 13322-1:2014, *Particle size analysis - Image analysis methods - Part 1: Static image analysis methods*

ISO 13322-2:2006, *Particle size analysis - Image analysis methods - Part 2: Dynamic image analysis method*

ISO 29301:2010*, Microbeam analysis - Analytical transmission electron microscopy - Methods for calibrating image magnification by using reference materials having periodic structures*

6.3.12 Scanning electron microscopy (SEM)

In scanning electron microscopy (SEM), an electron beam is produced, accelerated by a high voltage, focused and scanned on the surface of the sample. At each scanned point on the surface, electron-sample interaction yields specific signals among which secondary electron imaging gives a representation of the surface morphology, backscattered imaging gives information on local chemical composition and X-ray photons can be used to obtain information on local chemical composition. SEMs can also work in transmission mode facilitating the measurement of size and shape.

Automated image analysis may also be used. Image thresholding is more difficult than in TEM because the contrast in secondary imaging, which gives the best lateral resolution, is not as strong and is dependent on the object thickness and atomic number, as well as the local orientation of the surface with respect to the electron beam. The ultimate resolution achievable is 1 nm to 5 nm, depending on the SEM instrument used. It may not be sufficient to distinguish very small (<10 nm) particles. SEM can differentiate between primary particles and those that are aggregates and agglomerates.

Aerosol particles are collected on filters by specific pumping devices at low flow rates or at high flow rates. These devices can be fitted with different filter heads to sample all particulate matter or those below 10 µm, 2,5 µm or 0,1 µm. These filters can be further metallized to allow their observation in SEM after transfer to a suitable support or stub. Care should be taken with the deposition density in order to obtain a low enough density such that examination and measurement of individual particles is possible.

6.3.13 Relevant standards

ISO/TR 27628:2007, *Workplace atmospheres - Ultrafine, nanoparticle and nano-structured aerosols - Inhalation exposure characterization and assessment*

ISO 13322-1:2014, *Particle size analysis - Image analysis methods - Part 1: Static image analysis methods*

ISO 13322-2:2006, *Particle size analysis - Image analysis methods - Part 2: Dynamic image analysis method*

6.4 Measurands related to size and shape measurement in powders

6.4.1 Overview

Table 3 provides a summary of the measurands and methods used to determine size and shape of nano-objects in powders.

Table 3 — Measurands related to the size and shape measurement in powders

Overarching measurand	Measurand(s) specific to method	Method	Size range	Resolution	Limitation	Reference (see Bibliography)
3D Size and shape of NOAA	2D-projected size and shape of NOAA. Number-weighted geometric size and shape distributions	Scanning electron microscopy (SEM)	1 nm to 1 mm	1 nm to 5 nm	Metal deposition is generally necessary.	[8]
Mass specific surface area	mass of adsorbed gas (giving total surface area of the sample being measured)	Gas adsorption using BET method	1 nm to 1 µm	A few nanometres	Needs relatively large amount of sample material (depending on the expected specific surface area). Needs dry, outgassed sample	[9]
Volume-weighted size distribution (size being the equivalent geometric diameter)	Angular distribution of scattered light	Laser diffraction (LD)	30 nm to 1 mm	10 nm	Underestimation of submicron particles for polydispersed samples	[10]
Volume weighted mean diameter	Broadening of X-ray diffraction peaks	X-ray diffraction (XRD)	5 nm to 100 nm	5 nm	Not adapted for polycrystalline or amorphous materials	
volume weighted mean diameter of carbon nanotubes	Frequency shift	Raman spectroscopy	0,5 nm to 2 nm	0,05 nm	Not straight forward for multiwall nanotubes	[11, 12]

NOTE TEM is not included here as sample preparation for TEM often requires that the powder containing nano-objects is dispersed in a suitable liquid dispersant. TEM is discussed in 6.3.10 and 6.5.12.

6.4.2 Relevant standards

CEN ISO/TS 17200:2015, *Nanotechnology - Nanoparticles in powder form - Characteristics and measurements*

ISO 26824:2013, *Particle characterization of particulate systems – Vocabulary*

6.4.3 Scanning electron microscopy (SEM)

Nano-objects and their agglomerates and aggregates in the form of powder can be spread on suitable stubs designed to fit on SEM specimen stages. Convenient deposition techniques are, for instance, the use of a double-sided, conductive, adhesive tape to fix the objects onto the stub. Care should be taken with the deposition density in order to obtain a low enough density such that examination and measurement of individual particles is possible.

SEM is able to provide information relative to size and shape of particles but with some limitations (see 6.3.12 for details and principle of operation).

In particular for powders, the tendency to agglomerate when deposited on a substrate is a severe drawback for subsequent image analysis. Particle size distributions of powders are thus difficult to obtain in SEM. SEM is however very useful to describe shape of NOAA, by visual interpretation of the pictures. For this reason, it is routinely used in many NOAA production or research sites.

6.4.4 Relevant standards

ISO/TS 10798:2011, *Nanotechnologies - Characterization of single-wall carbon nanotubes using scanning electron microscopy and energy dispersive X-ray spectrometry analysis*

ISO 16700:2016 *Microbeam analysis – Scanning electron microscopy – Guidelines for calibrating image magnification*

6.4.5 Gas adsorption, the BET method

The Brunauer, Emmett and Teller (BET) method consists of the adsorption of a monolayer of gas (usually nitrogen, but krypton, argon and carbon dioxide are also used) on the surface of objects constituting the powdered sample. In the case of nitrogen, the adsorption isotherm is determined at the boiling point and atmospheric pressure. The total amount of the adsorbed gas in the monolayer is derived from the adsorption isotherm. The size of the adsorbed nitrogen molecule being known, the total surface area of the sample is derived. It is converted to mass specific surface area by dividing by the mass of the sample. This measurand can be used to characterize NOAA powders. If the density is known, it may also be converted in a mass weighted mean geometric diameter, assuming a spherical shape for the objects and assuming that the objects are non-porous. The measurand is the mass specific surface area and mass weighted geometric mean diameter.

6.4.6 Relevant standards

ISO 9277:2010, *Determination of the specific surface area of solids by gas adsorption – BET method*

6.4.7 Laser diffraction (LD)

An object illuminated by a laser beam scatters to different angles and intensities where the intensities depend upon particle size. The Mie solution to Maxwell's equations describes the scattering of light by particles, whatever their size with respect to the wavelength. Small objects scatter light at large angles, larger objects at small angles.

The specific measurand is the angular distribution of scattered light. It is converted to a volume-weighted size distribution, assuming a spherical shape for the objects. The refractive index shall be known.

NOAA in powder form can be measured by laser diffraction devices. Ultrasonic energy is generally applied in the device itself prior to measurement, to break agglomerates. No information is given about the shape. As for many other techniques, uncertainties increase for non-spherical objects. The size range is about 30 nm to

1 mm. In a very polydispersed sample, the relative amount of sub-micrometre particles may be underestimated. It should be noted that size measurement of powders can also be realized in liquid form, by dispersion in a suitable liquid matrix usually followed by ultrasonic treatment to avoid excessive agglomeration. Techniques described in 6.5 can then be applied.

6.4.8 Relevant standards

ISO 13320:2009, *Particle size analysis - Laser diffraction methods*

6.4.9 X-ray diffraction (XRD)

This is the basic method for the characterization of the crystalline structure of materials. The description of this technique and additional information on sample preparation, applications, benefits and limitations are given in 7.2.10.

XRD can also provide information on volume weighted mean diameter of primary crystalline domains. Monocrystalline nano-objects have only one crystalline domain, therefore the crystallite size measured in XRD will correspond to the dimensions of the nano-object. In the case of polycrystalline nano-objects, the measured size will be smaller than the external size of the nano-object.

This information on the crystallite size is derived from the broadening of X-ray diffraction peaks generated by the sample. Instrumental profile, microstrains and local disorder shall be taken into account since they also have an influence on peak broadening. This broadening occurs when the crystalline domains are smaller than about 100 nm. In the case of non-isotropic crystalline materials, the broadening of X-ray diffraction peaks will depend on the dimension of the crystals along the direction orthogonal to the atomic planes that generate the peak.

6.4.10 Relevant standards

EN 13925-1:2003, *Non-destructive testing - X-ray diffraction from polycrystalline and amorphous material – Part 1: General principles*

EN 13925-2:2003, *Non-destructive testing - X-ray diffraction from polycrystalline and amorphous material – Part 2: Procedures*

EN 13925-3:2005, *Non-destructive testing - X-ray diffraction from polycrystalline and amorphous materials - Instruments*

6.4.11 Raman spectroscopy

Raman spectroscopy is normally used for surface chemical analysis; however it can be used in certain cases to determine size, for example in carbon nanotubes or the layer thickness of graphene flakes. The Raman effect is the inelastic scattering of light with a change of frequency, due to the transfer of energy between the sample and incident light. This shift of frequency gives information on the vibrational modes in a molecule (or, in the case of carbon nanotubes, a specific molecular assembly).

In the case of carbon nanotubes, one specific vibrational mode is the “radial breathing mode (RBM)” corresponding to cyclic radial expansion and contraction of the tube under excitation by light. The frequency of this mode is directly linked to the diameter of the nanotube. Therefore, the RBM frequency shift of RBM gives volume weighted mean diameter of single wall carbon nanotubes.

6.5 Measurands related to size and shape measurements of nano-objects in liquid dispersions

6.5.1 Overview

Table 4 provides a summary of the measurands and methods used to determine size and shape of nano-objects in liquids.

Table 4 — Measurands related to the size and shape measurement in liquids

Overarching Measurand	Measurand(s) specific to method	Method	Size range	Resolution	Limitation	Reference (see Bibliography)
Mass-weighted size distribution (size being the equivalent hydrodynamic diameter)	Stokes diameter in CLS (Equivalent hydrodynamic diameter based on sedimentation velocity of objects in a suspending medium)	Centrifugal liquid sedimentation (CLS)	20 nm to 1 000 nm	5 nm	Relative high concentrations needed (>10 g/l), for devices using X-ray absorption detectors. Requires known density of particles.	[13]
Volume-weighted size distribution (size being the equivalent hydrodynamic diameter)	Autocorrelation function of scattered light at a given angle.	Dynamic light scattering (DLS)	6 nm to 1 000 nm	10 nm	Not applicable to concentrated, coloured or very polydisperse samples.	[13]
Volume-weighted size distribution (size being the equivalent geometric diameter)	Angular distribution of scattered light	Laser diffraction	30 nm to 1 mm	10 nm	Underestimation of submicron particles for polydispersed samples	[10]
Volume-squared-weighted size distribution(size being the equivalent geometric diameter), Fractal dimension	Angular distribution of scattered X-rays.	Small angle X-ray scattering (SAXS)	1 nm to 300 nm	20 nm	Complex models shall be used to extract the specific measurands. Not suitable for polydisperse samples.	[14]
Number-weighted hydrodynamic size distribution	Diffusion coefficient	Particle tracking analysis (PTA)	10 nm to 2 000 nm	10 nm	Not applicable to concentrated or very polydispersed samples.	[15]

3D particle size and shape distribution	2D-projected size and shape of NOAA. Number-weighted geometric size and shape distributions	Cryo-microscopy	3 nm to 500 nm	1 nm	Not applicable to concentrated samples.	[16]
3D particle size and shape distribution	2D-projected size and shape of NOAA. Number-weighted geometric size and shape distributions	Scanning electron microscopy (SEM)	1 nm to 1 mm	1 nm to 5 nm	Needs sample preparation onto a substrate. Slow, individual particle measurement.	
3D particle size and shape distribution	2D-projected size and shape of NOAA. Number-weighted geometric size and shape distributions	Transmission electron microscopy (TEM)	0,5 nm to 10 µm	0,2 nm	Needs sample preparation onto a TEM grid. Slow, individual particle measurement	

6.5.2 Centrifugal liquid sedimentation (CLS)

Centrifugal liquid sedimentation (CLS) or differential centrifugal sedimentation (DCS) as it is also known is a technique based on the measurement of the settling rate (specific measurand) of objects dispersed in a fluid. This rate is related to the diameter and density of the objects. The density and viscosity of the fluid shall be known and the density of the objects shall also be known. Disc centrifuge sedimentation is the most widely used variant of this technique. Typically a sucrose density gradient is created by gently overlaying lower concentrations of sucrose on higher concentrations in a centrifuge tube. Alternatively gradient mixers or gradient makers can be used to form a gradient. The dilute dispersion containing the particles of interest is injected on top of the gradient and centrifuged at forces in excess of 150 000 relative centrifugal force. The high speed spinning of the disk causes radial separation of objects with respect to size. A light or X-ray detector continuously records the mass concentration at a given radial position along the disk. Using the Stokes law, an extinction intensity-weighted hydrodynamic size distribution is obtained and transformed into a volume-weighted or number-weighted size distribution (the density shall be known and also the refractive index if light detectors are used).

The applicable size range is about 20 nm to 1 000 nm, depending upon relative densities of particles and dispersing liquid. X-ray detection is mainly suitable for inorganic particles. To obtain sufficient X-ray extinction, relative high dispersion concentrations are needed (usually in the range 10 g/l to 100 g/l, depending upon the nature of the dispersed material).

6.5.3 Relevant standards

ISO 13318-1:2001, *Determination of particle size distribution by centrifugal liquid sedimentation methods – Part 1: General principles and guidelines*

ISO 13318-3:2004, *Determination of particle size distribution by centrifugal liquid sedimentation methods – Part 3: Centrifugal X-ray method*

ISO 13318-2:2007, *Determination of particle size distribution by centrifugal liquid sedimentation methods – Part 2: Photocentrifuge method*

6.5.4 Dynamic light scattering (DLS)

In a liquid, the Brownian motion of dispersed objects causes temporal fluctuations of local number concentration. These fluctuations result in fluctuations of scattered light. Large particles have slow Brownian motions and scatter light at small angles and high intensities. Conversely, small particles with fast Brownian motion scatter light at high angles and low intensities. Hence, the determination of the autocorrelation function of scattered light at a given angle (specific measurand), allows the determination of the distribution of the diffusion coefficient of dispersed objects. Diffusion coefficient is converted into hydrodynamic diameter if the temperature and the viscosity of the dispersing medium are known. It should be noted that objects are assumed to be spherical, thus uncertainties increase for non-spherical objects. Taking into account all these considerations, a scattering intensity-weighted size distribution is obtained, which can be further converted into volume-weighted size distributions (overarching measurand).

Large polydispersity will lead to underestimation of smallest objects, since their low scattered-light signal will be masked by huge signal arising from biggest objects as the scattering intensity is proportional to diameter of the object to the 6th power. DLS is limited to non-absorbing samples and is not applicable to large concentrations, due to multiple light scattering effects. The size range is approximately 3 nm to 1 000 nm.

6.5.5 Relevant standards

ISO 13321:1996, *Particle size analysis - Photon correlation spectroscopy*

ISO 21501-2:2007, *Determination of particle size distribution - Single particle light interaction methods – Part 2: Light scattering liquid-borne particle counter*

ISO 22412:2008, *Particle size analysis - Dynamic light scattering (DLS)*

ASTM E2490-09, *Standard guide for measurement of particle size distribution of nanomaterials in suspension by Photon Correlation Spectroscopy (PCS)*

6.5.6 Laser diffraction (LD)

This technique described in 6.4.7 for powders also allows the characterization of PSD’s for liquid dispersions.

A simple sample preparation (dispersion of NOAA in water, eventually with the help of ultrasonic treatment and/or surface active agents) in a concentration range of 0,1 g/l to 1 g/l allows a volume-weighted size distribution to be obtained for NOAA. Benefits and limitations are the same as for powders (see 6.4.7).

6.5.7 Relevant standards

ISO 13320:2009, *Particle size analysis - Laser diffraction methods*

6.5.8 Small angle X-ray scattering (SAXS)

SAXS technique uses synchrotron radiation or laboratory scale commercial X-ray sources. The principle is essentially the same as laser diffraction. The very small wavelength of X-rays gives access to size and shape information in the nanometre range in favourable cases (existence of a fractal domain over a certain size range, low polydispersity of elemental particles).

The specific measurand is the angular distribution of scattered X-rays. The overarching measurands are a volume-squared-weighted size distribution of elemental particles (using Guinier approximation), a fractal dimension of aggregates and, in some cases, a mean size of agglomerates. All these measurands are obtained by modelling the experimental scattered intensity / angle curve.

6.5.9 Relevant standards

ISO 17867, *Particle size analysis - Small-angle X-ray scattering*

6.5.10 Particle tracking analysis (PTA)

This technique uses an optical microscope fitted with a laser beam. The scattered light of each particle is detected by a CCD camera. The motion of each particle is tracked from frame to frame by image analysis software. The Brownian motion of each particle (specific measurand), related to its hydrodynamic diameter, is recorded. A number-weighted hydrodynamic size distribution is therefore obtained.

As in DLS, the viscosity of the dispersing medium shall be known. This technique applies to rather dilute specimens in the range 10 nm to 2 000 nm. This range depends to upon the chemical nature of the sample. For polydispersed samples, large counting statistics shall be used to reduce uncertainties in the size distribution.

6.5.11 Relevant standards

ISO/DIS 19430:2015, *Particle size analysis - Particle Tracking Analysis (PTA) Method*

ASTM E2834-12, *Standard Guide for Measurement of Particle Size Distribution of Nanomaterials in Suspension by Nanoparticle Tracking Analysis (NTA)*

6.5.12 Electron microscopy

Nano-objects dispersed in liquids can be examined in SEM or TEM. For this purpose, it is better to choose a good dispersion media to avoid excessive agglomeration. As an example, metal oxide nano-objects often exhibit a hydrophilic character, due the presence of hydroxyl groups on the surface. Water, or water/ethanol mixtures are often good dispersion media in this case. In contrast, carbon nanotubes are strongly hydrophobic and are better dispersed in non-polar solvents.

For SEM, a small amount of dispersion (5 µl to 50 µl) can be transferred onto a flat support, for instance a glass disk, and allowed to dry. With older instruments it may be necessary to coat non-conductive particles by a conductive film through metal sputtering but this is not generally necessary with modern instruments operating at low accelerating voltages. For TEM, 2 µl to 10 µl of dispersion can be transferred onto a TEM grid, and then covered with a carbon membrane. In the case of aqueous dispersions, hydrophilisation of substrates, prior to deposition, can be a considerable advantage since it will prevent artefactual agglomeration upon drying. This is easily achieved by the use of a glow-discharge apparatus which is able to fix electric charges on the supports.

Cryo-TEM technique is a combination of a cryogenic sample preparation and observation on a dedicated sample holder at liquid nitrogen temperature. A very thin (100 nm to 500 nm) film of the liquid sample, prepared on a TEM grid, is very rapidly frozen by quenching in liquid ethane or propane. In the case of aqueous dispersions, the cooling rate is so high that ice crystal formation is prevented. For dispersions based on organic solvents, rapid freezing in liquid nitrogen shall be employed.

Objects then instantly have a fixed position: agglomeration cannot occur. The TEM grid is then transferred using the cryo-specimen holder for observation. This technique has the unique advantage to be able to image liquid dispersions in their natural state, since drying artefacts are avoided.

Size and shape measurements of either dried dispersions in SEM and TEM or Cryo-TEM samples can be made as described previously (6.3.10 and 6.3.12).

6.6 Measurands related to size and shape measurement on surfaces (microscopy techniques)

6.6.1 Overview

Table 5 provides a summary of the measurands and methods used to determine size and shape of nano-objects where the nano-objects are mounted on a surface.

Table 5 — Measurands related to the size and shape measurement on surfaces

Overarching measurand	Measurand(s) specific to method	Method	Size range	Resolution	Limitation	Reference (see Bibliography)
3D Size and shape of NOAA	2D-projected size and shape of NOAA. Number-weighted geometric size and shape distributions	Scanning electron microscopy (SEM)	1 nm to 1 mm	1 nm to5 nm	Needs sample preparation onto a substrate. Slow, individual particle measurement	
3D topographic map of the surface	Contact force	Atomic force microscopy (AFM)	1 nm to 1 000 nm	0,1 nm	Use z height of particles as resolution limited by probe size in *x* and *y* directions	[17]

6.6.2 Scanning electron microscopy (SEM)

Nano-objects can easily be examined in SEM. A small piece of material exhibiting the surface is fitted on a suitable SEM support, by means of conductive paste. For observation in classical (high vacuum) SEM, the sample surface may need to be made conductive by metal sputtering in a vacuum coater, although this may not be necessary with modern instruments which can operate at low accelerating voltages and hence less charging. Specific properties of the sample (like a high amount of adsorbed water) may however lead to bad conductivity even after metal sputtering. Low-vacuum SEM's allow observation without the need of this treatment, due to a special design of the backscattered electron detector.

Image analysis will be possible if the size of the objects is compatible with the lateral resolution of the instrument. The roughness of the surface has to be very low, otherwise local contrast fluctuations due to topography may hinder the detection of objects on the base of image grey level analysis. The surface concentration shall be well below the percolation threshold to allow identification of individual objects.

6.6.3 Atomic force microscopy (AFM)

The surface of the sample is scanned on a rectangular raster by a very sharp tip (usually silicon, with a radius of curvature in the range 5 nm to 10 nm). Piezoelectric components are used to generate motion in the *x, y, z* motion of a tip mounted on a cantilever relative to sample. At the immediate proximity of the surface, various forces are experienced by the tip which are generally detected via deflection of the cantilever which is monitored using a laser beam coupled to an optical detector. In the constant force contact mode, the total force exerted on the tip is maintained at a constant level by adjusting the z height of the tip relative to the sample. This feedback signal leads to the overarching measurand of a topographic image of the surface. The specific measurand is then a contact force (for example Van der Waals, electrostatic), converted to a laser beam deflection and finally to a three-dimensional map of the surface.

In contact mode, the tip has a tendency to stick to or damage the surface of many materials, under the action of attractive forces due to adsorbed liquid layers. The intermittent contact mode avoids this by oscillating the *z* motion of the cantilever such that the probe tip makes contact with the sample surface for a fraction of the sinusoidal oscillation. In this mode, the change in the amplitude arising from the intermittent contact can be used to control the relative heights of the sample and tip in the scanned image leading to the topographic image.

6.6.4 Relevant standards

ISO 11952:2014, *Surface chemical analysis - Scanning-probe microscopy - Determination of geometric quantities using SPM: Calibration of measuring systems*

ISO 11775:2015, *Surface chemical analysis - Scanning-probe microscopy - Determination of cantilever normal spring constants*

ISO 13095:2014, *Surface Chemical Analysis - Atomic force microscopy - Procedure for in situ characterization of AFM probe shank profile used for nanostructure measurement*

7 Measurands related to chemical analysis of nano-objects and their agglomerates and aggregates

7.1 Introduction

It is important to characterize the chemical composition of nano-objects as it provides information about the chemical nature of components, the additives, the localization of the chemical species, and the surface chemical states. Some measurements can also help to investigate the contamination of nano-objects and their agglomerates and aggregates such as residual organic components (from initial preparation) or metallic contamination. Some information can be determined on volatile components using thermal analysis studies with identification of gases evolved during the heating (for example by the EGA method). The techniques presented in this chapter are not specifically designed for use for nano-objects and often do not give nanoscale resolution but can provide very valuable information on them.

The characterization process of nano-objects should also take into account the possibility of their complex structure. Such structures (for example core-shell structure or complex surface molecules) require characterization methods which provide detailed information about chemically active entities. Additionally, the development of nano-composites requires the knowledge of the chemical properties of core-shell structure. The properties of nano- composite materials containing nano-fillers can be significantly impacted by the mixture ratio between the organic matrix and the nano-fillers. For this purpose the degree of dispersion is needed throughout the sample.

The manufacturing process for nano-objects can contaminate the material. The measurand techniques related to chemical analysis described in this chapter can be helpful to distinguish different types of contamination for nano-objects. The techniques can help to identify impurities located on the surface of nano-objects or in solution.

Many various types of nano-objects are prepared in the form of aqueous dispersion. The nano-objects in such dispersions can exist as primary particles, agglomerates, or aggregates. The stability of the dispersion depends on the effect of all forces, which are determined mainly by the properties of the particle and the dispersing medium and particle surface properties, i.e. surface chemistry. It is important to consider the fundamental relevance of surface treatment or modifications of nanomaterials. Otherwise many nano-objects will tend to form large agglomerates and the primary particles will not disperse in water. In addition, nano-objects might interact with the liquid phase components, partially or totally yielding degradation or transformation products that might influence the overall toxicity and fate processes.

7.2 Measurands related to surface chemical analysis of nano-objects and their agglomerates and aggregates

7.2.1 Measurands

The measurands are given in Table 6 and described in more detail along with the methods in the subsequent sections.

Table 6 — Measurands related to the surface chemical analysis of nano-objects and their agglomerates and aggregates

Overarching measurand	Measurand specific to method	Method	Lateral resolution of the method	Depth resolution of the method	Limitation	Reference (see Bibliography)
Chemical identification	kinetic energies of the electrons [eV]	Auger electron spectroscopy (AES)	> 10 nm	2 nm to 20 nm	Samples analysed under high vacuum, charging of non-conducting samples Sensitivity (0,3 at.%)	[18, 19, 20, 21]
Composition, chemical bonding, surface properties	Measures the changes in the energy distribution of an electron beam transmitted through a thin specimen [eV]	Electron energy loss spectroscopy (EELS)	0,1 nm	10 nm	Need very thin specimens, < 30 nm, Intensity weak for energy losses > 300 eV Can only be undertaken with a TEM	[22, 23, 24]
Elemental, isotopic, or molecular composition of the surface	Unified atomic mass units [u]	Secondary ion mass spectroscopy (SIMS)	> 200 nm	1 nm approximately 1 nm (inorganic) approximately 10 nm (organic)	Quantification challenging Samples analysed under vacuum	[20, 21, 25, 26, 27, 28]
Chemical, elemental analysis	Fluorescence spectrum [Intensity vs wavelength in cm^{-1}]	X-ray fluorescence spectroscopy (XRF)	1 nm to 100 µm	5 µm to 20 µm	The normal quantitative limit is 10 to 20 ppm (parts per million). In combination with a synchrotron radiation (SR) X-ray microbeam, it	[21, 29, 30, 31, 32]

					is possible to achieve absolute detection limits at the level of around 100 ppb (parts per billion)	
Crystalline size, crystallographic phase, lattice parameters, structure	Angles and intensities of diffracted X-ray beams (intensity, degree)	X-ray diffraction (XRD)	50 µm	5 µm to 20 µm	Is more accurate for measuring large crystalline structures rather than small ones.	[21, 25, 33]
Composition, electronic structure of materials. Core levels, valence and conduction band.	kinetic energies of the electrons [eV]	X-ray photoelectron spectroscopy (XPS)	> 10 µm	> 1nm	Samples analysed under vacuum Sensitivity (0,3 at.%)	[18, 20, 21, 26, 34]
Composition	The interaction between an electron beam and the surface of the sample produces photons	Energy dispersive X-ray spectrometry (EDS or EDX)	0,5 µm	0,3 µm to 5 µm	For EDX using SEM the specimens shall be conductive, well-polished. The composition is relative	[21, 25, 35]

7.2.2 Auger electron spectroscopy (AES)

This method provides information about the chemical identification of materials and works in ultra-high vacuum. This technique uses the Auger effect, which is based on the analysis of energetic electrons emitted from an excited atom after a series of internal relaxation process. The Auger effect is an electronic process of AES resulting from the inter- and intra-state transitions of electrons in an excited atom. In Auger spectroscopy the charging effects in non-conducting samples are the most common limitation.

It has high lateral resolution and precise chemical sensitivity. Surface sensitivity in AES arises from the fact that emitted electrons usually have energies ranging from 50 eV to 3 keV, which leads to detection limits of approximately 0,1 atomic percent (at.%) to 1 atomic percent (at.%) [18, 19, 26, 36].

7.2.3 Relevant standards

ISO 16531:2013, *Surface chemical analysis - Depth profiling - Methods for ion beam alignment and the associated measurement of current or current density for depth profiling in AES and XPS*

ISO 18118:2015, *Surface chemical analysis - Auger electron spectroscopy and X-ray photoelectron spectroscopy - Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials*

ISO 16242:2011, *Surface chemical analysis - Recording and reporting data in Auger electron spectroscopy (AES)*

ISO 29081:2010, *Surface chemical analysis - Auger electron spectroscopy - Reporting of methods used for charge control and charge correction*

ISO/TR 14187:2011, *Surface chemical analysis - Characterization of nanostructured materials*

ISO 16531:2013, *Surface chemical analysis - Depth profiling - Methods for ion beam alignment and the associated measurement of current or current density for depth profiling in AES and XPS*

ISO 15471:2016, *Surface chemical analysis - Auger electron spectroscopy - Description of selected instrumental performance parameters*

7.2.4 Electron energy loss spectroscopy (EELS)

In this technique material is exposed to a beam of electrons with a known, narrow range of kinetic energies, where some of the electrons will undergo inelastic scattering. The amount of energy loss can be measured via an electron spectrometer and interpreted in terms of what caused the energy loss. It operates in a TEM and can be thought of as complementary to energy-dispersive X-ray spectroscopy (EDS) but with detectability 10 times higher than EDS and much better for low atomic number elements. Signal includes chemical information and direct information on the structure of solids and oxidation state of the elements. EELS is capable of measuring atomic composition, chemical bonding, valence and conduction band electronic properties. It gives better discrimination between elements than EDS. The samples for EELS investigation in the TEM required careful preparation and are thin slices of a material that can be provided by focused ion beam (FIB) or ultramicrotome [22, 23, 24, 37, 38].

7.2.5 Relevant standards

ISO/TR 14187:2011, *Surface chemical analysis - Characterization of nanostructured materials*

7.2.6 Secondary ion mass spectroscopy (SIMS)

SIMS is a technique used in materials science and surface science to analyse the composition (identification of trace elements, organic molecules and polymers on surfaces, with higher than 1 ppm sensitivity) of solid surfaces by sputtering the surface of the specimen with a focused primary ion beam and collecting and analysing ejected secondary ions. The mass/charge ratios of these secondary ions are measured with a mass spectrometer to determine the elemental, isotopic, or molecular composition of the surface to a depth of 1 nm to 2 nm. Despite the fact that this method has approximately 200 nm lateral resolution it can be used for nano objects and materials that contain them for chemical identification. It is a highly sensitive method for investigating the surface chemistry (top 1 nm) of samples [25, 26, 27, 28, 36].

7.2.7 Relevant standards

ISO 20341:2003, *Surface chemical analysis - Secondary-ion mass spectrometry - Method for estimating depth resolution parameters with multiple delta-layer reference materials*

ISO 18114:2003, *Surface chemical analysis - Secondary-ion mass spectrometry - Determination of relative sensitivity factors from ion-implanted reference materials*

ISO 23830:2008, *Surface chemical analysis - Secondary-ion mass spectrometry - Repeatability and constancy of the relative-intensity scale in static secondary-ion mass spectrometry*

ISO 22048:2004, *Surface chemical analysis - Information format for static secondary-ion mass spectrometry*

ISO/TR 14187:2011, *Surface chemical analysis - Characterization of nanostructured materials*

7.2.8 X-ray fluorescence spectroscopy (XRF)

XRF is a technique used for elemental chemical analysis of materials. An X-ray source is used to irradiate the specimen and to cause the elements in the specimen to emit (or to excite) their characteristic X-rays. A detection system (wavelength dispersive) is used to measure the peaks of the emitted X-rays for qualitative and quantitative measurements of the elements and their amounts. The technique was extended in the 70's to analyse thin films. XRF is routinely used for the simultaneous determination of elemental composition and film thickness. When the materials are excited with high-energy short wavelength radiation (like X-rays) they can become ionized. If the energy of the radiation is sufficient to dislodge a tightly-held inner shell electron, the atom becomes unstable and an outer shell electron replaces the missing inner electron. Apart from its non-destructive nature, this technique is fast and multi-elemental and is successfully applied in chemical studies of different types of materials. Before XRF measurements, there is no need for any restoration or cleaning process, except for the mechanical removal of contamination from the surface of samples, undertaken under microscope visualization. All analyses are performed in vacuum in order to detect light elements. The elements in the samples are identified based on characteristic X-ray lines and can be used in a wide range of elements, from sodium (atomic number 11) to uranium (atomic number 92) and provides detection limits in ppm. It is a fast technique (the chemical compositions to be determined in seconds) and easy to use. The analysed volume is very large compared to any surface contamination. Reference materials are needed for calibration. Despite the fact that this method has approximately 100 nm lateral resolution it can be used for nano objects and materials that contain them for chemical identification [29, 30, 31].

Total reflection X-ray fluorescence (TXRF) is similar to energy dispersive XRF technique but operates at set geometry. Here, an incident beam impinges upon a sample at an angle below the critical angle of external total reflection for X-rays resulting in reflection of almost 100 % of the excitation beam photons. The advantage of is reduced measurement background contributions by elimination of sample scattering resulting in increased elemental measurement sensitivity. TXRF is also a well-established technique for chemical analysis and is mainly employed for electronic industry quality control. Due to the high sensitivity in heavy metal detection, TXRF is suitable for environmental chemical nanoscale metrology. Given appropriate standards, in the future TXRF could be considered for routinely quantitative analyses of environmental matrices. Moreover, the extension of TXRF to measure the angle dependence fluorescence signal shows increased interest to thin layer analysis of nano-particles.

7.2.9 Relevant standards

ISO 14706:2014, *Surface chemical analysis - Determination of surface elemental contamination on silicon wafers by total-reflection X-ray fluorescence (TXRF) spectroscopy*

ISO/TS 18507:2015, *Surface chemical analysis - Use of Total Reflection X-ray Fluorescence spectroscopy in biological and environmental analysis*

7.2.10 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a method is used for determining the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of X-rays to diffract into many specific directions. The method is suitable for characterization and identification of various polycrystalline phases.

XRD is a basic method for the characterization of the crystalline structure of materials. An important feature of X-ray radiation is the fact that it cannot be focussed easily, so the information about the structure of material is usually provided from a relatively large area (approximately 50 µm). Powdered samples are positioned on a flat plate sample holder. In powder diffraction it is important to have a sample with a smooth plane surface. The benefits of this method are that non-destructive structure analysis can be used for a small amount of the powder and the measurements can be conducted with increasing temperature. For nano-object analysis, it is likely that broadening of the diffraction lines will be observed, which makes phase analysis difficult.

XRD can measure the average spacing between layers or rows of atoms, determine the orientation of a single crystal or grain, find the crystal structure of an unknown material as well as internal stress of small crystalline regions and determine structural properties such as lattice parameters, strain, grain size, epitaxy, phase composition [25, 39, 40].

7.2.11 Relevant standards

ISO/TR 14187:2011, *Surface chemical analysis – Characterization of nanostructured materials*

7.2.12 X-ray photoelectron spectroscopy (XPS)

In X-ray photoelectron spectroscopy (XPS) a sample is irradiated with X-rays that penetrate the sample. When X-ray photons hit and transfer energy to a core-level electron, the electron is emitted from its initial state with a kinetic energy dependant on the incident X-ray and the binding energy of the atomic orbital from which it originated. These electrons are released, detected and counted as a function of their energy (spectroscopic). The energy and intensity of these emitted electrons are analysed to identify and determine the concentrations of the elements present. The X-ray beams in some standard systems can be as small as 5 µm and penetrate deep into the surface. This is much bigger than a nanoparticle diameter. However, the escape depth of the freed electrons is of the order of less than 10 nanometres so information is obtained from within this depth.

XPS can be applied to identify the elements present in a piece of surface of a sample, which is typically 5 µm wide and a few nm thick. XPS can be applied to obtain more general information on the elements present in the sample, but has a relatively high detection limit (about 0,01 mass%, or about 0,1 g/kg to 0,8 g/kg depending on the element). XPS is more sensitive to heavy elements than to lighter elements. It only detects the elements in a very thin layer close to the surface (about 10 nm). XPS can give an indication on the presence of a coating surrounding the nano-objects and their agglomerates and aggregates.

Careful sample preparation is essential to ensure good quality data. Samples should preferably be smooth, flat and free from contamination. Typical samples for XPS are 0,5 cm^2 to 1 cm^2 in size and up to 4 mm thick. Powder samples shall have a small particle size to avoid differential charging, and therefore broadening of peaks. Magnetic powders should only be analysed using electrostatic mode.

XPS operates in ultra-high vacuum. It can be used with a cooling stage to cool samples down to 150 K. An argon ion sputter beam and electron flood gun can neutralize charging samples and remove any organic shell material. 3D profiling through material is also possible with the correct sputter guns.

XPS provides quantitative chemical state/bonding information and detects elements from lithium to uranium with surface sensitivity ranging from 5 angstroms to 75 angstroms mapping (x,y) with < 10 µm resolution is possible. Both conducting and insulating materials can be tested. XPS can detect elements with an abundance of 0,1 atomic % in a layer as thick as 5 nm [18, 25, 26, 34, 35, 36].

7.2.13 Relevant standards

ISO/TR 14187:2011, *Surface chemical analysis - Characterization of nanostructured materials*

ISO 16243:2011, *Surface chemical analysis - Recording and reporting data in X-ray photoelectron spectroscopy (XPS)*

ISO 16531:2013, *Surface chemical analysis - Depth profiling - Methods for ion beam alignment and the associated measurement of current or current density for depth profiling in AES and XPS*

ISO 13424:2013, *Surface chemical analysis - X-ray photoelectron spectroscopy - Reporting of results of thin-film analysis*

7.2.14 Energy dispersive X-ray spectroscopy (EDS or EDX)

Energy Dispersive X-ray analysis (EDX) is often used in conjunction with SEM and TEM. An electron beam strikes the surface of a conducting sample. The energy of the beam is typically in the range 10 keV to 20 keV. This causes X-rays to be emitted from the point where the material is irradiated by the primary electron beam. The energy of the X-rays emitted depends on the local chemical composition of the material under examination.

It gives information about elemental composition from (atomic number 4) beryllium to (atomic number 99) einsteinium with a detection limit of approximately 0,1 at.%. Non-conducting samples do pose a problem with EDX, because the bombardment of the sample with electrons starts to charge the sample itself, which prohibits the X-rays from coming out in an efficient way. However elements of low atomic number can be difficult to detect and analyse by EDX because of overlap between the characteristic X-ray peaks [25, 35, 36].

7.3 Measurands related to the chemical analysis of nano-objects as bulk samples

7.3.1 Measurands

The measurands described in this section can be used to test the chemical properties of the entire sample which contains nano-objects. Most of the methods presented allow the testing of nano-objects and their agglomerates and aggregates in various forms. It can be powders, thin films, products contained nano-objects like composites and dispersions. The measurands are summarized in Table 7.

Table 7 — Measurands related to the chemical analysis of nano-objects and their agglomerates and aggregates

Overarching measurand	**Measurand(s) specific to method**	**Method**	**Lateral resolution**	**Depth resolution**	**Limitation**	**Reference (see Bibliography)**
Structure, Composition of rough surfaces	Chemical vibrations are measured in wave number [cm^{-1}].	Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT)	> 15 µm	0,1 µm to2,5 µm depending on the wavelength of light, angle of incidence, refractive index of the sample	Mostly can be performed on dry powders. Sensitive to CO_2 and H_2O	[41]
Thermal properties of reaction and phase transformation	Heat flow difference between sample and reference [mW/mg] J/g: endothermic or exothermic reactions J/(g·°K): heat capacity, specific heat	Calorimetry and differential scanning calorimetry (DSC)	> 1 µm Depending on heating rate	Depending on heating rate	T = −180 °C to 800°C	[42, 43, 44, 45, 46]
Structure, Composition	Intensity over a narrow range of wavelengths at a time. Chemical vibrations are measured in wave number difference	Fourier transform infrared spectroscopy (FTIR)	> 15 µm	0,1 µm to 2,5 µm	Mostly can be performed on dry powders. Sensitive to CO_2 and H_2O Molecule shall be active in the infrared region. Sensitivity and	[21, 42, 47]

	[cm^{-1}].				Detection Limits Routine is 2 %; under most favourable conditions and special techniques, it is 0,01 %.	
Composition, identification of released gases from the sample	Current ion [A·s] Wavenumber [cm^{-1}], Quantitative Loss of sample mass [mg]	Thermal analysis with evolved gas analyser (EGA) like FTIR or quadrupole mass spectrometer (QMS)	n/a	n/a	Typically: QMS 2–150 amu FTIR 400 cm^{-1}to 5 500 cm^{-1} T = room temperature −1 500 °C 0,1 ppm −50 %	[21, 48, 49]
Composition, Thermal properties	Contents of volatile components, Loss of sample mass [g]	Thermogravimetric analysis (TGA)	> 1 µm Depending on heating rate	Depending on heating rate	Required samples 0,1 mg to 5 000 mg	[21, 44]
Concentration, composition	Absorption spectrum plotting absorbance versus wavelength [nm]	Ultraviolet–visible spectroscopy (UV-Vis)	N/A	N/A	Corrections for scattering may be required Solid samples require reflectance accessory	[50]
Structure, Composition	Shift of frequency of the inelastic scattering of light in wave number difference [cm^{-1}].	Raman spectroscopy	0,5 nm to 10 nm	0,5 nm	Cannot be used for metals or alloys. Fluorescence of impurities or of the sample itself can hide the Raman spectrum Sample heating through the intense laser radiation can destroy the sample or cover the Raman spectrum	[51]

7.3.2 Differential scanning calorimetry (DSC)

DSC is a technique of thermal analysis in which the difference in the amount of heat flow required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. A small amount of sample (5 mg to 10 mg) is used for DSC measurements. Large temperature range testing from −180 °C to 700 °C or from room temperature to 1 600 °C is possible.

This method provide information about phase transition, glass transition temperature, fusion of nano-objects and crystallization [42, 43, 44, 45].

7.3.3 Relevant standards

EN ISO 11357-7:2015, *Plastics - Differential scanning calorimetry (DSC) - Part 7: Determination of crystallization kinetics (*ISO 11357-7:2015*)*

EN ISO 11357-1:2009, *Plastics - Differential scanning calorimetry (DSC) - Part 1: General principles (*ISO 11357-1:2016*)*

7.3.4 Fourier transform infrared spectroscopy (FTIR)

Fourier transformed infrared spectroscopy (FTIR) has the capability and versatility to depth profile materials. There are different types of depth profiling but for a molecular picture of the sample’s interphase FTIR is superior. There are many different ways of depth profiling samples with FTIR. Thus far, attenuated total reflectance (ATR), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) and photoacoustic spectroscopy (PAS) are three different infrared (IR) methods suitable for depth profiling. They differ not only in terms of their theoretical and physical origin, but also in relation to penetration depth and thus give information at different depths below the sample surface.

FTIR provides specific information about chemical bonding and molecular structures, making it useful for analysing organic materials and certain inorganic materials. Chemical bonds vibrate at characteristic frequencies, and when exposed to infrared radiation, they absorb the radiation at frequencies that match their vibration modes. Measuring the radiation absorption as a function of frequency produces a spectrum that can be used to identify functional groups and compounds. FTIR can be used to identify the type and site of chemical functionalization of nano-objects and their agglomerates and aggregates and to recognize different active sites in metal and metal oxide based nano-objects.

Little or no preparation is required with many types of sample holders and cells available. Water should be removed from the sample if possible. The benefits are that it is a very quick measurements with a large database of materials tested and is typically non-destructive.

When coupled with attenuated total reflection (ATR) crystals, it can detect ultra-thin (monolayer thickness) film or molecular species in aqueous phase (special setup needed). The estimated time to obtain spectrum from a routine sample varies from 1 min to 10 min depending on the type of instrument and the resolution required. Many FTIR systems provide an automatic calibration with an accuracy of better than 0,01 cm^{-1}. This eliminates the need for external calibrations.

The DRIFT method is an infrared spectroscopy technique used on powder samples (with high surface area-rough surfaces) with no preparation. The penetration depth into the sample is dependent on physical and optical properties of the sample as well as that of the diluting powder used for depth profiling. It can be used as an alternative to pressed-pellet technique. DRIFT can easily differentiate between organic and inorganic materials.

The sample is added to a sample cup and the data are collected. The infrared light on a sample is reflected and transmitted to different degrees depending on the bulk properties of the material. The diffuse reflection is produced by the sample's rough surfaces' reflection of the light in all directions and is collected by use of an ellipsoid or paraboloid mirror. The particle size should be smaller than the wavelength of the incident light, so this would suggest that it should be less than 5 µm for mid-range infrared spectroscopy. The spectra are plotted in units of log inverse reflectance (log 1/R) versus wavenumber.

The sample can be analysed either directly in bulk form or as dispersions in IR-transparent matrices such as potassium bromide and potassium chloride. Dilution of the analyte in a non-absorbing matrix increases the proportion of diffuse reflectance in all the light reflected. Typically the solid sample is diluted homogeneously to 5 % to 10 % by weight using potassium bromide.

Many FTIR systems provide an automatic calibration with a stated accuracy of better than 0,01 cm^{-1}. This can eliminate the need for external calibrations. FTIR enable high throughput, high signal-to-noise ratio and high wavelength accuracy. The large penetration depth, means that spectra can be acquired for low bandgap semiconductors. Minimal elemental information is given for most samples. Background solvent or solid matrix shall be relatively transparent in the spectral region of interest.

It is possible to obtain an IR spectrum from samples in many different forms, such as liquid, solid, and gas. However, many materials are opaque to IR radiation and shall be dissolved or diluted in a transparent matrix in order to obtain spectra. Alternatively, it is possible to obtain reflectance or emission spectra directly from opaque samples [41, 42, 47].

7.3.5 Relevant standards

ISO 10640:2011, *Plastics - Methodology for assessing polymer photoageing by FTIR and UV/visible spectroscopy*

ISO/TS 14101:2012, *Surface characterization of gold nanoparticles for nanomaterial specific toxicity screening: FT-IR method*

7.3.6 Thermal analysis with evolved gas analyser (EGA) plus FTIR or QMS

This method is used to study the gas released from the heated sample that undergoes decomposition or desorption. By coupling the thermal analysis instrument (DSC or TGA) with a quadrupole mass spectrometer (QMS) or FTIR the detection of released gasses from the sample and their analysis is possible in real time allowing correlation with other thermal analysis signals (mass loss or endothermic transition).

For the DSC test a small amount of sample (5-10 mg) is used and the samples should be purged by inert gas to provide stability of measurement condition. Before the experiment, a blank test with thermal analysis instrument and spectrometer should be carried out using the same settings that are used for the sample.

Thermal analysis gives the determination of chemical composition of material in solid or gas-phase, and the identification of the type and site of chemical functionalization of nano-objects and their agglomerates and aggregates. By using QMS and FTIR spectrometer together with thermal analysis device complementary results can be obtained [48, 49].

Thermogravimetric analysis (TGA) is a method of thermal analysis in which changes in sample mass of material is measured as a function of increasing temperature with constant heating rate [43, 44].

7.3.7 Relevant standards

EN ISO 11358-1:2014, *Plastics - Thermogravimetry (TG) of polymers – Part 1: General principles (*ISO 11358-1:2014*)*

ISO 21870:2005, *Rubber compounding ingredients - Carbon black - Determination of high-temperature loss on heating by thermogravimetry*

ISO/TS 11308:2011, *Nanotechnologies - Characterization of single-wall carbon nanotubes using thermogravimetric analysis*

7.3.8 Ultraviolet–visible spectroscopy (UV-Vis)

This method can be used to identify some functional groups in molecules and can be used for assaying. In nanotechnology, UV-Vis spectroscopy can provide important information about nano-objects through surface plasmon resonance (SPR) studies. This absorption strongly depends on the particle size, dielectric medium and chemical surroundings. The resolution of a UV-Vis spectrophotometer is related to its spectral band width. The smaller the spectral band width, the finer the resolution. The spectral band width depends on the slit width and the dispersive power of the monochrometer. For diode array instruments, the resolution also depends on the number of diodes in the array. The wavelength range is 190 nm to 900 nm with a resolution of 0,1 nm [50].

The technique gives the absorption properties for some nano-objects, provides information on sizes and the quantification of amount of material.

7.3.9 Relevant standards

ISO 10640:2011, *Plastics - Methodology for assessing polymer photoageing by FTIR and UV/visible spectroscopy*

ISO/TS 10868:2011, *Nanotechnologies - Characterization of single-wall carbon nanotubes using ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopy*

7.3.10 Raman spectroscopy

Raman spectroscopy makes use of the Raman effect which is the inelastic scattering of light with a change of frequency, due to the transfer of energy between the sample and incident light. This shift of frequency gives information on the vibrational modes in the sample and hence chemical information. In certain circumstances it can give size information, see 6.4.11.

7.3.11 Inductively coupled plasma (ICP) techniques

In inductively coupled plasma (ICP) techniques, a liquid dispersion sample is sprayed into a plasma at high temperature where the atoms are ionized and detected The detector can be a based on mass spectrometry (ICP-MS) or optical emission spectrometry (ICP-OES) also known as atomic emission spectroscopy (ICP-AES). In this latter technique the intensity of each peak at a given wavelength is compared to reference elements of known concentration in order to calculate the concentration of each element. This enables chemical and concentration information to be obtained.

For single particle ICP-MS (sp-ICP-MS), the observation time for a particular element is split into smaller enough time windows such that single particles are detected with the intensity of the signal propositional to the number of atoms which it contains. This provides chemical information along with some measure of size.

7.3.12 Contact Angle

The contact angle is the measured angle between a liquid and a surface. It defines the wettability of the surface by the liquid. Dynamic contact angles can also be measured. These are typically measured using the sessile drop method where the angle of a drop on a surface is measured optically. This method is not for measuring the properties of a single nano-object, rather a continuous covering of nano-objects on a surface should be used and can be obtained from a liquid dispersion. The contact angle obtained is dependent on both the chemistry and topography of the surface.

8 Measurands related to mass and density

8.1 Introduction

This section covers measurands associated with mass and density. The main measurands are:

a) Nano-object mass and mass distribution;

b) Nano-object density and density distribution and;

c) Nano-object volume and size measurands as detailed in Clause 6

8.2 Aerosols

8.2.1 Measurands

The measurands are given in Table 8 and described in more detail along with the methods in the subsequent sections.

Table 8 — Measurands associated with mass and density measurement of nano-objects in an aerosol

Overarching measurand	Measurand(s) specific to method	Method	Range	Resolution	Limitation	Reference (see Bibliography)
Mass distribution	Mass to charge (m/z) distribution	Aerosol particle mass analyser	0,001~100 fg 10 nm to 10 µm	10 % (g/g) of centre mass of distribution	Relies on charged particles	[52]
Mass distribution	Time of flight mass-to-charge (m/z) distribution	TOF particle mass analyser	1 m/z to 1 200 m/z	m/Δm up to 4 000 for 0,05 µgm^{-3}	Relies on charged particles	[53]

8.2.2 Relevant standards

CEN ISO/TS 12025:2015, *Nanomaterials - Quantification of nano-object release from powders by generation of aerosols (*ISO/TS 12025:2012*)*

ISO 12154:2014, *Determination of density by volumetric displacement - Skeleton density by gas pycnometry*

ISO 8573-8:2004, *Compressed air - Part 8: Test methods for solid particle content by mass concentration*

ISO 9276-5:2005, *Representation of results of particle size analysis - Part 5: Methods of calculation relating to particle size analyses using logarithmic normal probability distribution*

EN ISO 10808:2010, *Nanotechnologies - Characterization of nanoparticles in inhalation exposure chambers for inhalation toxicity testing (*ISO 10808:2010*)*

8.2.3 Aerosol particle mass analyser (APM)

The analyser comprises of two cylindrical electrodes rotating around a common axis. The aerosol sample particles are charged and introduced into the annular gap and the electrodes are kept rotating at the same speed. When a voltage is applied to the inner electrode, the particles experience opposing centripetal and electrostatic forces. From the balance of these forces the particle mass can be calculated.

8.2.4 Time of flight mass spectrometry

This is a method of mass spectrometry in which a charged nanoparticle's mass-to-charge ratio is determined via a time of flight measurement. The particles are accelerated by an electric field of known strength. This acceleration results in charged particles of the same charge having the same kinetic energy. The velocity of the particle then depends on the mass-to-charge ratio. The time that it subsequently takes for the particle to reach a detector at a known distance is measured. This time will depend on the mass-to-charge ratio of the particle (heavier particles reach lower speeds and take higher times). From this time and the known experimental parameters, the mass-to-charge ratio of the nanoparticle is determined. This method can also be used to determine size distribution in aerosol form and the chemical analysis of aerosols.

8.3 Powders

8.3.1 Measurands

Nano-objects in powder form are generally either aerosolised or dispersed in a solvent for mass or density measurements and subsequently analysed by techniques described in 8.2 or 8.4 respectively. Care shall be taken to eliminate particle aggregation and agglomeration if individual particle size distribution is sought.

However, nano-objects powder density can be measured directly by gas pycnometry as listed in Table 9.

Table 9 — Measurands associated with mass and density measurement of nano-objects in powder form

Overarching measurand	Measurand(s) specific to method	Method	Range	Resolution	Limitation	Reference (see Bibliography)
Density	Gas displacement volume	Pycnometry	0,1 g/cm^3 to 10 g/cm^3	±0,01 %	Volume and mass measured separately and divided to give density.	[54]

8.3.2 Pycnometry

Pycnometry measures the density of solids, in this instance a nano-object powder, by gas displacement, employing the Boyle's law which governs volume-pressure relationship. The instrument measures gas volume displacement by the nanoparticle powder, and by measuring mass separately, the density can be calculated.

8.3.3 Relevant standards

ISO 12154:2014, *Determination of density by volumetric displacement – Skeleton density by gas pycnometry*

8.4 Liquid dispersions

8.4.1 Measurands

The measurands are given in Table 10 and described in more detail along with the methods in the subsequent sections.

Table 10 — Measurands related to mass and density for nano-objects in liquid dispersions

Overarching measurand	**Measurand(s) specific to method**	**Method**	**Range**	**Resolution**	**Limitation**	**Reference (see Bibliography)**
Density distribution	Optical transmission as a function of position Settling rate	Centrifugal liquid sedimentation (isopycnic method)	0,1 g cm^{-3} to 10 g cm^{-3}	±4 % (g/g)	Still in development stage	[13, 55]
Mass distribution	Optical transmission as a function of position Settling rate	Centrifugal liquid sedimentation (isopycnic method)	10^{-18} g to 10^{-11} g (1 ag to 10 pg)	±4 % (g/g)	Still in development stage	[13, 55]
Mass distribution	Scattering intensity as a function of angle Particle size distribution	Static light scattering	0,001 ag to 100 ag (1 kD to 10 MD) 0,05 µm to 2 000 µm	5 % (g/g)	The sample dispersion should be transparent and not absorb light of the wavelength used. Typically large sample volume (1 ml) required.	[56]
Mass distribution Density distribution	Individual particle mass	Resonant mass measurement	> 350 ag 50 nm to 5 µm	±3 % (g/g) 0,002 g cm^{-3}		[56]

8.4.2 Relevant standards

ISO 13318-1:2001, *Determination of particle size distribution by centrifugal liquid sedimentation methods – Part 1: General principles and guidelines*

EN ISO 16014-5:2012, *Plastics - Determination of average molecular mass and molecular mass distribution of polymers using size-exclusion chromatography - Part 5: Method using light-scattering detection (*ISO 16014-5:2012*)*

ISO 8573-8:2004, *Compressed air - Part 8: Test methods for solid particle content by mass concentration*

ISO 9276-5:2005, *Representation of results of particle size analysis - Part 5: Methods of calculation relating to particle size analyses using logarithmic normal probability distribution*

8.4.3 Centrifugal liquid sedimentation (Isopycnic method)

See 8.3.2. The particles settle at a level where their density matches that of the surrounding medium, hence the term isopycnic, which means “of the same density”. Their settling-rate gives mass, their equilibrium or non-equilibrium settling point gives density.

8.4.4 Static light scattering (SLS)

In static light scattering, a high intensity monochromatic light, typically a laser, is passed through a solution containing the nanoparticles. Single or multiple detectors are used to measure the scattered intensity at single or multiple angles. The angular dependence of scattered intensity is used to obtain both particle mass and size for nanoparticles of radius above 1 % to 2 % the incident wavelength. Depending on the orientation of the detector angles relative to the direction of incident light, low angle light scattering (LALS), right angle light scattering (RALS), multi-angle light scattering (MALS) are the various implementations of SLS.

8.4.5 Resonant mass measurement (RMM)

The resonant mass measurement (RMM) detects and counts particles in the size range 50 nm to 5 µm, and measures their buoyant mass, and size. RMM uses a microfluidic channel passing through a resonant cantilever to detect, count and measure the mass of the particles in the liquid passing through the channel. The mass of the particle changes the resonant frequency of the cantilever, which is directly related to the buoyant mass of the particle. The technique also allows to accurately count particles in the sample. Particles of same density as the solute will not be detected. The density value is required for size of volume evaluation.

9 Measurands related to charge - Liquid dispersions

9.1 Measurands

Electrokinetic potential or zeta potential is the electric potential in the interfacial double layer at the location of the slipping plane versus a point in the bulk fluid away from the interface. In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The measurands are given in Table 11 and described in more detail along with the methods in the subsequent sections.

Table 11 — Measurands related to charge

Overarching measurand	Measurand(s) specific to method	Method	Range	Resolution	Limitation	Reference (see Bibliography)
Charge zeta potential	Particle velocity	Electrophoretic light scattering	−500 mV to 500 mV	0,1 mV	Electro-osmosis at the walls of the sample cell can hinder measurements of very small particles.	[57]
Charge zeta potential	Dynamic electrophoretic mobility	Electroaccoustic phenomena measurements	−500 mV to 500 mV	0,1 mV	Interference from the presence of air bubbles	[58]

9.2 Relevant standards

ISO 13099-1:2012, *Colloidal systems - Methods for zeta-potential determination - Part 1: Electroacoustic and electrokinetic phenomena*

ISO 13099-2:2012, *Colloidal systems - Methods for zeta-potential determination - Part 2: Optical methods*

ISO 13099-3:2014, *Colloidal systems - Methods for zeta potential determination - Part 3: Acoustic methods*

9.3 Electrophoretic light scattering

Electrophoresis is the motion of dispersed particles relative to a fluid under the influence of a spatially uniform electric field. The zeta potential of the dispersion is measured by applying an electric field across the dispersion. Particles within the dispersion with a zeta potential will migrate toward the electrode of opposite charge with a velocity proportional to the magnitude of the zeta potential. This velocity is measured using laser Doppler anemometer. The frequency shift or phase shift of an incident laser beam caused by these moving particles is measured to reveal the particle mobility, and this mobility is converted to the zeta potential by considering the dispersant viscosity and dielectric permittivity and applying the Smoluchowski theories.

9.4 Electroaccoustic phenomena measurements

There are two electroacoustic effects used for measuring particle charge, i.e. the zeta potential: colloid vibration current and electric sonic amplitude. There instruments measure the dynamic electrophoretic mobility which depends on zeta potential.

Colloid vibration current arises when ultrasonic waves propagate through a fluid containing charged nano-particles. The pressure gradient in an ultrasonic wave moves the nano-particles relative to the fluid. Fluid motion relative to the particle drags the diffuse ions of the electrical double layer in the direction of one or the other poles. As a result of this drag, there is an excess of negative ions in the vicinity of one pole and an excess of positive surface charge at the other pole resulting in a particle dipole moment. These dipole moments generate an electric field which in turn generates an electric current.

Electric sonic amplitude is the reverse of colloid vibration current. It occurs under the influence of an oscillating electric field. This field moves nano-particles relative to the liquid, which generates ultrasound.

Electroacoustic techniques have the advantage of being able to perform measurements in as-produced samples, without dilution, at volume fractions up to 50 %. Calculation of zeta potential from the dynamic electrophoretic mobility requires information on the densities for particles and liquid. In addition, for larger particles exceeding 300 nm in size information on the particle size is additionally required.

10 Measurands related to crystallinity

10.1 Measurands

a) Degree of crystallinity

b) Crystal structure including lattice system and lattice parameters

c) Crystalline index – percentage of crystalline material

d) Melting point

e) Glass transition temperature

The measurands are summarized in Table 12. Here most of the techniques are for application to aggregates and powders. For single nano-objects the techniques for SEM, TEM and Raman crystallography can be applied.

Table 12 — Measurands related to crystallinity

Overarching measurand	Measurand(s) specific to method	Method	Range	Resolution (at best point in range)	Limitation	Reference (see Bibliography)
Lattice system Lattice constant	X-ray scattering angle and intensity	Small-angle X-ray scattering (SAXS)	1 nm to 150 nm	0,5 nm	Qualitative	[59, 60]
Lattice system Lattice constant	X-ray scattering angle and intensity	Ultra-small-angle X-ray scattering (USAXS)	1 nm to 2,5 um	0,1 nm	Qualitative Not ideal for two-component or amorphous systems	[61]
Lattice system Lattice constant	X-ray scattering angle and intensity	Wide-angle X-ray scattering (WAXS)	< 1 nm	< 0,1 nm	Qualitative	[60]
Lattice system Lattice constant Crystallinity Crystalline index	X-ray Scattering angle and intensity	X-ray scattering	0,1 nm to 2 nm 0 % to 100 %	0,05 nm to 0,5 nm	Resolution inversely proportional to unit cell size No phase information Hard to resolve light atoms in the presence of heavy atoms Requires relatively large crystals Qualitative	[62]
Lattice system Crystallinity Crystalline index	Electron scattering angle, amplitude and phase	TEM Electron diffraction (TEM)	50 µm to 0,5 nm	0,05 nm	Resolution scales inversely with scan area (Magnification). UHV techniques. Electron beam induced damage	[63]
Lattice system Crystallinity Crystalline index	Electron scattering angle, amplitude and phase	SEM Electron backscattering detection (EBSD) Reflection high-energy electron diffraction (RHEED) Low energy	1 nm to 1 000 µm	SEM 0,5 nm RHEED 0,5 nm LEED < 0,0 1 nm	Normally requires an electrically conductive sample or conductive coating Sample in vacuum	[64, 65]

		electron diffraction (LEED)				
Lattice system Crystallinity Crystalline index	Neutron scattering angle, amplitude and phase	Neutron diffraction	0,1 nm to 5 000 µm	0,1 nm	Needs powders or large crystals > 1 mm^3	[66]
Crystallinity Melting point Glass transition temperature Crystalline index	Heat flow	Differential scanning calorimetry (DSC)	−180 °C to 1 750 °C	0,02 °C		[67]
Crystallinity Crystalline index	Resonance frequency as a function of magnetic field	NMR (Nuclear magnetic resonance) crystallography	Up to 100 kDa	< 0,1 nm	Slow Expensive May require isotope labelling	[68, 69]
Crystallinity Chirality (of carbon nanotubes)	Raman scattering frequency shift	Raman crystallography				[70]

10.2 Small-angle/wide-angle X-ray scattering (SAXS/WAXS)

Small-angle/wide-angle X-ray scattering (SAXS/WAXS) involves the elastic scattering of X-rays of wavelength 0,1 nm to 0,2 nm by a sample containing nano-objects. The scattered X-rays are recorded at low angles (0,1° to 10°) or at high angles (10° to 90°). These techniques provide information about the shape and size of nanoparticles, characteristic distances of partially ordered materials, pore sizes, and other data. SAXS is capable of delivering structural information of nanoparticles between 5 nm and 25 nm. WAXS can resolve even smaller dimensions. Generally, WAXS is employed for studying highly ordered or crystalline structures while SAXS is more common for amorphous materials or non-homogeneous and two-component systems.

10.3 X-ray diffraction (XRD)

X-ray diffraction is a technique in which crystalline atoms cause a beam of X-rays to diffract into many well-defined directions. By measuring the angles and intensities of these diffracted beams, a three-dimensional picture of the density of electrons within the crystal is generated. From this electron density map, the positions of the atoms in the crystal is determined, as well as their chemical bonding states, nature of any disorder and various other information. As the crystal's unit cell becomes larger and more complex, the resolution of X-ray diffraction reduces. In the presence of heavy atoms with many electrons, it becomes harder to detect light atoms by X-ray diffraction. Total scattering or pair distribution function analysis utilizes not only Bragg scattering from a material but also the diffuse scattering in order to look beyond the average structure to examine the local, or short-range structure.

10.4 Scanning/ electron microscopy (SEM)

See 6.3.12.

10.5 High-resolution transmission electron microscopy (HRTEM)

HRTEM allows is capable of directly imaging the crystalline and atomic structure of a NOAA sample. In HRTEM, the nano-object is imaged by recording the 2D spatial wave amplitude distribution in the image plane, analogous to a light microscope. At present, the highest point resolution is realized in phase contrast TEM of 0,5 A. At this scale, individual atoms of a crystal and any defects can be resolved. For 3D crystals, it is necessary to combine several views, taken from different angles, into a 3D map.

10.6 Electron diffraction

Electron diffraction involves firing electrons at a NOAA sample and observing the resulting interference pattern of scattered electrons. The periodic structure of a crystalline solid acts as a diffraction grating, scattering the electrons in a corresponding manner. The structure of the crystal is therefore obtained by working backwards from the observed electron diffraction pattern. Electron diffraction is also used to study the short range order in amorphous nanoparticles. It can complement X-ray diffraction for studies of very small crystals (<0,1 µm) of inorganic, organic and biological materials such as proteins that cannot easily form the large 3-dimensional crystals required for XRD. Unlike XRD, crystallographic structure factor phase information can be experimentally determined in electron diffraction.

10.7 Neutron diffraction

Neutron crystallography involves the application of neutron scattering to determine the atomic and crystallographic structure of a NOAA material. A sample is placed in a beam of thermal or cold neutrons to obtain a diffraction pattern that provides information on the structure of the material. The technique is similar to X-ray diffraction but due to their different scattering properties, neutrons and X-rays provide complementary information. The technique is most commonly performed as powder diffraction on a polycrystalline NOAA powder. For single crystal neutron crystallography, the crystals shall be much larger (approximately 1 mm^3) than those used in X-ray diffraction and hence not suitable for nano-objects. Powder diffraction is a scientific technique using X-ray, neutron, or electron diffraction on powder or microcrystalline samples for structural characterization of materials. Single-crystal diffraction, as the name suggests, requires a single-crystal of the material. Although it possible to solve crystal structures from powder data alone, its single crystal analogue is a far more powerful technique for structure determination. Powder diffraction is mostly used to characterize and identify phases, and to refine details of an already known structure, rather than solving unknown structures.

10.8 Electron backscatter diffraction (EBSD)

Electron backscatter diffraction (EBSD) also known as backscatter Kikuchi diffraction (BKD) is used to examine the crystallographic orientation of NOAA materials, which in turn can be used to elucidate texture or preferred orientation of any crystalline or polycrystalline material. EBSD can be used to index and identify crystal systems, crystal orientation mapping, defect studies, phase identification, grain boundary and morphology studies, regional heterogeneity investigations, material discrimination, microstrain mapping, and using complementary techniques, physicochemical identification. Experimentally EBSD is conducted using an SEM equipped with an EBSD detector.

10.9 Reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED)

Reflection high-energy electron diffraction (RHEED) is used to characterize the surface of crystalline materials. The electron beam of 10 keV to 30 keV energy is incident on the sample at a very small angle relative to the sample surface. Incident electrons diffract from atoms at the surface of the sample, and a small fraction of the diffracted electrons interfere constructively at specific angles and form regular patterns on the detector.

Low-energy electron diffraction (LEED) is also used to determine the surface structure of crystalline materials using a collimated beam of low energy electrons (20 eV to 200 eV) and observing the diffracted electrons.

10.10 Differential scanning calorimetry (DSC)

See 7.3.2. DSC can be used to determine amount of crystallinity, glass transition temperature, melting point and phase changes.

10.11 Nuclear magnetic resonance (NMR) crystallography

The NMR spectra are obtained by samples placed in a strong magnetic field and probed by radio waves. The resultant set of resonances are analysed to give the atomic nuclei that are in proximity to one another and the local conformation of atoms that are bonded together.

10.12 Raman crystallography

Raman spectroscopy (also see 6.4.11) is used to observe the vibrational, rotational and other low-frequency phonon modes of a system. Raman scattering by an anisotropic crystal is used to obtain information about the crystal orientation. The wavelength and polarization of the Raman scattered light with respect to the crystal orientation and the incident laser light can be used to determine the crystal structure.

In the case of carbon nanotubes, Raman spectroscopy can also be used to determine the chirality or type of single-wall carbon nanotubes, by analysis of the position of the radial breathing mode and the shape and intensities of the G-mode components, which are due to the planar vibrations of carbon atoms.

10.13 Relevant standards

ISO 24173:2009, *Microbeam analysis - Guidelines for orientation measurement using electron backscatter diffraction*

ISO 25498:2010, *Microbeam analysis - Analytical electron microscopy - Selected-area electron diffraction analysis using a transmission electron microscope*

ISO 13067:2011, *Microbeam analysis - Electron backscatter diffraction - Measurement of average grain size*

ISO/TS 10797:2012, *Nanotechnologies - Characterization of single-wall carbon nanotubes using transmission electron microscopy*

ISO/TS 10798:2011, *Nanotechnologies - Characterization of single-wall carbon nanotubes using scanning electron microscopy and energy dispersive X-ray spectrometry analysis*

11 Optical properties measurands

11.1 Introduction

Optical properties of nano-objects and materials containing nano-objects include the properties of dry powders, aerosols in air, liquid dispersions, solid particles on solid surfaces, thin films, and composite materials. Measurands and techniques used to determine them depend on the type of material and the environment.

11.2 Measurands

The measurands are summarized in Table 13.

Table 13 — Measurands for optical properties

Overarching measurand	Measurand(s) specific to method	Method	Range	Resolution	Reference (see Bibliography)
Plasmon frequency Colour	Absorption spectrum	UV-Vis-NIR absorption spectroscopy	175 nm to 3 300 nm	0,05 nm to 0,2 nm depending on range	[71]
Optical absorption	Wavelength absorbed	Absorption spectroscopy	175 nm to 3 330 nm	0,05 nm (UV) to 0,2 nm (IR)	[71]
Optical emission	Wavelength emitted	Photoluminescence (fluorescence) spectroscopy	400 nm to 2 700 nm	0,05 nm (UV) to 0,2 nm (IR)	[72]
Optical emission	Wavelength emitted	Electroluminescence spectroscopy	400 nm to 2 700 nm	0,05 nm (UV) to 0,2 nm (IR)	
Colour	Wavelength transmitted or absorbed	Absorption spectroscopy	175 nm to 3 330 nm	0,05 nm (UV) to 0,2 nm (IR)	[71]
Fluorescence	Intensity	Spectrofluorometer	200 nm to 850 nm in wavelength	50 femtomolar fluorescein	[73]
Optical property	Absorption	UV-Vis-NIR Spectroscopy	175 nm to 3 300 nm	0,05 nm to 0,2 nm depending on range	[71]

Optical properties of nano-objects, nanomaterials and nanostructures originate from the fundamental interaction of light with material. In the case of quantum dots, the confined electron state in a quantum dot results in absorption and emission of a well-controlled frequency of optical radiation (length scale 3 nm to 20 nm). In the case of the photonic materials the repeated structure of the material leads to a number of nonlinear effects (length scale 200 nm to 400 nm).

Quantum dots (similar to other nanomaterials or products) degrade over time as their properties such as fluorescence or spectral width change with time. The degradation time or amount of degradation per year should be included in the specifications for materials. The fluorescence is measured through a parameter known as emittance which is the ratio of the radiant exitance of a quantum dot and the radiant exitance of a blackbody at the same temperature.

11.3 Spectroscopy techniques

A number of standardized optical spectroscopies may be used to evaluate emittance, full emission spectrum, peak position (colour) and peak width. Most optical spectroscopic equipment splits incoming light into spectral components and then measures intensity of these spectral component to determine the optical information.

Optical absorption spectroscopy (UV-Vis-NIR): absorption spectroscopy refers to spectroscopic techniques that measure the absorption of radiation, as a function of frequency or wavelength, due to its interaction with a sample. The sample absorbs energy, i.e. photons, from the radiating field. The intensity of the absorption varies as a function of frequency, and this variation is the absorption spectrum. Spectroscopic techniques are not nanoscale-specific but some nanoscale parameters such as film thickness, particle size and particle concentration may be inferred from spectroscopic measurements. The technique involves directing a beam of radiation at a sample and detecting the intensity of the radiation that passes through it. The transmitted energy can be used to calculate the absorption. Absorption spectroscopy can be used to characterize nanomaterials such as single-wall carbon nanotubes or the size and concentration of quantum dots in a dispersion.

Photoluminescence (PL) (or fluorescence) spectroscopy, also called optical emission spectroscopy measures the dispersion of light emission from a nano-object stimulated by the absorption of photons. It is a contactless, non-destructive method to probe the opto-electronic properties of materials. Light is directed onto a sample, where it is absorbed and where a process called photo-excitation can occur. The photo-excitation causes the material to jump to a higher energy electronic state, and will then release energy (photons) as it relaxes and returns back to a lower energy level. The emission of light, or luminescence through this process is photoluminescence (PL).

Electroluminescence (EL) is an opto-electronic phenomenon in which a nano-object emits light when stimulated by the passage of an electric current or by a strong electric field. Electrons and holes can be separated either by doping the nano-object to form a p-n junction or through excitation by impact of high-energy electrons accelerated by a strong electric field. The excited electrons and holes then radiatively recombine to release light, and the spectroscopic characterization of the emitted light is known as EL spectroscopy.

11.4 Relevant standards

ISO/TS 17466:2015, *Use of UV-Vis absorption spectroscopy in the characterization of cadmium chalcogenide colloidal quantum dots*

ISO/TS 10868:2011, *Nanotechnologies - Characterization of single-wall carbon nanotubes using ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopy*

12 Electrical and electronic measurands

12.1 Measurands

(a) Specific conductance/resistance (conductivity/resistivity): is the resistance or conductance of a nanoparticle normalized for its volume (cross sectional area and length). It is considered an intrinsic electrical property of a material.

(b) In plane sheet resistance: used especially for 2-dimensional nano-materials, such as graphene. It is defined as resistance of a square area of the material.

(c) Band-gap: the energy gap between the valance and the conduction band of a semiconductor nano-object. Band gap of metallic nano-objects is defined as zero. Band-gap can be either direct or indirect, i.e. whether an electron from the valence band can be excited into the conduction band with or without a chance in associated momentum.

The measurands related to electrical and electronic properties of nano-objects are summarized in Table 14.

Table 14 — Measurands related to electrical and electronic measurements

Overarching measurand	Measurand(s) specific to method	Method	Range	Resolution	Limitation	Reference (see Bibliography)
Specific conductance/ resistance (conductivity /resistivity)	Conductance/ resistance (together with particle dimensions)	2-probe or 4-probe electrical measurement	Resistivity 0 Ω.m to 10^{16} Ω.m	0,1 µΩ.m		[74, 75]
In plane Sheet resistance	Resistance (together with thickness)	4-point probe, e.g. Van der Pauw method	Zero (superconductor) to infinity (insulator)	0,1 µΩ		[74, 75]
Band gap	Photoemission intensity as a function of angle	Angle resolved photoemission spectroscopy (ARPES)		1 meV		
Band gap	Resistance	Measure resistance as a function of temperature	Generally 0,5 eV to 5 eV	0,1 eV at 300 K	Research stage	
Band gap	Absorption of light	Optical (UV/Vis/IR) absorption spectroscopy	Generally 0,5 eV to 5 eV	0,1 eV at 300 K	Requires very dilute dispersions of nano-objects, works best with individually dispersed nano-objects	[71]
Band gap	Optical absorption/ emission wavelength	Photoluminescence (fluorescence) spectroscopy	Generally 0,5 eV to 5 eV	0,1 eV at 300 K	Requires individually dispersed nano-objects	[72]
Band gap	Raman peak position, which gives object dimension	Raman spectroscopy	Generally 0,5 eV to 5 eV	0,1 eV at 300 K	Only applicable to specific Raman active nano-objects such as carbon nanotubes	
Band gap	Tunnelling current	Scanning tunnelling microscopy (Scanning tunnelling spectroscopy)	0,1 eV to 5 eV Resolution: 0,1 eV at 300 K	0,1 nm	UHV technique, special sample preparation and conductive substrate essential.	[76]
Nanoscale conductivity	Current	Conducting atomic force microscopy	10 µm x 10 µm scan field; Currents of a few pA up to 500 nA	0,1 nmto approximatively 10 nm	Limited to conducting samples. Also limited by the range of the scanner	[77, 78]

Piezoelectric Coefficient	Surface charge and displacement	Piezoforce microscopy	10 µm x 10 µm scan field; Currents of a few pA up to 500 nA	0,1 nm to approximatively 10 nm	Limited by scan range of the scanner	[79]

12.2 Techniques

12.2.1 2 or 4 point conductance measurements

The conductance measurement may be performed by 2-point or 4-point conductance measurements. Non-contact eddy-current based methods can also be used to measure sheet-resistance. Such measurements have been proven to be useful in coating conductivity measurements. Solid coatings are best defined as nanostructures or nanoscale films rather than nano-objects which is the focus of this document. The band-gap of a nano-material can be measured by measuring the resistance as a function of temperature, and fitting the resulting curve. It can be measured using optical absorption and emission, such as photoluminescence spectroscopy (also known as fluorescence spectroscopy) and Raman spectroscopy.

12.2.2 Angle-resolved ultraviolet photoemission spectroscopy (ARPES)

The band gap can also be measured using photoemission spectroscopy techniques such as angle-resolved ultraviolet photoemission spectroscopy (ARPES). ARPES is a direct experimental technique to observe the distribution of the electrons in the reciprocal space of solids. Information can be gained on both the energy and momentum of an electron, resulting in detailed information on band dispersion and Fermi surface.

12.2.3 Scanning tunnelling microscopy (STM)

The band gap can also be measured using scanning tunnelling spectroscopy (STS), which is an extension of scanning tunnelling microscopy (STM) and provides information about the density of electrons in a sample as a function of their energy.

The STM technique is based on the ability to position a conducting sample and an atomically sharp conducting tip at a tunnelling distance from each other. The tunnelling current from tip to the sample when sample is biased has a very strong dependence on the sample to tip distance (tunnelling gap). The equipment is able to maintain such a constant distance by monitoring the tunnelling current while scanning over the sample surface. The sample and the tip are most commonly positioned using piezoelectric actuators. At any point on the surface a current versus voltage (I-V) curve may be taken in a spectroscopic mode. The technique allows for sub atomic resolution as well as atomic manipulate (controlled movement of atoms on the sample surface).

12.2.4 Conductive atomic force microscopy

Conductive AFM is a variation of atomic force microscopy (see 6.6.3) that records local electrical conductivity as well as a topographic image of the sample. A conducting probe tip is required, for example a silicon cantilever is coated with conducting material such as gold or diamond. The conductivity is measured as current flowing between tip and the sample surface at a constant bias. Currents of 10^{-12} ampere to 10^{-6} ampere may be applied to the tip. The lower boundary is dictated by the noise level in the system. At specific points of interest local I-V curves can be measured in a spectroscopic mode.

12.2.5 Piezoforce microscopy (PFM)

Piezoelectricity is the ability of a material to produce electric charge on mechanical deformation or be mechanically deformed by the application of an electric field. The relationship between the electric field and the mechanical extension is known as the piezoelectric coefficient which is a key measurand for such material. The materials exhibiting piezoelectricity are normally ceramics or composites that are often used in thin film applications.

Three distinct types of piezoelectric coefficients are known depending on the orientation of the applied force and the piezoelectric axis: transverse effect [a force is applied along a neutral axis (y) and the charges are generated along the (x) direction], longitudinal effect (charge in x-direction is released by forces applied along x-direction) and shear effect.

There are three main measurement methods to characterize the piezoelectric coefficient: frequency method, laser interferometry method and the quasi-static method. In most methods a potential is applied to the sample in a parallel plate capacitor or other configuration and the extension is measured. The only method capable of achieving nanoscale spatial resolution is based on the conductive AFM technique that is known as piezoforce microscopy (PFM). It may also be used to image the nano-scale features of domains in the piezoelectric thin films and to probe localized piezoelectric parameters.

13 Magnetic measurands

13.1 Introduction

Magnetic nano-objects that are known in some communities as “nanomagnets” derive their properties from the contribution of the classical (bulk) magnetic properties of the demagnetising field and the magnetic ordering force also known as “exchange interaction”. The latter originates from the quantum mechanical processes and is only strong at the short range of the order of exchange length.

Similar to other measurands there are techniques able to access spatially distributed magnetic properties and some techniques that make a bulk (spatially averaged) measurement of a property. Spatially averaged measurands such as net magnetisation, Curie temperature, coercivity and others are often very useful for industry and are non-nano-specific measurement techniques. It should be noted that in some applications the introduction of magnetic nano-objects into a non-magnetic matrix such as plastic or ceramic adds a specific property but may not require high spatial resolution.

13.2 Measurands

A summary of the relevant measurands are shown in Table 15.

Table 15 —Measurands related to magnetic properties of solid nano-composite materials

Overarching measurand	Measurand(s) specific to method	Method	Range	Resolution	Limitation	Reference (see Bibliography)
Saturation Magnetization	Inductive impedance	Resistor, inductor and capacitor (RLC) circuit measurement of an inductive circuit component. vibrating sample magnetometer (VSM) and alternating gradient force magnetometer (AGFM) may be used for this measurement	1,2 4MA/m < H_{max} < 4 MA/m m_{max}: 1 Am^2	H: 0,1 kA/m M: 10^{-9} Am^2	Volume of the sample may need to be known.	[80, 81, 82]

Curie temperature	Change of magnetic susceptibility or magnetization or emitted energy	Magneto-optical Kerr effect magnetometry (MOKE) with a temperature control Vibrating sample Magnetometer (VSM) with a temperature control. Differential scanning calorimetry (DSC)	2,2 K < T < 500 K	From ± 0,1 K to ± 1 K based on stability of temperature control.	Magnetometry measurements require slow temperature change. DSC is limited by a very small change in heat	[80, 81, 82, 83]
Magnetic Susceptibility	Slope of the magnetisim versus magnetic field strength (M-H)	RLC measurement of an inductive circuit component. VSM and AGFM may be used for this measurement.	1,2 MA/m < H_{max} < 4 MA/m m_{max}: 1 Am^2	H: 0,1 kA/m M: 10^{-9} Am^2	This is a bulk measurement technique.	[80, 81, 82]
Surface magnetisation	Force Kerr rotation and ellipticity Hall effect emf related directly to stray magnetic field	Magnetic force microscope (MFM) Magneto-optical Kerr effect microscopy (MOKE) Scanning Hall effect magnetometer	Typically low magnetic field strengths (H) H up to 0,3T	Limited by the tip Limited by the optical resolution. ±3 % to 5 %	The tip field may alter the sample and only give information on stray fields Only probes sample depth comparable to laser (light) skin depth Gives information of stray fields	[80, 81, 84]
Coercive field	Inductive signal, Kerr rotation (for MOKE),	Inductive magnetometry or optical magnetometry that allow full saturation of the material	1,2 MA/m < H_{max} < 4 MA/m m_{max}: 1 Am^2	H: 0,1 kA/m M: 10^{-9} Am^2		[80, 81]

13.3 Techniques

13.3.1 Superconducting quantum interference device (SQUID)

A SQUID (superconducting quantum interference device) is a very sensitive magnetometer used to measure extremely small magnetic fields, based on Josephson junctions. There are two main types of SQUID: direct current (DC) and radio frequency (RF). RF SQUIDs can work with only one Josephson junction, which makes them cheaper but are less sensitive.

NOTE The magnetic field measurement limits for SQUID is 5×10^{-18} T.

13.3.2 Vibrating sample magnetometer (VSM)

A vibrating sample magnetometer measures the magnetization of a sample of magnetic material placed in an external magnetizing field and oscillated sinusoidally, by converting the dipole field of the sample into an AC electrical signal.

NOTE The magnetic field measurement limits for VSM is 10^{-17} emu.

13.3.3 Mössbauer spectroscopy

Mössbauer spectroscopy is a spectroscopic technique based on the Mössbauer effect which consists of recoil-free, resonant absorption and emission of gamma rays in solids. Mössbauer spectroscopy probes tiny changes in the energy levels of an atomic nucleus in response to its environment. Three types of nuclear interactions are observed in Mossbauer spectroscopy: an isomer shift, also known as a chemical shift; quadrupole splitting; and magnetic or hyperfine splitting, also known as the Zeeman Effect. Mössbauer spectroscopy is unique in its sensitivity to small changes in the chemical environment of the nucleus including oxidation state changes, the effect of different ligands on a particular atom, and the magnetic environment of the sample.

13.3.4 Electron paramagnetic resonance (EPR) spectroscopy

Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) spectroscopy is a technique for studying materials with unpaired electrons. A collection of paramagnetic centres, such as free radicals, is exposed to microwaves at a fixed frequency. When the spin-splitting under external magnetic field matches the energy of the microwaves, there is enhanced absorption. The derivative of the absorption spectrum is the most common way to record and publish EPR spectra.

13.3.5 Magneto-optical Kerr-effect (MOKE)

The magneto-optical Kerr effect (MOKE) measures the rotation of polarized light reflected off the surface of a magnetic sample.

NOTE MOKE measurements are limited typically to reflectivity changes smaller than 0,02 % and polarization changes small than 0,005°.

A scanning MOKE setup requires an optical microscope with the polarization analysis option. This technique gives the contrast of the image related to the orientation of the magnetization on the sample surface. The technique is limited by the optical resolution of the microscope but an apertureless MOKE with scanning capability may increase that resolution. A typical scanning range of 10 µm x 10 µm is often used. Spatial resolution of approximately 50 nm is achievable.

13.3.6 Magnetic force microscopy (MFM)

Magnetic force microscopy (MFM) is a variation of AFM (see 6.6.3) where the tip has a strong magnetic moment that interacts with the magnetic field of the sample. MFM detects stray fields from the sample and records the deflection of the cantilever. The force on the tip is proportional to the stray field gradient and may be converted into the surface magnetization using a number of micromagnetic assumptions. The range of scanning is approximately 10 µm x 10 µm with special resolution of approximately 10 nm. Limitations are linked to the tip to sample interaction where the sample magnetisation may be altered by the presence of the tip. Measurements may be performed in air and room temperature.

13.3.7 Scanning Hall effect microscopy

A Hall effect magnetometer sensor may be scanned over the magnetic surface to obtain the distribution of magnetic field in vicinity of the surface. The signal is proportional to the field strength and may be converted into the state of the surface magnetization. The lateral resolution of this technique heavily depends on the design and size of the hall sensor unit. The scan range is typically 15 µm x 15 µm with a lateral resolution below 1 µm.

13.3.8 Spin-polarized scanning tunnelling microscopy (SP-STM)

SP-STM is a variation of STM (see12.2.3) where the STM tip has a net magnetic polarization at the atomically sharp apex. This results in a spin-polarized tunneling current flowing between time and the sample. If the sample magnetization is in the same orientation the tunneling probability is higher than if it is antiparallel. In addition to topography the localized magnetic polarization (or in fact the spin-polarized tunneling probability) is mapped with STM special resolution. For most systems the SP-STM is operated under ultrahigh vacuum (lower than 10^{-7} mbar) and under low temperature (below 66 K).

13.3.9 Relevant standards

ASTM A342 / A342M – 14, *Standard Test Methods for Permeability of Weakly Magnetic Materials*

IEC 80000-6:2008, *Quantities and units - Part 6: Electromagnetism*

14 Thermal measurands

14.1 Measurands

Materials containing nano-objects and their agglomerates and aggregates might have specific thermal properties that are achieved from the addition of the nano-objects to the composite matrix or from layering and thin film generation. In some cases, thermal conductivity of materials might be enhanced by the addition of carbon nanotubes or thermal capacity can be enhanced through addition of nano-objects. Thermal expansion of the composite material may also be controlled by appropriate additives. So the critical measurands for the solid composites containing nano-objects and their agglomerates and aggregates are thermal conductivity, specific heat capacity and thermal expansion. In some areas thermal diffusivity and thermal effusivity are also considered as primary measurands which can give the other three quantities. These measurands are summarized in Table 16.

Table 16 — Measurands related to thermal properties

Overarching measurand	Measurand(s) specific to method	Method	Range	Resolution	Limitation	Reference (see Bibliography)
Heat Capacity	Specific Heat Capacity (J/(K kg)	Calorimetry and Differential scanning calorimetry (DSC)	from room temperature to 1 500°C	> 1 µm Depending on heating rate	Large scale samples needed	[85]
Spatially resolved thermal conductivity	Thermal conductivity (W/(m·K))	Scanning thermal microscopy (SThM)	Scanning range 100 µm x 100 µm	50 nm to100 nm for lateral resolution, probe T resolution < 0,1°C	Tip-sample contact (heating) volume difficult to determine	

NOTE It should be noted that thermal measurements are not nano-specific. For most of the commonly used thermal measurements of nano-enhanced properties (e.g. high heat capacity) please refer to conventional metrology texts [86].

14.2 Techniques

14.2.1 Measurement of specific heat capacity

Specific heat capacity in solids refers to the ability of the material to store heat. It can be measured by a number of techniques such as calorimetry and differential scanning calorimetry (DSC) [7.3.2]

14.2.2 Scanning thermal microscopy (SThM)

Scanning thermal probe microscopy offers the combination of spatial resolution, imaging and localized measurement of temperature and thermal conductivity. The SThM is uses the methodology of the scanning probe microscopy to achieve high special resolution by scanning a probe over the sample. Topography of the sample may be obtained as well as the localized measurement of temperature and thermal conductivity. The localized temperature may be monitored by a thermocouple junction at the probe tip and resistive or bolometer probes where the probe temperature is monitored by a thin film resistor at probe tip. As the tip is placed in direct contact with the sample the heat flows to the sample and thermal conductivity may be determined. This gives high lateral resolution of thermal conductivity with the ability to correlate topography and thermal information.

It should be noted that the heat exchange between tip and the sample may take place by direct (solid-solid) contact, which results in the conductivity mapping, by tip and sample surface liquid convection (solid-liquid) and by air convection (solid-gas) convection. The scanning range of the technique depends on the scanning stage used and is of the order of 100 µm by 100 µm. The temperature precision of less than 0,1 °C may be achieved.

15 Other performance related measurands

15.1 Introduction

In this chapter, we detail other performance related measurands for characterizing nano-objects in different forms. This covers dustiness, solubility and dispersibility and mechanical properties.

15.2 Powders - Dustiness

Dustiness is not an intrinsic physical or chemical defined property of a powder, it is defined as “the propensity of a material to generate airborne dust during its handling” [87]. Dustiness depends on a number of factors including the physical characteristics of the powders [e.g. forms (powder, granules, pellets) and moisture content], the physicochemical properties of the particles contained in the powder (e.g. size and shape, surface area, type of coating, hydrophobicity and hydrophilicity properties, aggregation of particles), the environment (e.g. moisture, temperature), the type of aerosol generation (activation energy or energy input) and the interaction between particles during agitation (e.g. friction shearing, van der Waals forces). Therefore different values may be obtained by different test methods.

A summary of the measurands related to dustiness is given in Table 17.

Table 17 — Measurands related to Dustiness

Overarching measurand	Measurand(s) specific to method	Method	Size range	Resolution / accuracy	Limitation	Reference
Dustiness values in terms of mass and particle number	Dustiness values in terms of particle number, particle size distribution (equivalent aerodynamic diameter or electrical mobility diameter) and morphology. Dustiness values in terms of biological (inhalable, thoracic and respirable) mass fractions as defined by EN 481	Examples: - Rotating drum method - Continuous drop method - Small rotating drum method - Vortex shaker (Standards in development)	Few nm to approximately 10 µm for dustiness values in terms of particle number, particle size distribution and morphology. For dustiness values in terms of mass fractions as defined by EN 481.	Depends on methods and measuring instrumentations	Biologically relevant mass method are standardized based on EN 15051–1, to 3. Non-gravimetric methods, standardization under development.	EN 481 EN 15051–1 to 3 CEN ISO/TS 12025

15.3 Liquid dispersions

15.3.1 Introduction

This class of materials is also known as a suspension of solid nano-objects in liquids. The presence of nano-objects may change mechanical, thermal, electrical or optical properties of this liquid.

Table 18 — Measurands related to properties of suspension of nano-objects in liquids

Overarching measurand	Measurand(s) specific to method	Method	Range	Resolution	Limitation	Reference (see Bibliography)
Viscosity	Viscosity (Pa s)	Viscometer	0,3 Pa s < η < 10 000 Pa s	Accuracy ± 1 % of full range	For Rolling ball method density of liquid is required. Rotating disk viscometer requires large sample sizes	
Viscosity	Viscosity (Pa s) Viscoelastic behaviour: storage modulus and loss modulus	Rheometer	0,01 Pa s < η < 10000 Pa s	Accuracy ± 1 % of full range		
Dispersibility	Transmitted and reflected intensity	Static multiple light scattering (SMLS)	10 nm to 1 000 µm in size 0,01 % v/v to 95 % v/v in concentration	5 % of mean particle size.	Requires some independent calibration and yields only mean particle size or particle concentration.	

15.3.2 Viscosity

15.3.2.1 Overview

The viscosity of a liquid is often a function of temperature and other external factors. The suspension of nano-objects in liquid may have a more complex behaviour resulting in a change in viscosity. For that reason if a fine powder of magnetic material (such as Fe or Fe_2O_3) is dispersed in oil or water the combined liquid may have the viscosity that varies as a function of externally applied magnetic field. Such a fluid is also known as ferro-fluid.

In most practical situations the viscosity of a dispersion is measured in exactly the same way as that of a pure liquid. The effect of dispersed nano-objects may be therefore obtained by well-established methods such as rotational viscometer, flow cups, gravimetric capillary principle, rolling ball method and rheometry. It should be noted that none of these methods are specific to nanoscale measurements but they are commonly used for complex suspensions of nanomaterials. The units of viscosity are Pascal times second (Pa·s = kg/(s·m)).

15.3.2.2 Rotational viscometer

This type of viscometer consists of a sample-filled cup and the testing bob. In most cases the bob is rotated (Searle Principle). EN ISO 3219 deals with nanomaterial suspensions specifically even though it is used for other viscous liquids.

15.3.2.3 Gravimetric capillary principle

The rate of flow of a viscous liquid through a vertical tube or capillary under the force of gravity may be used to determine the liquid viscosity. This method is often used for polymers and biological samples. This method has an advantage of being miniaturisable to nano-litre sample sizes. With tubes as small as 30 to 300 micrometres in diameter and measurement times of the order of 100 s one can achieve a 3 % accuracy in the measurements.

15.3.2.4 Rolling or falling ball principle

The rolling ball method uses the gravity drag on the ball travelling through a capillary tube filled with the sample. The tube may be at an angle to the vertical allowing the drag to be changed. Modern rolling ball viscometers operate between 5 °C and 100 °C and could be applied to samples from 0,3 mPa s up to 10 000 mPa s with volumes of the order of 100 µl. Measurement times are of the order of tens of seconds.

15.3.2.5 Rheometry

Rheometry in general aims to test for the properties of fluids as they respond to applied pressure. It is most often used for liquids that cannot be described by one value of viscosity (complex suspensions, slurry, etc). The liquids with viscosity values from 0,3 mPa s to 100 Pa s may be studied. Some rheometers use microfluidic technology requiring sample volumes as low as 100 µl with an accuracy of ± 2 % and repeatability of ± 0,5 %. Temperature range for such measurements is approximately 4 °C to 65 °C. Larger temperature ranges 5 °C to 500 °C under conditions of high force (or pressure) and/or high shear rate may be achieved using capillary twin screw rheometers that are often used for resins or plastics.

15.3.2.6 Relevant standards

EN ISO 2431:2011, *Paints and varnishes - Determination of flow time by use of flow cups (*ISO 2431:2011*)*

EN ISO 3104:1996, *Petroleum products - Transparent and opaque liquids - Determination of kinematic viscosity and calculation of dynamic viscosity (*ISO 3104:1994*)*

EN ISO 3219:1994, *Plastics - Polymers/resins in the liquid state or as emulsions or dispersions - Determination of viscosity using a rotational viscometer with defined shear rate*

ISO 1628-1, *Plastics - Determination of the viscosity of polymers in dilute solution using capillary viscometer - Part 1: General principles*

ISO 1628-2, *Plastics - Determination of the viscosity of polymers in dilute solution using capillary viscometer - Part 2: Poly(vinyl chloride) resins*

ISO 1628-3, *Plastics - Determination of the viscosity of polymers in dilute solution using capillary viscometer - Part 3: Polyethylenes and polypropylenes*

EN ISO 2884-1:2006, *Paints and varnishes - Determination of viscosity using rotary viscometers - Part 1: Cone-and-plate viscometer operated at a high rate of shear*

EN ISO 2884-2:2006, *Paints and varnishes - Determination of viscosity using rotary viscometers - Part 2: Disc or ball viscometer operated at a specified speed*

EN ISO 12058-1:2002, *Plastics - Determination of viscosity using a falling-ball vsicometer - Part 1: Inclined-tube method*

ISO 4575:2007, *Plastics - Poly(vinyl chloride) pastes - Determination of apparent viscosity using the Severs rheometer*

ISO 16790:2005, *Plastics - Determination of drawing characteristics of thermoplastics in the molten state*

ISO 11443:2014, *Plastics - Determination of the fluidity of plastics using capillary and slit-die rheometers*

ISO 6721-10:2015, *Plastics - Determination of dynamic mechanical properties - Part 10: Complex shear viscosity using a parallel-plate oscillatory rheometer*

ISO 13145:2012, *Rubber - Determination of viscosity and stress relaxation using a rotorless sealed shear rheometer*

15.3.3 Dispersibility

Dispersion of nano-objects in a liquid is often qualified in the uniformity or stability terms. Nano-objects tend to aggregate and aggregate and then flocculate or sediment. For the formulation of a product that depends on the uniformity of such a dispersion with respect to time or other conditions (such as temperature) the parameter of dispersibility is critical.

A number of techniques are available to determine the uniformity and time stability of the dispersion:

One method is static multiple light scattering (SMLS), this allows testing of very dense (undiluted dispersions) and can yield the mean particle size as well as the particle concentration as function of time and position in the test vessel.

Static multiple light scattering is based on the static light scattering principle applied to concentrated media. It consists of successive scattering of the radiation within the scattering medium. In concentrated samples, the incoming light is scattered successively numerous times, thereby rapidly losing the memory of the incident direction. The intensity of the multi-scattered light depends on the emitted light wavelength, the particles concentration, the particle size, the refractive index of continuous and dispersed phase, the absorbency and the sensor position.

NOTE The combination of vertical scanning and multiple acquisitions over sample height enables the recording of heterogeneities local to the sample, dispersion state and its time evolution (physical stability).

No sample preparation is required (i.e. no dilution required even for high concentrated samples) as it covers a wide range of concentration (0,01 % v/v to 95 % v/v). It can measure a wide range of particle size (10 nm to 1 000 µm) and is sensitive to dispersion state. It offers time dependent analysis of dispersion state on the very same sample: and hence is sensitive to destabilization mechanisms (i.e. sedimentation) when coupled to scanning technology.

The limitations of the technique are that the method only gives mean particle size rather than a size distribution. Volume fraction and refractive indexes are required for mean particle size calculation and absorbency may limit some measurements.

15.3.4 Relevant standards

ISO/TR 13097:2013, *Guidelines for the characterization of dispersion stability*

15.3.5 Solubility and rate of dissolution

The solubility refers to the maximum mass of a nano-object which can be dissolved in a solvent so that a single, homogenous, temporally stable phase results. Solubility occurs when the material is surrounded by solvent at the molecular level.

It is important not to confuse solubility and dispersibility, as we are interested in the potential of a material to lose its particulate character and to change its form to a smaller molecular or ionic form. This is to be stressed as the distinction can be difficult in the case of colloidal suspensions of nanomaterials.

The terms miscible and immiscible may be encountered when considering the solubility of one liquid in another where miscible means soluble without limits. When findings are available on the solubility of nanomaterials in biological media, these shall be primarily used for the assessment of biopersistence. Solubility in water may be used as a yardstick for biopersistence. With good water solubility, a good solubility in biological media may normally be assumed. But this does not apply across the board. In individual cases, poor solubility in water may nonetheless be associated with good solubility in biological media. Metallic cobalt, for example, is not soluble in water, but it shows good solubility in serum. Internationally, there is no uniform definition of concentration ranges to describe solubility in water. A number of nano-objects are purposely manufactured to have a specific coating that inadvertently affects their solubility. In such cases it is not appropriate to use the solubility data of the core to estimate the biopersistance of the whole nanoparticle. Coated nano-objects may be more or less soluble than their uncoated equivalents

The measurand for solubility is the maximum mass or concentration of the solute, in this case nano-objects that can be dissolved in a unit mass or volume of the solvent at a specified (or standard) temperature and pressure; unit: [kg/kg] or [kg/m^3], or g/l or [mole/mole]).

Many factors affect the solubility, these include:

(a) Pressure, the pressure on the surface of a solution has very little effect on the solubility of solids and liquids.

(b) Temperature, the solubility of solids and liquids usually increases as the temperature increases.

(c) Forces between particles, one factor that affects solubility is the nature of the intermolecular forces or interionic forces in both the solute and the solvent. When one substance dissolves in another, the attractive forces in both shall be overcome. The dissolving solute shall be able to break up the aggregation of molecules in the solvent, and the molecules of the solvent shall have sufficient attraction for the solute particles to remove them one by one from their neighbours in the undissolved solute. If the solute is ionic, only a very polar solvent like water provides enough interaction to affect dissolution. In those ionic insoluble compounds, the interaction between the ions is greater than can be overcome by interaction with the polar water molecules. If the solute particles are polar molecules, polar solvents such as alcohols can usually affect dissolution. If the solute is nonpolar, it might dissolve only in nonpolar solvents, not because polar solvent molecules are unable to overcome the weak dispersion forces between the solute molecules, but because these dispersion forces are too weak to overcome the dipole-dipole interaction between the solvent molecules. For this reason the solubility value shall be measured for each solvent-solute combination and can be characterized as a function of temperature, impurity concentrations and other external parameters.

The dissolution rate generally depends on the surface area, temperature and the amount of locally available solute. Some estimation of this rate can be obtained by studying the rate of change of nano-object size as a function of time. Although, care shall be taken to differentiate between sedimentation and dissolution.

15.3.6 Relevant standards

EN ISO 7579:2009, *Dyestuffs - Determination of solubility in organic solvents - Gravimetric and photometric methods (*ISO 7579:2009*)*

ISO/TR 13014, *Nanotechnologies - Guidance on physico-chemical characterization of engineered nanoscale materials for toxicologic assessment*

15.4 Mechanical properties

15.4.1 Introduction

The addition of nano-objects, to matrix materials such as plastic, rubber or making solids out of nano-objects as in the case of ceramics changes the matrix materials mechanical properties as well as other parameters. The key mechanical parameters of such a composite can be classed as bulk measurands where no spatial resolution is implied or spatially resolved parameters measured with high resolution probes on a nano-scale. Some techniques allow for spatially resolved property measurements (such as AFM) while others only measure the whole material properties. The results of local hardness or electrical conductivity may be significantly different from larger scale measurements. These mechanical properties should be measured by the same test methods that have been developed over many years for conventional materials.

NOTE A good compendium of test methods is given in reference [86].

Table 19 — Measurands related to mechanical properties of solid nano-composite materials

Overarching measurand	**Measurand(s) specific to method**	**Method**	**Range**	**Resolution**	**Limitation**	**Reference**
Large scale elastic properties	Young's modulus, Poisson Ratio, Shear Modulus	Linear variable differential transformer or strain gauge.	100 nm to2 500 mm	Bulk measurement	cryogenic temperatures or up to 650 °C Accuracy of 5 % to 7 %	ASTM E111–04
Large scale elastic properties	Resonant frequency	Ultrasonic pulse technique, free-vibration technique, free resonance by impulse excitation, free resonance by continuous excitation	Only small oscillations	Bulk measurement	Only applicable to low strain measurements Accuracy 0,1 % to 1 %	ASTM E1875–13, ASTM E1876–09
Local elastic and plastic deformation properties	Young's modulus (Pa), Hardness (Pa), Also potentially yield strength, maximum plastic strain and ductility, and creep parameters and viscoelastic properties	Instrumented indentation or nanoindentation Atomic force microscopy	Probing on a nm to µm length scale	Localized testing. resolution can be in nanoscale	Typical load resolution: < 1 nN and displacement resolution: 0,000 4 nN	EN ISO 14577-1 EN ISO 14577-2, also EN ISO 14577-3 and EN ISO 14577-4
Mechanical properties	Yield strength (Pa), Young's modulus, UTS	Tensile testing	Depends on the method used	Typical uncertainty is 1 % to5 %		EN ISO 6892-1:2016
Tribological performance	Wear rate (m^3/Nm), coefficient of friction, abrasion resistance, erosion resistance	Tribometry	Typically: 1 mm to 1 000 mm	Large scale testing technique	Poor spatial resolution	

15.4.2 Measurement of elastic constants by static methods

Static loading experiments yield a number of parameters related to elastic and plastic deformation properties of solids. Key parameters include Young's modulus (ASTM E111-04), Poisson's ratio (ASTM E132-04) and Shear Modulus (ASTM E143-13).

For macro sized samples made of ceramics or other materials such as concretes the Young's modulus can be measured by 3-point and 4-point bending methods (ASTM C1341-13). For fibres made of metals, ceramic or glass the Young's modulus may be obtained from the extension measurements and the cross-sectional area. Plastic or polymer sheets are tested in tension following the procedure prescribed in detail in ASTM D882-12. The accuracy of the measurement may be only 5 % to 7 %. Some benefits are the possibility for testing a wide length rage of measurement 10 mm to 2 500 mm and at a wide range of temperatures from approximately 75 °C to 1 200 °C.

15.4.3 Relevant standards

ASTM E111-04 (2010), *Standard test method for Young's modulus, tangent modulus, and chord modulus*

ASTM E132-04 (2010), *Standard test method for Poisson's ratio at room temperature*

ASTM E143-13, *Standard test method for shear modulus at room temperature*

ASTM C1341-13, *Standard Test Method for Flexural Properties of Continuous Fibre-Reinforced Advanced Ceramic Composites*

ASTM D882-12, *Standard test method for tensile properties of thin plastic sheeting*

15.4.4 Measurement of elastic constants by dynamic methods

Dynamic methods for measuring the elastic properties such as Young's modulus, shear modulus and Poisson's ratio for a number of solid materials offer great accuracy and avoid the large stain effects such as creep or elastic hysteresis. The dynamic methods for determining elastic constants include ultrasonic pulse technique, free-vibration technique, free resonance by impulse excitation, and free resonance by continuous excitation.

There are two types of dynamic tests in practice. One method uses the measurement of the time of flight of an ultra-sound pulse, yields the ultrasound velocity in the material of well-known dimensions and density, which leads to the Young's modulus with a precision of the order of 0,1 %. Another method mechanically excites the freely vibrating rod (specimen) to find the resonant frequency. The specimen dimensions are used to calculate the elastic parameters. The benefits are that large strain complex effects such as creep or elastic hysteresis are avoided. Experimental frequencies from 500 Hz to 30 kHz are used.

15.4.5 Relevant standards

ASTM C623-92 (2015), *Standard test method for young's modulus, shear modulus, and poisson's ratio for glass and glass-ceramics by resonance*

ASTM E1875-13, *Standard test method for dynamic young's modulus, shear modulus, and poisson's ratio by sonic resonance*

ASTM E1876-09, *Standard test method for dynamic young's modulus, shear modulus, and poisson's ratio by impulse excitation of vibration*

15.4.6 Measurement of elastic and plastic properties by instrumented indentation methods

Most elasticity measurements refer to the macro scale properties such as Young's modulus or Poisson's ratio and surface hardness however in some cases the macro scale measurement is simply not possible or not appropriate where the measurement of specific components of a materials system are required such as the individual phases in a composites or for coatings.

In this case an indentation is made into the surface of the sample. A known force is applied (with piezoelectric elements, electrostatically or electromagnetically) and the displacement is measured by a variety of gauges (capacitive sensors, linear variable differential transformers or laser interferometers). The indenters can have a shape of 4 or 3 faceted pyramids (or cube corner geometry) as well as spherical. The latter is difficult to fabricate but yields good elastic deformation data. The deformation is often a combination of plastic and elastic deformation in the sample. The load versus displacement curve can be analysed to yield hardness from the permanent depth of the indentation, and Young's modulus from the slope of the unloading curve, but this analysis relies on a well calibrated test system including the calibration of the tip shape and input of the value of Poisson's ratio (estimated or measured by other techniques), but a result for Young's modulus with an error of 5 % can be obtained. Other parameters plastic deformation parameters such as yield strength, maximum plastic strain and ductility, and viscoelastic properties for viscoelastic materials can be evaluated from this method. These tests provide a localized measure of the elastic and plastic material parameters *in situ*.

15.4.7 Relevant standards

EN ISO 14577-1:2015, *Metallic materials - Instrumented indentation test for hardness and materials parameters - Part 1: Test method (*ISO 14577-1:2015*)*

EN ISO 14577-2:2015, *Metallic materials - Instrumented indentation test for hardness and materials parameters - Part 2: Verification and calibration of testing machines (*ISO 14577-2:2015*)*

EN ISO 14577-3:2015, *Metallic materials - Instrumented indentation test for hardness and materials parameters - Part 3: Calibration of reference blocks (*ISO 14577-3:2015*)*

EN ISO 14577-4:2007, *Metallic materials - Instrumented indentation test for hardness and materials parameters - Part 4: Test method for metallic and non-metallic coatings (*ISO 14577-4:2007*)*

15.4.8 Measurement of surface properties and wear

Mechanical wear may be measured by a number of methods either at the micro and macro scale or at the nanoscale through the use of atomic force microscopy (AFM). The appropriate test method depends on the mechanism of wear that is being studied. Wear occurs through the interaction of two surfaces with different types of wear including sliding, rolling contact, erosion and abrasion. Different test methods are available for these different types of mechanical contact. Most mechanical wear tests are not specifically nano-scale related, but the magnitude of wear and the friction that is generated are nearly always controlled by the micro and nanoscale phenomena that occur at the contact interface. Key measurands are the coefficient of friction and the wear rate which are related to the normal load and sliding distance as well as material properties.

15.4.9 Relevant standards

ISO/TR 11811:2012, *Nanotechnologies - Guidance on methods for nano- and microtribology measurements*

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