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**Nanotechnologies — Requirements  
and recommendations for the  
identification of measurands that  
characterise nano-objects and  
materials that contain them**

*Nanotechnologies – Exigences et recommandations pour  
l'identification des mesurandes qui caractérisent les nano-objets et les  
matériaux les contenant*

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## Foreword

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

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

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

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

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

This document was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*, and IEC/TC 113, *Nanotechnology for electrotechnical products and systems*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at [www.iso.org/members.html](http://www.iso.org/members.html).

## 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 nm to 100 nm). Specific size dependent properties are usually exhibited in this size range, even if they do not disappear abruptly beyond these limits. Nano-objects, either natural or manufactured, can 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 (NOAAs) 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 physical and chemical properties, performance and lifetime. 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 the development of new techniques and adaptation of existing ones.

The method selection is often strongly influenced by its initial cost and availability, time and sample compatibility. However, an aspect that is easily forgotten is whether the selected method truly targets the physical or chemical material property that is intended to be measured (“the measurand”). This can sound trivial, but in practice, insufficient knowledge or consideration about the actual measurement principle and/or the property measured can impede a correct assessment of the measurement results.

Measurement techniques and methods are typically classified according to the material properties they can measure. One definition of “measurand” used in many ISO standards is the “quantity intended to be measured”. In nanotechnologies popular material properties often considered as this “intended measurand” can be size, shape, chemical composition, surface charge. However, in reality, due to their different underlying physical measurement principles, results obtained by different techniques, for a common material property, can differ significantly. The logical reason for this is that these different techniques measure not the intended measurand but different measurands, which are specific to the technique but are closely related to the intended measurand.

For intended use in biological systems and therapeutic purposes, additional characterization beyond those mentioned in the document may be required.

This document describes measurands used to characterize nano-objects, and their agglomerates and aggregates. This document is split into 10 main clauses covering:

- [Clause 6](#): size and shape measurands;
- [Clause 7](#): chemical analysis measurands;
- [Clause 8](#): mass and density;
- [Clause 9](#): charge measurands;
- [Clause 10](#): crystallinity measurands;
- [Clause 11](#): optical properties measurands;
- [Clause 12](#): electrical and electronic measurands;
- [Clause 13](#): magnetic measurands;
- [Clause 14](#): thermal measurands;
- [Clause 15](#): other performance related measurands.

# Nanotechnologies — Requirements and recommendations for the identification of measurands that characterise nano-objects and materials that contain them

## 1 Scope

This document specifies requirements and recommendations 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 recommendations for relevant measurement.

## 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 20579-4, *Surface chemical analysis — Guidelines to sample handling, preparation and mounting — Part 4: Reporting information related to the history, preparation, handling and mounting of nano-objects prior to surface analysis*

ISO/TS 80004-1:2015, *Nanotechnologies — Vocabulary — Part 1: Core terms*

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

ISO/TS 80004-6:2021, *Nanotechnologies — Vocabulary — Part 6: Nano-object characterization*

## 3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004-1:2015, ISO/TS 80004-2:2015 and ISO/TS 80004-6:2021 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at <https://www.electropedia.org/>
- ISO Online browsing platform: available at <https://www.iso.org/obp>

### 3.1 General core terms

#### 3.1.1

##### **nanoscale**

length range approximately from 1 nm to 100 nm

Note 1 to entry: Properties that are not extrapolations from a larger size are predominately exhibited in this length range.

[SOURCE: ISO/TS 80004-1:2015, 2.1]

### 3.1.2

#### **nano-object**

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

Note 1 to entry: The second and third external dimensions are orthogonal to the first dimension and to each other.

[SOURCE: ISO/TS 80004-1:2015, 2.5]

### 3.1.3

#### **agglomerate**

collection of weakly bound *particles* (3.1.5) 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* (3.1.6).

[SOURCE: ISO/TS 80004-6:2021, 3.10]

### 3.1.4

#### **aggregate**

*particle* (3.1.5) 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* (3.1.6).

[SOURCE: ISO/TS 80004-6:2021, 3.11]

### 3.1.5

#### **particle**

minute piece of matter with defined physical boundaries

Note 1 to entry: A physical boundary can also be described as an interface

Note 2 to entry: A particle can move as a unit

Note 3 to entry: This general particle definition applies to *nano-objects* (3.1.2)

[SOURCE: ISO 26824:2013, 1.1]

### 3.1.6

#### **primary particle**

original source *particle* (3.1.5) of *agglomerates* (3.1.3) or *aggregates* (3.1.4) or mixtures of the two

Note 1 to entry: Constituent particles of agglomerates or aggregates at a certain actual state may be primary particles, but often the constituents are aggregates.

Note 2 to entry: Agglomerates and aggregates are also termed secondary particles.

[SOURCE: ISO 26824:2013, 1.4]

### 3.1.7

#### **constituent particle**

identifiable, integral component of a larger *particle* (3.1.5)

Note 1 to entry: The constituent particle structures may be *primary particles* (3.1.6) or secondary particles.

[SOURCE: ISO/TS 80004-2:2015, 3.3]

## 3.2 Measurand related 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* (3.1.5) 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: ISO 26824:2013, 1.5]

### 3.2.3

#### **particle size distribution**

distribution of the quantity of *particles* (3.1.5) 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).

Note 2 to entry: The quantity can be, for example, number, mass, or volume based.

[SOURCE: ISO/TS 80004-6:2021, 4.1.2]

### 3.2.4

#### **particle shape**

external geometric form of a *particle* (3.1.5)

[SOURCE: ISO/TS 80004-6:2021, 4.1.3]

### 3.2.5

#### **aspect ratio**

ratio of length of a *particle* (3.1.5) to its width

[SOURCE: ISO/TS 80004-6:2021, 4.1.4]

### 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* (3.1.5) being measured

Note 1 to entry: Physical properties are, for example, the same settling velocity or electrolyte solution displacing volume or projection area under a microscope. The physical property to which the equivalent diameter refers should be indicated using a suitable subscript (see ISO 9276-1:1998), e.g. subscript "V" for equivalent volume diameter and subscript "S" for equivalent surface area diameter.

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

Note 3 to entry: Other parameters, e.g. the effective density of the particle in a fluid, are used for the calculation of the equivalent diameter such as Stokes diameter or sedimentation equivalent diameter. The parameters used for the calculation should be reported additionally.

Note 4 to entry: For inertial instruments, the *aerodynamic diameter* (3.2.9) is used. Aerodynamic diameter is the diameter of a sphere of density  $1\ 000\ \text{kg m}^{-3}$  that has the same settling velocity as the particle in question.

[SOURCE: ISO/TS 80004-6:2021, 4.1.5]

### 3.2.7

#### **light scattering**

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

[SOURCE: ISO/TS 80004-6:2021, 4.2.5]

### 3.2.8

#### **hydrodynamic diameter**

*equivalent diameter* (3.2.6) of a *particle* (3.1.5) in a liquid having the same diffusion coefficient as a spherical particle with no boundary layer in that liquid

Note 1 to entry: In practice, nanoparticles in solution can be non-spherical, dynamic, and solvated.

Note 2 to entry: A particle in a liquid will have a boundary layer. This is a thin layer of fluid or adsorbates close to the solid surface, within which shear stresses significantly influence the fluid velocity distribution. The fluid velocity varies from zero at the solid surface to the velocity of free stream flow at a certain distance away from the solid surface.

[SOURCE: ISO/TS 80004-6:2021, 4.2.6]

### 3.2.9

#### **aerodynamic diameter**

diameter of a sphere of density  $1\ \text{g/cm}^3$  with the same terminal velocity due to gravitational force in calm air as the *particle* (3.1.5), under prevailing conditions of temperature, pressure and relative humidity

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

[SOURCE: ISO 23210:2009, 3.1.1]

**3.2.10****mobility diameter****particle mobility diameter****particle mobility equivalent diameter****mobility equivalent diameter**

diameter of a sphere carrying a single elementary charge with the same drift speed in an electric field as the *particle* (3.1.5) 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 involving its capacitance, i.e. its capacity to become electrically charged by bipolar air ions), but not of its density.

[SOURCE: EN 16966:2018]

**3.2.11****mass specific surface area**

absolute surface area of the sample divided by sample mass

Note 1 to entry: The mass specific surface area has units of m<sup>2</sup>/kg.

[SOURCE: ISO/TS 80004-6:2021, 4.6.1]

**3.2.12****photoluminescence**

luminescence caused by absorption of optical radiation

[SOURCE: ISO/TS 80004-6:2021, 5.3]

**3.2.13****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: ISO/TS 80004-6:2021, 5.9]

**3.2.14****lattice parameters**

linear and angular dimensions of the crystallographic unit cell

[SOURCE: ISO 21432:2019, 3.19]

**3.2.15****scattering angle**

angle between the direction of the incident *particle* (3.1.5) or photon and the direction that the particle or photon is travelling after scattering

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

**3.2.16****zeta potential****electrokinetic 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: ISO/TS 80004-6:2021, 6.4.5]

**3.2.17****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: ISO/TS 80004-6:2021, 4.5.12]

**3.2.18**

**Curie temperature**

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

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

**3.2.19**

**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<sup>2</sup>/s

[SOURCE: ISO 13826:2013, 2.1]

**3.2.20**

**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]

**3.2.21**

**dispersibility**

qualitative or quantitative characteristic or property of a particulate source material assessing the ease with which said material can be dispersed within a continuous phase

Note 1 to entry: Spatially uniform distribution (homogeneity) of the dispersed phase is considered an integral part of the desired end point.

Note 2 to entry: *Particle size* (3.2.2) or *particle size distribution* (3.2.3) is often used as an end point relative to defined criteria specific to the application.

Note 3 to entry: Dispersibility refers to a specific dispersion process and specific process time.

Note 4 to entry: Dispersion stability, though a related phenomenon, should not be confused with *dispersibility*.

[SOURCE: ISO/TS 22107:2021, 3.6]

**4 Abbreviated terms**

For the purposes of this document, the following 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 method	Brunauer, Emmet and Teller method
CLS	centrifugal liquid sedimentation
CPC	condensation particle counter
CVC	colloid vibration current
DC	direct current
DCS	differential centrifugal sedimentation
DEMC	differential electrical mobility classifier
DLS	dynamic light scattering
DMAS	differential mobility analysis system
DRIFT	diffuse reflectance infrared Fourier transform spectroscopy
DSC	differential scanning calorimetry
EBS	electron backscatter diffraction
EDX	energy dispersive X-ray spectroscopy NOTE EDS is another acronym for this method.
EELS	electron energy loss spectroscopy
EGA	evolved gas analyser
EL	electroluminescence
ELPI	electrical low-pressure impaction
EPR	electron paramagnetic resonance
ESA	electrokinetic sonic amplitude
ESR	electron spin resonance
FFF	field-flow fractionation
FIB	focused ion beam
FTIR	Fourier transform infrared spectroscopy
HRTEM	high-resolution transmission electron microscopy
LD	laser diffraction
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectroscopy

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ICP-OES	inductively coupled plasma optical emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometry
IR	infrared
LALS	low angle light scattering
LEED	low-energy electron diffraction
LEIS	low-energy ion scattering
MALS	multi-angle light scattering
MFM	magnetic force microscopy
MOKE	magneto-optical Kerr effect
NP	nanoparticle
NIR	near infrared
NMR	nuclear magnetic resonance
NOAA	nano-objects, and their agglomerates and aggregates
OPC	optical particle counter
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 spectrometry
SLS	static light scattering
SMLS	static multiple light scattering

SMPS	scanning mobility particle spectrometer
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 Procedure

The selection of measurands to characterize NOAAs is defined by the type and quality of information required by the user. Multiple methods or techniques are usually available for a specific measurand, and thus the method(s) or technique(s) chosen should be fit for purpose and compatible with the sample material.

In this document, measurands from different categories are described. Use one or more of the measurands to characterize NOAAs. The measurands that shall be used depend on the information that the user requires. Very often the user requires more than one measurand, for example size, shape, charge and chemistry therefore measurands from different subclauses of this document should be selected where required.

The user should not confuse 'measurand' with 'method', the latter being a means to obtain the former. The user should also be aware that different methods that nominally provide the same type of information, for example size, can in fact yield different results due to method-dependent difference and other factors. Therefore, an orthogonal approach (use of multiple orthogonal methods), when

practical, should be applied toward measurand determination when method dependencies are known or suspected. On the other hand, if different methods are targeting exactly the same measurand, where this measurand is specifically defined for example by fundamental or structural principles, then results should always be comparable and independent from the method used provided the methods are correctly calibrated.

### 5.2 Types of measurands

To aid the user in the selection of measurands and specific methods or techniques, this document describes the measurands for characterizing nano-objects based on commonly used techniques and separated into different 'types' of measurands. Tables and text in each subclause 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. Results obtained by different techniques can be significantly different from one another due to differences in the techniques' underlying physical measurement principles.
- c) Range and resolution of particular techniques: these are given in units that depend on the particular measurand and are for typical current commercial instruments. State of the art research instruments can have higher resolution than those stated. The resolution of each measurand and technique is different and calculated via different means. Depending on the technique, it can be a percentage of the measurand size, the ability to resolve two peaks or ultimate performance of an instrument. Resolution is provided only as a guide and not discussed in detail here.
- d) Limitations and references: references to ISO standards are stated where they are available. These should be consulted for detailed information. Limitations refer to limitations of the technique.

### 5.3 State of nano-objects

Nano-objects exist in a number of different states, a summary of which is provided in [Table 1](#). For analysis, different techniques require the nano-objects to be in different forms or dispersed phases.

The material under test can be composed entirely of nano-objects or it can contain a percentage of nano-objects where the percentage can be measured via different measurands, for example number or mass, and hence different techniques. The degree and nature of the dispersion of the nano-objects is also important and should be considered, see [Clause 15](#).

**Table 1 — Different states of nano-objects**

Continuous phase	Dispersed phase		
	Solid	Liquid	Gas
<b>Solid</b>	Nano-composite, nano-(structured) powder mixture	Nano-porous material	Nano-porous material Solid nanofoam
<b>Liquid</b>	Nano-suspension / colloid	Nano-emulsion	Liquid nano-foam
<b>Gas</b>	Nano-aerosol (solid)	Nano-aerosol (liquid)	(does not apply)

Other factors that need to be considered include sample preparation. Here, the state of nano-objects before, during and after sample preparation and prior to analysis can vary considerably and effect the measured results. Examples include the type and duration of sonication and extraction and deposition parameters and methods.

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

### 6.1 General

The shape, mean size, and particle size distribution of 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 examples.

During their life cycle, nano-objects and the materials that contain them need to be characterized. Several time identifiable steps can be identified where characterization can be appropriate. These include after synthesis, after shipping, after storage and processing before use. This characterization allows checking whether they exhibit the properties they are designed for. This is the case even if the relationship between intrinsic characteristics of the nano-objects and the desired application property (e.g. optical, electrical, and mechanical) is not fully understood. Regarding size and shape, their characterization should 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 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 can 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 can 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

#### 6.2.1 Overview

PSD is a list of numerical values that represent the relative, or in rare cases the absolute number 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 (types), 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;
- 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. DLS). 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 NOAA's 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 elongation (the ratio between maximum Feret diameter and minimum Feret diameter where the Feret diameter is the distance between two parallel

tangential lines in a specific direction), aspect ratio (the ratio of length of a particle to its width) 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.

NOTE Care needs to be taken when applying the definition of an aspect ratio (a 2D parameter) to different shaped materials (which are 3D). The relevant lengths are dependant on the morphology of the nano-object, for example, particle versus rod versus plate.

## 6.2.2 General relevant standards

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

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

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

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

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

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

ISO 26824, *Particle characterization of particulate systems — Vocabulary*

ISO/TS 80004-6, *Nanotechnologies — Vocabulary — Part 6: Nano-object characterization*

## 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 in which they are distributed. 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 document, 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 – gives 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, for example, 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. The real-time techniques measure size only whereas the microscopy techniques can measure shape as well as size.

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

Overarching measurand	Measurand specific to the method	Method	Size range	Resolution	Limitations	References
Number-weighted size distribution, where "size" is the particle equivalent aerodynamic diameter	Electrical detection from 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/m <sup>3</sup> to 100 mg/m <sup>3</sup> . 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 – electrical mobility size distribution	Electrical mobility	DMAS	3 nm to 1 000 nm	sub-nm	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	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-weighted aerodynamic size distribution	Velocity	APS	0,5 µm to 20 µm	0,1 µm	The resolution is lower for non-spherical particles.	[4]
Size and shape of NOAA	2D-projected size and shape of NOAA. Number-weighted geometric size and shape distributions.	Particle sampler with TEM and image analysis	1 nm to 10 µm	0,2 nm	Typical sampling efficiency has a minimum (10 %) at 20 nm to 30 nm. TEM is not a real time technique.	[5],[6]
Size and shape of NOAA	2D-projected size and shape of NOAA. Number-weighted geometric size and shape distributions.	SEM on filters	5 nm to 1 mm	5 nm	Needs sample preparation onto a substrate. Slow, individual particle measurement. SEM is not a real time technique.	[7]

NOTE In [Table 2](#) and subsequent tables the parameters size range, resolution and limitations relate to the measurement method.

### 6.3.2 General relevant standards

ISO/TR 18196, *Nanotechnologies — Measurement technique matrix for the characterization of nano-objects*

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

### 6.3.3 Electrical low-pressure impaction

In ELPI, 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 ones accumulate on the 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 or 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 SEM to obtain shape information.

#### 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 reentrainment, and enhance collection efficiency. This results in sharper cut-size characteristics and more accurate mass-weighted size distributions.

NOTE Typical electrical impactors determine the 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<sup>3</sup> to 100 mg/m<sup>3</sup>.

#### 6.3.5 Differential mobility analysing system

A differential mobility analysis system, also known as SMPS, is the combination of a DEMC and a 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 to deflect the path of charged objects entering the DEMC. Since this deflection is proportional to the electrical mobility, each voltage setting extracts a specific size class of objects from the system. The DEMC essentially acts as a band pass filter, allowing only objects of a specific mobility size to exit the column. Electrical mobility is determined by the charge-to-size ratio. For singly-charged spheres, the size is equivalent to the geometric spherical diameter of the object. For non-spherical objects, the size is the equivalent spherical mobility diameter exhibiting the same drag force as the measured object. A CPC placed at the outlet records the number concentration of each class using an optical-based technique. A mobility size distribution is thus obtained in a typical size range from 3 nm to 1 000 nm, although novel instruments are improving the size range down to 0,5 nm. Different columns (DEMCs) cover different size ranges in the classical DMAS and different CPCs exhibit different limits of detection. The specific measurand involved in this technique is the electrical mobility, directly linked to charge and aerodynamic diameter of objects since their charge law is known. Information on the shape of the objects cannot be directly obtained, but models exist to fit data to a known shape function to extract, for example, length distributions. For highly anisotropic objects like nanofibres, the charging law can be unpredictable, resulting in large uncertainties in the results.

Some alternate DEMC designs exist, where one of the electrodes is divided into a number of segments, each connected to highly sensitive electrometers. This allows the extension of the size range of the technique, typically from 10 nm to 10 µm. The fast mobility particle size spectrometer is an example of such a design and can measure particles in the range from 5,6 nm to 560 nm with a total of 32 channels.

These designs are much faster than a classical DMAS since they can perform measurements at more than 1 Hz.

### 6.3.6 Relevant standards

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

ISO 27891, *Aerosol particle number concentration — Calibration of condensation particle counters*

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

### 6.3.7 Optical particle counter

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 spherical diameter can be derived from Mie theory. For precise size distributions, the refractive index of particles shall be known. Usually the instrument is calibrated using a monodisperse aerosol of known refractive index such as polystyrene latex. The resulting size distribution displayed by the instrument is based on an equivalent diameter. Mie scattering calculations have been used to both model the response of the instruments and invert the resulting data but are limited by knowledge of the particle's refractive indices and shape. Number-weighted optical equivalent size distribution ranging from 0,3  $\mu\text{m}$  to 20  $\mu\text{m}$  can be measured using such counters. This size range can be seen as irrelevant for the nanoscale but is complementary to SMPS measurements since nanoparticles are often found in aerosols under the form of aggregates and agglomerates.

### 6.3.8 Relevant standards

ISO 13320, *Particle size analysis — Laser diffraction methods*

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

### 6.3.9 Aerodynamic particle sizing

In 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  $\mu\text{m}$  to 20  $\mu\text{m}$  so this technique is only suitable for measuring aggregates and agglomerates of nano-objects and not the nano-objects themselves.

### 6.3.10 TEM combined with TEM grid samplers

TEM is a microscopy technique in which a beam of electrons is transmitted through a thin specimen to form an image. Number-weighted geometric size and shape distributions can be obtained by means of image analysis of TEM micrographs, with some limits and restrictions. It is usually not possible to obtain separate PSD's for nano-objects since primary particles are very difficult to isolate in an aggregate or agglomerate especially with automatic criteria used by the software. Very long nanofibres, like carbon nanotubes, can be difficult to separate as individual fibres 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 can limit the counting statistics whereas high concentrations can 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 certified reference materials.

Image analysis software gives access to number-weighted geometric size or shape distributions (expressed in equivalent circular 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 and is generally limited to two-dimensional information. Shape distributions can also be obtained, for instance by measuring individual aspect ratio of NOAA (length divided by width). TEM allows the differentiation between constituent particles which can be the 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. Soluble HEPA filters can also be used.

**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<sup>[5]</sup>.

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

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

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

ISO 21363, *Nanotechnologies — Measurements of particle size and shape distributions by transmission electron microscopy*

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

ISO 29301, *Microbeam analysis — Analytical electron microscopy — Methods for calibrating image magnification by using reference materials with periodic structures*

### 6.3.12 Scanning electron microscopy

In 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 can 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 nano-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. Size and shape information is generally limited to two-dimensional information.

The instrument under use possibly does not have sufficient resolving power to distinguish very small (<10 nm) particles. SEM can differentiate between constituent 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.

SEM and other microscopy techniques can also be used to study the properties of nanocomposites and other materials with nanoscale surface features.

### 6.3.13 Relevant standards

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

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

ISO 19749, *Nanotechnologies — Measurements of particle size and shape distributions by scanning electron microscopy*

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

## 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 the size and shape of nano-objects in powders.

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

Overarching measurand	Measurand specific to the method	Method	Size range	Resolution	Limitations	References
Size and shape of NOAA	2D-projected size and shape of NOAA. Number-weighted geometric size and shape distributions	SEM	5 nm to 1 mm	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	LD	30 nm to 1 mm	10 nm	Underestimation of the relative number of submicron particles for polydispersed samples	[10]
Volume-weighted mean diameter	Broadening of X-ray diffraction peaks	XRD	5 nm to 100 nm	5 nm	Is more accurate for measuring large crystalline structures rather than small ones.	[11]
Volume-weighted mean diameter of carbon nanotubes	Frequency shift	Raman spectroscopy	0,5 nm to 2 nm	0,05 nm	Not straightforward for multi-wall carbon nanotubes	[12],[13]

NOTE TEM is not included in this table, as sample preparation for TEM often requires the powder that contains nano-objects to be dispersed in a suitable liquid dispersant. TEM is discussed in [6.3.10](#) and [6.5.12](#).

### 6.4.2 Relevant standards

ISO 17200, *Nanotechnology — Nanoparticles in powder form — Characteristics and measurements*

ISO/TS 21356-1, *Nanotechnologies — Structural characterization of graphene — Part 1: Graphene from powders and dispersions*

ISO 26824, *Particle characterization of particulate systems — Vocabulary*

### 6.4.3 Scanning electron microscopy

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 can 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 the shape of NOAA, by visual interpretation of the micrographs. For this reason, it is routinely used in many NOAA production or research sites.

### 6.4.4 Relevant standards

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

ISO 16700, *Microbeam analysis — Scanning electron microscopy — Guidelines for calibrating image magnification*

### 6.4.5 Gas adsorption, the BET method

The 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 (77 K) over a range of relative partial pressures. The total amount of the adsorbed gas in the monolayer is derived by fitting the adsorption isotherm to the BET formula and converting to standard temperature of 273,15 K and atmospheric pressure of  $1,013 \times 10^5$  Pa. The size of the adsorbed nitrogen molecule being known, the total surface area of the sample is obtained. This value is then converted to mass specific surface area by dividing by the dry mass of the sample. This measurand can be used to characterize NOAA powders. If the density is known, it can also be converted to 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. One limitation is that the BET result tends to be representative of the powder sample, and not necessarily the particles themselves.

### 6.4.6 Relevant standard

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

### 6.4.7 Laser diffraction

A dispersion (e.g. aerosolized powder) 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 and refractive indices. While larger particles scatter more light toward low angles, smaller particles scatter light weakly and more isotropically. Therefore, detectors placed at low and high scattering angles are utilized in LD to capture the scattering pattern for a wide range of sizes. Multiple laser wavelengths can also be used to enhance detection of objects at the low end of the applicable range, allowing measurements down to roughly 10 nm; note that conventional LD instruments (low angle scattering) are not intended for the analysis of nano-objects and generally are limited to sizes greater than 100 nm.

The angular and wavelength-dependent differences are used in the analysis of the scattering data. The specific measurand is the angular distribution of scattered light. It is converted to a volume-weighted size distribution using Mie analysis and assuming a spherical shape for the objects. The refractive index shall be known.

NOAA in powder form is typically delivered to the measurement cell in LD using a vibratory feeder followed by compressed air or vacuum acceleration in a venturi nozzle, with or without impaction. LD does not provide shape information; all sizes are presented as equivalent spherical diameters. Hence, as with many other techniques that use a spherical model, uncertainties increase for non-spherical objects. The applicable size range is dependent on the optical configuration, but can range from tens of nanometres up to approximately 1 mm. In a highly polydisperse sample, the relative amount of sub-micrometre particles can 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 agglomeration. Care should be taken to optimize the time and energy of the ultrasonic treatment in order to try to maintain the same level of agglomeration as in dry powder form. Techniques described in 6.5 can then be applied.

#### 6.4.8 Relevant standard

ISO 13320, *Particle size analysis — Laser diffraction methods*

#### 6.4.9 X-ray diffraction

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 corresponds to the dimensions of the nano-object. In the case of polycrystalline nano-objects, the measured size is 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 considered 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 depends 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 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 “RBM” corresponding to cyclic radial expansion and contraction of the tube under excitation by light. The frequency of this mode is inversely proportional to the diameter of the nanotube.

## 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 the size and shape of nano-objects in liquids.

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

Overarching measurand	Measurand specific to the method	Method	Size range	Resolution	Limitations	References
Mass-weighted size distribution (size being the equivalent hydrodynamic diameter)	Stokes diameter in CLS (equivalent hydrodynamic diameter based on sedimentation rates of objects in a suspending medium)	CLS	20 nm to 1 µm	5 nm	Relative high concentrations needed (>10 g/l), for devices using X-ray absorption detectors. Requires known effective density and refractive index of particles.	[14]
Volume-weighted size distribution (size being the equivalent hydrodynamic diameter)	Autocorrelation function of scattered light at a given angle and the translational diffusion coefficient.	DLS	6 nm to 1 000 nm	10 nm	Not applicable to concentrated, coloured or very polydisperse samples.	[14]
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	SAXS	1 nm to 150 nm	20 nm	Complex models shall be used to extract the specific measurands. Not suitable for polydisperse samples.	[15]
Number-weighted hydrodynamic size distribution	Diffusion coefficient	PTA	10 nm to 2 µm	10 nm	Not applicable to concentrated or very polydispersed samples. Applicable size range can depend on sample type.	[16]
Particle size and shape distribution	2D-projected size and shape of NOAA. Number-weighted geometric size and shape distributions	SEM	5 nm to 1 mm	5 nm	Needs sample preparation onto a substrate. Slow, individual particle measurement.	
Particle size and shape distribution	2D-projected size and shape of NOAA. Number-weighted geometric size and shape distributions.	TEM	0,5 nm to 10 µm	0,2 nm	Needs sample preparation onto a TEM grid. Slow, individual particle measurement	
Particle size and molar mass	Angular distribution of scattered light, autocorrelation function of scattered light at a fixed angle, UV-Vis absorption at one or more wavelengths.	FFF including asymmetrical flow and centrifugal	1 nm to ≈50 µm	Depends on the detector(s) used, typically 1 nm	Requires method development and validation. Long analysis times for highly polydisperse samples (>1 h)	[17],[18]
Number-weighted particle size distribution	Spherical equivalent diameter from measured mass of analyte and assumed particle density.	sp-ICP-MS	10 nm to 2 µm	10 nm	Requires proper dilution (not directly applicable to high number concentration). Requires known density and shape of particles.	[19]

### 6.5.2 Centrifugal liquid sedimentation

CLS 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 effective density of the objects. The temperature dependent density and viscosity of the fluid 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 disc. 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 and density. A light turbidity or X-ray detector continuously records the light attenuation or mass concentration at a given radial position along the disc. The measured sedimentation time is related to an equivalent diameter using Stokes law. The acquired PSD's are either light extinction-weighted (turbidity detector) or mass-weighted (X-ray detector). The light extinction-weighted PSD can be transformed into a volume-weighted distribution and eventually to a number-weighted size distribution by applying Mie theory. In this case, the material's refractive index, including its imaginary part shall be known.

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, *Determination of particle size distribution by centrifugal liquid sedimentation methods — Part 1: General principles and guidelines*

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

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

### 6.5.4 Dynamic light scattering

In a liquid, the Brownian motion of dispersed objects result in time-dependent fluctuations of scattered light due to randomized constructive and destructive interference. In DLS, these rapid fluctuations are measured and analysed using autocorrelation spectroscopy (time domain) or frequency analysis (spectral domain). Larger objects move more slowly than smaller objects, and therefore exhibit slower Brownian motion characterized by a smaller diffusion coefficient. Hence, the determination of the autocorrelation function or power spectrum of scattered light at a given angle (specific measurand), allows the determination of the distribution of the diffusion coefficients of dispersed objects. The average diffusion coefficient is converted into an average hydrodynamic diameter using the Stokes-Einstein equation. The method requires that the temperature and the dynamic viscosity of the dispersing medium are known. It should be noted that in this analysis objects are assumed to be spherical, thus measurement uncertainties can significantly increase for results obtained measuring non-spherical objects. Taking into account all these considerations, a scattered light intensity-weighted harmonic mean size (often referred to as the z-average) and polydispersity index (relative variance) are obtained via the well-known cumulants analysis. Additionally, and subject to the ill-conditioned inverse problem, a scattered light intensity-weighted size distribution can be produced using common algorithms such as non-negative least squares, which can be further converted into a volume-weighted size distribution using the known refractive index of the scatterers. Polydispersity in a sample can lead to underestimation of the smallest objects, since their low scattered-light signal is masked by the much larger signal arising from the more massive objects, as the scattering intensity is proportional to diameter of the object to the sixth power. Generally, DLS is not appropriate for highly polydispersed samples. DLS is typically limited to non-absorbing samples, although absorbing particles can be measured as long as sufficient scattering exists. It is not applicable to high concentrations due to multiple light scattering effects, although multiple scattering can be mitigated by the use of special cells,

focusing at a shallow point in the cell or using cross correlation DLS. The size range is approximately 6 nm to 1 000 nm.

#### 6.5.5 Relevant standards

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

ISO 22412, *Particle size analysis — Dynamic light scattering (DLS)*

ISO/TR 22814, *Good practice for dynamic light scattering (DLS) measurements*

ASTM E2490-09, *Standard guide for measurement of particle size distribution of nanomaterials in suspension by Photon Correlation Spectroscopy (PCS)*<sup>[20]</sup>

ASTM E3247-20, *Standard Test Method for Measuring the Size of Nanoparticles in Aqueous Media Using Dynamic Light Scattering*<sup>[21]</sup>

#### 6.5.6 Laser diffraction

The laser diffraction 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 an aqueous solution, sometimes with the help of either an ultrasonic treatment or surface-active agents, or both) 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 standard

ISO 13320, *Particle size analysis — Laser diffraction methods*

#### 6.5.8 Small angle X-ray scattering

The SAXS technique uses synchrotron radiation or laboratory scale commercial X-ray sources. The principle is essentially the same as laser diffraction, but in SAXS the scattering intensity is proportional to (is inherently weighted by) the square of the electron density difference within the particles and that of the surrounding medium. The very small wavelength of X-rays gives access to physical dimensions and agglomerate or surface structure information in the nanometre range in favourable cases (existence of a fractal domain over a certain size range).

The specific measurand is the angular distribution of scattered X-rays for a specified X-ray wavelength. The overarching measurands are a volume-weighted size distribution of elemental particles, their total surface area per unit sample volume, the fractal exponent of fractal aggregates and, in some cases, a mean size of agglomerates. All these measurands are obtained by fitting appropriate models to the experimental scattered intensity curve, measured as a function of scattering angle, while using a specified X-ray wavelength.

#### 6.5.9 Relevant standard

ISO 17867, *Particle size analysis — Small angle X-ray scattering (SAXS)*

#### 6.5.10 Particle tracking analysis

PTA 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.

The viscosity of the dispersing medium shall be known. This technique applies to dilute specimens consisting of NOAA in the range 10 nm to 2 000 nm. This range depends to upon the scattering properties

of the particles. For example, the lower limit stated is for particles composed of materials with a high refractive index, such as gold and silver. For particles such as polystyrene and silica, which scatter light much weaker, the lower limits are about 40 nm and 80 nm, respectively [22]. For polydispersed samples, large counting statistics shall be used to reduce uncertainties in the size distribution.

#### 6.5.11 Relevant standards

ISO 19430, *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)* [23]

#### 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 and 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  $\mu\text{l}$  to 50  $\mu\text{l}$ ) can be transferred onto a flat support, for instance a glass disk or silicon substrate, and allowed to dry. For analysis of non-conductive samples, it can be necessary to coat them through metal sputtering to bypass charging effects that hinders the imaging process. However, utilizing lower accelerating voltages often allow imaging without the need for metal coatings. For TEM, 2  $\mu\text{l}$  to 10  $\mu\text{l}$  of dispersion can be transferred onto a TEM grid, and then covered with a carbon membrane. In the case of aqueous dispersions, hydrophilization of substrates, prior to deposition, can be a considerable advantage since it prevents artefactual agglomeration upon drying (e.g. drop casting). This is easily achieved using a glow-discharge (gas plasma) apparatus which is able to fix electric charges on the supports. Wet oxygen plasma has been used to both clean and oxidize silicon surface used for deposition. Electrostatic deposition onto charged substrates is commonly used to avoid drying artefacts. Besides using a negatively charged native oxide, the substrate can be modified chemically to produce an electrostatic charge that is opposite to the analyte nano-objects. Poly-l-lysine and amino-silanes have been widely used for this purpose (when the analyte is negatively charged).

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) and relevant standards listed in 6.3.11 and 6.3.13.

#### 6.5.13 Field flow fractionation

FFF is a group of related separation techniques where separation of dissolved, suspended and dispersed sample constituents in the size range of 1 nm to approximately 50  $\mu\text{m}$  is achieved within a thin, ribbon-like channel without a stationary phase. FFF offers the capacity to fractionate diverse populations of NOAAs with minimal perturbation of the sample. FFF is a modular technique to which multiple detectors can be arranged in tandem. In this manner, particle size, concentration, molar mass and composition can be determined for eluting bands following separation based on one or more fields applied perpendicular to the direction of flow. The thickness of the channel is less than 1 mm (typically 350  $\mu\text{m}$ ) to maintain laminar flow between the lower plate, referred to as the accumulation wall, and upper plate, referred to as the depletion wall. Depending on the applied force field, FFF can be divided into different sub techniques. Commercially available instruments that are used for the analysis of

NOAAs include asymmetrical-flow FFF, centrifugal FFF and electrical FFF (used in conjunction with asymmetrical-flow FFF).

For asymmetrical-flow FFF, the separation mechanism or mode depends on the particle size. For particles smaller than about 500 nm, normal mode separation dominates, and smaller particles elute before larger particles. From approximately 500 nm to 10 µm, steric mode separation results in particles eluting in reverse size order. Above approximately 10 µm, hyperlayer mode dominates, also resulting in reverse size elution. Typically, for NOAAs FFF works with particles in the normal mode range. It is not generally possible to perform a fractionation in which particle size falls into both the normal and steric/hyperlayer range without resulting complications of mixed modes of separation.

FFF, as used for nano-object characterization, is an integrated measurement system combining upstream separation with downstream multi-detector analysis. Advantages of FFF include relatively small sample size requirements, the ability to match the mobile phase to the sample, the lack of a solid phase (compare to size exclusion chromatography), the capacity to separate polydisperse samples for high resolution size analysis or for off-line analysis by many techniques, and the wide range of online detectors available.

The most common detectors relevant to the analysis of NOAAs include DLS, MALS and UV-Vis absorbance. In an ideal case, the determination of particle diameter would be based on retention time and applying the FFF theory. However, as the FFF separation is often affected by interactions between particles and the membrane, which is located on top of the accumulation wall, a direct measurement of size is preferable to retention-based size measurement, though sizing methods have limitations in terms of the detectable range of size and concentration. FFF, when coupled with DLS and MALS, can also provide some shape information, for example measuring rod aspect ratio.

With regards to online concentration measurements, UV-Vis absorbance, refractive index detector and ICP-MS are the most commonly used in FFF systems. These methods are generally sensitive to the mass of analyte present. As ICP-MS is a destructive method, it is used as the final detector in tandem analysis. ICP-MS based methods have very low detection limits (approximately down to the ng/l regime depending on the instrument and element) and are element specific for metal-containing nano-objects. In contrast to ICP-MS methods, UV-Vis detection limits depend on the absorptivity and scattering properties of the materials, and it is not element specific. UV-Vis works best for optically active materials that exhibit a characteristic absorption band or where only a single absorbing species is present. Linearity of absorption should be confirmed for the analyte over the relevant concentration range. In contrast to online analysis, off-line analysis procedures (sizing and concentration evaluation after fractions are collected following separation) make it possible to use additional detection methods such as electron microscopy and atomic force microscopy. Even though the results of the microscopic analysis are dependent on sample preparation methods, the visualized information can be of significant benefit for the characterization of NOAAs.

Finally, molar mass can be obtained for polymeric nano-objects using a differential refractometer by measuring the increment change in the refractive index with respect to change in concentration and combined with MALS results using well-established relationships.

### 6.5.14 Relevant standard

ISO/TS 21362, *Nanotechnologies — Analysis of nano-objects using asymmetrical-flow and centrifugal field-flow fractionation*

### 6.5.15 Single particle ICP-MS

sp-ICP-MS can simultaneously provide information on size, size distribution, particle number concentration, and ionic content for the analysis of highly dilute nanoparticle suspensions. Single particle ICP-MS relies on the principle that one NP is detected at a time. Measurements are acquired using short (microsecond to millisecond), consecutive, measurement periods. Each nanoparticle is atomized and ionized in the plasma, producing a spatially concentrated packet of ions measured as a transient signal spike superimposed on the steady-state signal produced by any dissolved analyte. The intensity of the transient signal from a single particle, after subtraction of the dissolved signal intensity,

is proportional to the number of atoms in the particle which can be converted to element mass and thus diameter to the third power, assuming a spherical particle shape. Particle density and shape shall be known. The number of pulses counted is proportional to the nanoparticle number concentration. The intensity of the continuum signal provides a measure of the dissolved analyte. Automated counting tools have been developed to increase time efficiency and accuracy.

Detection limits depend on the elemental composition, the particle density, the dissolved analyte content, and the sensitivity of the commercial instrument being used. For chemically homogenous NPs composed of a monoisotopic element (i.e. Au) and containing low mass concentration of ions, size detection limits of 10 nm can be obtained. The upper size range for low density, metal oxide particles can reach 2 000 nm. Number concentrations in the range of  $10^3$  per ml to  $10^5$  per ml can be measured. Ionic concentrations at part per trillion levels in the diluted sample are measurable.

#### 6.5.16 Relevant standard

ISO/TS 19590, *Nanotechnologies — Size distribution and concentration of inorganic nanoparticles in aqueous media via single particle inductively coupled plasma mass spectrometry*

### 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 specific to the method	Method	Size range	Resolution	Limitations	References
Size and shape of NOAA	2D-projected size and shape of NOAA. Number-weighted geometric size and shape distributions.	SEM	5 nm to 1 mm	5 nm	Needs sample preparation onto a substrate. Slow, individual particle measurement.	
3D topographic map of the surface	Contact force to give 3D size and shape	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.	[24]

#### 6.6.2 Scanning electron microscopy

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 can 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) can 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 is 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 can 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

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 (e.g. 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. Hence, AFM can provide useful information on 3D shape information for example on nanorods and two-dimensional materials for which thickness and lateral size can be measured.

#### 6.6.4 Relevant standards

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

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

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

ASTM E2859-11, *Standard Guide for Size Measurement of Nanoparticles Using Atomic Force Microscopy*<sup>[25]</sup>

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

### 7.1 General

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. Such characterization will sometimes be of individual nano-objects and sometimes of an ensemble of nano-objects or a whole system, for example nano-objects along with a substrate. 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 (e.g. by the EGA method). The techniques presented in [Clause 7](#) 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 consider the possibility of their complex structure. Such structures (e.g. core-shell structure or complex surface molecules) require characterization methods which provide detailed information about chemically active entities. Additionally, the development of nanocomposites 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 [Clause 7](#) 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 dispersions. 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 nano-objects. Otherwise many nano-objects tend to form large agglomerates and the primary particles does not disperse in water. In addition, nano-objects can interact with the liquid phase components, partially or totally yielding degradation or transformation products that can 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 subclauses. As the object size becomes smaller, surfaces make up an increasingly large fraction of the analysis “volume”. Sample preparation and careful handling are essential to minimize contamination and ensure correct analysis. The lateral and depth resolutions given in [Table 6](#) are typically of current commercial instrumentation.

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

Overarching measurand	Measurand specific to the method	Method	Lateral resolution of the method	Depth resolution of the method	Limitations	References
Chemical identification	Kinetic energies of the electrons (eV)	AES	10 nm	2 nm to 20 nm	Samples analysed under high vacuum; care needed for non-conducting samples. Sensitivity (0,3 at. %). Matrix effects in quantitative AES of multicomponent samples to be considered.	[26],[27],[28],[29]
Composition, chemical bonding, surface properties	Changes in energy distribution of an electron beam transmitted through a thin specimen (eV)	EELS with TEM	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.	[29],[30],[31]
Elemental, isotopic, or molecular composition of the surface	Unified atomic mass units (u)	SIMS	200 nm	≈1 nm (inorganic), ≈10 nm (organic)	Quantification challenging. Samples analysed under vacuum.	[29],[32],[33]
Chemical, elemental analysis	Fluorescence spectrum (intensity versus wavelength in $\text{cm}^{-1}$ )	XRF	1 nm to 100 $\mu\text{m}$	5 $\mu\text{m}$ to 20 $\mu\text{m}$	Normal quantitative limit: 10 ppm to 20 ppm (parts per million). With synchrotron radiation source, absolute detection limits: 100 ppb (parts per billion).	[34],[35],[36]
Crystalline size, crystallographic phase, lattice parameters, structure	Angles and intensities of diffracted X-ray beams (intensity, degree)	XRD	50 $\mu\text{m}$	5 $\mu\text{m}$ to 20 $\mu\text{m}$	Is more accurate for measuring large crystalline structures rather than small ones.	[37]
Surface composition, chemistry of coating, surface functionalisation	Kinetic energies of the electrons (eV)	XPS	>10 $\mu\text{m}$	>1 nm	Samples normally analysed under vacuum. Sensitivity (0,1 at. %).	[26],[28],[29]
Composition	Interaction between electron beam and sample produces photons	EDX	0,5 $\mu\text{m}$	0,3 $\mu\text{m}$ to 5 $\mu\text{m}$	For EDX using SEM the specimens shall be conductive, well-polished. The composition is relative.	[29],[30]
Coating thickness	Scattering of noble gas ions	LEIS	0,01 mm to 0,5 mm	1 nm to 10 nm	Species adsorbed on nano-objects should be removed before analysis.	[29]

### 7.2.2 Auger electron spectroscopy

AES provides information about the chemical identity of materials and works in ultra-high vacuum. This technique uses the Auger effect, a non-radiative decay of an electron impact created core hole leading to energetic Auger electrons emitted from an excited atom and analysed by an electron spectrometer. In Auger spectroscopy the charging effects in non-conducting samples are the most common limitation, although with care analysis of non-conducting nano-objects placed on a conductive substrate and using an electron flood gun is possible. It delivers semi-quantitative elemental and chemical state information. Surface sensitivity in AES arises from the fact that emitted electrons usually have energies ranging from 50 eV to 3 keV. Detection limits of approximately 0,1 atomic percent (at. %) to 1 atomic percent (at. %), depending on the element analysed, are reached. The method can be used to analyse ensembles and individual nano particles and for an acquisition of element maps.

### 7.2.3 Relevant standards

ISO/TR 14187, *Surface chemical analysis — Characterization of nanostructured materials*

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

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

ISO 16531, *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 18116, *Surface chemical analysis — Guidelines for preparation and mounting of specimens for analysis*

ISO 18117, *Surface chemical analysis — Handling of specimens prior to analysis*

ISO 18118, *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 20579-4, *Surface chemical analysis — Guidelines to sample handling, preparation and mounting — Part 4: Reporting information related to the history, preparation, handling and mounting of nano-objects prior to surface analysis*

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

### 7.2.4 Electron energy loss spectroscopy

In EELS, a material is exposed to a beam of electrons with a known, narrow range of kinetic energies, where some of the electrons 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 EDX but with detectability 10 times higher than EDX 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 can measure atomic composition, chemical bonding, valence, and conduction band electronic properties. It gives better discrimination between elements than EDX. The samples for EELS investigation in the TEM required careful preparation and are thin slices of a material that can be provided by FIB or ultramicrotomer.

### 7.2.5 Relevant standard

ISO/TR 14187, *Surface chemical analysis — Characterization of nanostructured materials*

### 7.2.6 Secondary ion mass spectroscopy

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. The lateral resolution of this method is typically 200 nm, so ensembles of nano-objects analysed, some configurations allow 50 nm to 100 nm resolution dependant on the material. It is a highly sensitive method for investigating the surface chemistry (top 1 nm) of samples, which in this case would be ensembles of nano-objects.

### 7.2.7 Relevant standards

ISO/TR 14187, *Surface chemical analysis — Characterization of nanostructured materials*

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

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

ISO 20579-4, *Surface chemical analysis — Guidelines to sample handling, preparation and mounting — Part 4: Reporting information related to the history, preparation, handling and mounting of nano-objects prior to surface analysis*

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

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

### 7.2.8 X-ray fluorescence spectroscopy

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 1970s 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, 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<sup>[30],[31],[32]</sup>.

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 total external reflection for X-rays resulting in reflection of almost 100 % of the excitation beam photons. The advantage of this method 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 can 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 nanoparticles.

### 7.2.9 Relevant standards

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

ISO/TS 18507, *Surface chemical analysis — Use of total reflection X-ray fluorescence spectroscopy in biological and environmental analysis*

### 7.2.10 X-ray diffraction

XRD is a method used for determining the atomic and molecular structure of a crystal, in which the 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 focused 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 is 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 and composition.

### 7.2.11 Relevant standard

ISO/TR 14187, *Surface chemical analysis — Characterization of nanostructured materials*

### 7.2.12 X-ray photoelectron spectroscopy

In XPS, a sample is irradiated with X-rays that penetrate the sample. When the X-ray photons excite a core-level photo electron, it is emitted with a kinetic energy dependent on the incident X-ray and the binding energy of the atomic orbital from which it originated. In an XPS, photo electrons are released, detected and counted as a function of their kinetic energy. Kinetic energy and intensity of photo electrons are analysed to identify and determine the surface concentrations of the elements present and the chemical state or bonding situation of the emitter atom. XPS detects elements from lithium to uranium. XPS can detect elements with a surface concentration of approximately 0,1 at. %. The sensitivity depends on the respective photo-ionization cross-section of an element. Both conducting and insulating materials can be tested. For non-conductors, either neutralizer devices as electron flood guns or Argon ion guns, or both, are used to stabilize the surface charge in a controlled manner.

The X-ray beams in some commercial imaging systems can be as small as 10 µm. Chemical mapping with ≈10 µm lateral resolution is possible. However, the lateral resolution is too low to address an individual nanoparticle, therefore ensembles of nanoparticles have to be measured. The X-ray beams also penetrate deep into the surface; however, the escape depth of the photo electrons is of the order of less than 10 nm and therefore information is obtained from within this information depth. XPS can be used to measure the chemistry and also the thickness of coatings surrounding nano-objects, for example, the shell of core-shell nanoparticles and surface chemical functionalisation.

Careful sample preparation is essential to ensure good quality of data (see ISO 20579-4). XPS operates in ultra-high vacuum and can be used with heating and cooling stages.

NOTE In future, XPS analysis of nano-objects can be undertaken using near ambient pressure XPS or liquid jet technologies where the nano-objects are dispersed in the liquid. These new techniques are under-development<sup>[38]</sup>.

### 7.2.13 Relevant standards

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

ISO/TR 14187, *Surface chemical analysis — Characterization of nanostructured materials*

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

ISO 16531, *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 18116, *Surface chemical analysis — Guidelines for preparation and mounting of specimens for analysis*

ISO 18117, *Surface chemical analysis — Handling of specimens prior to analysis*

ISO 20579-4, *Surface chemical analysis — Guidelines to sample handling, preparation and mounting — Part 4: Reporting information related to the history, preparation, handling and mounting of nano-objects prior to surface analysis*

### 7.2.14 Energy dispersive X-ray spectroscopy

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 (such as nitrogen, carbon) can be difficult to be detected and analysed by EDX because of overlap between the characteristic X-ray peaks. The spatial resolution for EDX in combination with SEM is typically for bulk samples in the range of one micrometre. At lower excitation energies (below 10 keV) or when the nano-objects are prepared on electron-transparent films, the resolution can be reduced well below 100 nm<sup>[39]</sup>. When EDX is applied with a TEM, the resolution is below 1 nm and high-resolution EDX elemental distributions (maps) can be carried out on composite nano-objects such as core-shell nanoparticles.

### 7.2.15 Low energy ion scattering

In LEIS the sample is bombarded with noble gas (He, Ne, Ar) ions of a few keV, some are backscattered by the surface atoms. Noble gas ions are scattered from the sample and collected at a fixed scattering angle resulting in an energy spectrum of the scattered ions. The energy loss in the scattering process contains information on the mass of the atom that the helium ion is scattered from and the depth at which the scattering event occurred. The area under a peak directly relates to the number of atoms of a certain species present in the analysed surface.

LEIS analysis is performed in ultra-high vacuum. It can be used to measure the shell thickness of core-shell nanoparticles with reasonable agreement with XPS<sup>[40]</sup>.

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

### 7.3.1 Measurands

The measurands described in [7.3](#) can be used to test the chemical properties of the entire sample which contains nano-objects or for some techniques a larger analysis volume and depth than just the surface region. 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 specific to the method	Method	Lateral resolution of the method	Depth resolution of the method	Limitations	References
Structure, composition of rough surfaces	Chemical vibrations are measured in wave number ( $\text{cm}^{-1}$ ).	DRIFT	$>15 \mu\text{m}$	$0,1 \mu\text{m}$ to $2,5 \mu\text{m}$ depending on the wavelength of light, angle of incidence, refractive index of the sample	Mostly can be performed on dry powders. Sensitive to $\text{CO}_2$ and $\text{H}_2\text{O}$ .	[41],[42]
Structure, composition	Intensity over a narrow range of wavelengths at a time. Chemical vibrations are measured in wave number difference ( $\text{cm}^{-1}$ ).	FTIR	$>15 \mu\text{m}$	$0,1 \mu\text{m}$ to $2,5 \mu\text{m}$	Mostly can be performed on dry powders. Sensitive to $\text{CO}_2$ and $\text{H}_2\text{O}$ Molecule shall be active in the infrared region. Sensitivity and detection limits: 2 %; with special techniques: 0,01 %.	[42],[43]
Composition, identification of released gases from the sample	Current ion (A-s) Wavenumber ( $\text{cm}^{-1}$ ), Quantitative loss of sample mass (mg)	Thermal analysis (e.g. TGA) with EGA like FTIR or QMS	N/A	N/A	Typically: QMS 2-150 amu; FTIR $400 \text{ cm}^{-1}$ to $5\,500 \text{ cm}^{-1}$ ; T = room temperature – $1\,500 \text{ }^\circ\text{C}$ 0,1 ppm – 50 %	[44],[45]
Concentration, composition	Absorption spectrum plotting absorbance versus wavelength (nm)	UV-Vis	N/A	N/A	Corrections for scattering can be required. Solid samples require reflectance accessory.	[29]
Structure, composition	Shift of frequency of the inelastic scattering of light in wave number difference ( $\text{cm}^{-1}$ )	Raman spectroscopy	$0,5 \text{ nm}$ to $10 \text{ nm}$	$0,5 \text{ nm}$	Cannot be used for metals or alloys. Fluorescence of impurities or sample can hide the Raman spectrum. Sample heating by intense laser radiation can damage the sample.	[46]
Elemental composition and mass per particle	Elemental mass per particle; particle number concentration; dissolved (ionic) element mass fraction	sp-ICP-MS (see also 6.5.15)	N/A	N/A	Requires proper dilution (not directly applicable to high number concentration); see <a href="#">Table 4</a> .	[47],[48],[49]
Elemental composition and mass (ICP-MS, ICP-OES, ICP-AES); isotopic composition (ICP-MS)	Total elemental mass concentration (sum of particulate and ionic species)	ICP-MS, ICP-OES, ICP-AES	N/A	N/A	Requires acidic decomposition and complete solubilization of sample.	[50]

In this table, the depth resolution primarily refers to the depth of analysis into a sample that the technique detects from.

### 7.3.2 Fourier transform infrared spectroscopy

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 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  $0,01 \text{ cm}^{-1}$ . This eliminates the need for external calibrations. The DRIFT method is an infrared spectroscopy technique used on powder samples (with high surface area). 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 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 suggests that it should be less than  $5 \mu\text{m}$  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 approximately 5 % to 10 % by weight using potassium bromide.

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.

### 7.3.3 Relevant standards

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

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

### 7.3.4 Thermal analysis with evolved gas analyser plus FTIR or QMS

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. 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 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 mg to 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. TGA with EGA typically gives qualitative information on the composition, but quantification is challenging, whether by FTIR or QMS.

### 7.3.5 Relevant standards

ISO/TS 11308, *Nanotechnologies — Characterization of carbon nanotube samples using thermogravimetric analysis*

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

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

### 7.3.6 Ultraviolet-visible spectroscopy

UV-Vis spectroscopy 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 SPR studies and provides information on sizes and the quantification of amount of material. The absorption strongly depends on the particle size, dielectric medium and chemical surroundings. The resolution of a UV-Vis spectrophotometer is normally 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 monochromator. 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 <sup>[45]</sup>.

### 7.3.7 Relevant standards

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

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

### 7.3.8 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, and is complimentary to IR spectroscopy. Raman can differentiate between isotopes. In certain circumstances, it can give size information; see [6.4.11](#).

### 7.3.9 Inductively coupled plasma techniques

In 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 ICP-MS or ICP-OES also known as a ICP-AES. The intensity of each peak at a given mass to charge ratio (ICP-MS) or wavelength (ICP-OES/AES) is compared to reference elements of known mass concentration in order to calculate the concentration of each element. This enables chemical and concentration information to be obtained.

For sp-ICP-MS, see also [6.5.15](#), the measurement time for a particular elemental mass to charge ratio is split into small enough time windows such that single particles are detected with the intensity of the signal proportional to the number of atoms each particle contains. This provides chemical information along with a measure of the elemental mass of each particle and in combination with the measured number concentration, yields the particle mass concentration.

### 7.3.10 Relevant standards

ISO 11885, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*

ISO/TS 13278, *Nanotechnologies — Determination of elemental impurities in samples of carbon nanotubes using inductively coupled plasma mass spectrometry*

ISO 17294-1, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 1: General guidelines*

ISO 17294-2, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 2: Determination of selected elements including uranium isotopes*

### 7.3.11 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 General

[Clause 8](#) covers measurands associated with mass and density. The main measurands are:

- nano-object mass and mass distribution;
- nano-object density and density distribution;
- 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 subclauses.

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

Overarching measurand	Measurand specific to the method	Method	Range	Resolution	Limitations	References
Mass distribution	Mass to charge (m/z) distribution	Aerosol particle mass analyser	0,001 fg $\approx$ 100 fg; 10 nm to 10 $\mu$ m	Mass fraction of 10 % of centre mass of distribution	Relies on charged particles	<a href="#">[51]</a>
	Time of flight mass to charge (m/z) distribution	TOF particle mass analyser	1 m/z to 1 200 m/z	m/ $\Delta$ m up to 4 000 for 0,05 $\mu$ gm <sup>-3</sup>		<a href="#">[52]</a>

#### 8.2.2 Relevant standards

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

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

ISO 10808, *Nanotechnologies — Characterization of nanoparticles in inhalation exposure chambers for inhalation toxicity testing*

ISO/TS 12025, *Nanomaterials — Quantification of nano-object release from powders by generation of aerosols*

ISO 12154, *Determination of density by volumetric displacement — Skeleton density by gas pycnometry*

### 8.2.3 Aerosol particle mass analyser

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 depends 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 specific to the method	Method	Range	Resolution	Limitations	References
Density	Gas displacement volume	Pycnometry	0,1 g/cm <sup>3</sup> to 10 g/cm <sup>3</sup>	±0,01 %	Volume and mass measured separately and divided to give density.	[53],[54], ISO 12154

### 8.3.2 Pycnometry

Pycnometry measures the bulk or skeletal 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, *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 are described in more detail along with the methods in the subsequent subclauses.

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

Overarching measurand	Measurand specific to the method	Method	Range	Resolution	Limitations	References
Density distribution	Optical transmission as a function of position settling rate	Centrifugal liquid sedimentation (iso-pycnic and multi-velocity methods)	0,1 g cm <sup>-3</sup> to 10 g cm <sup>-3</sup>	Mass fraction of ±4 %	Still in development stage	[14],[29]
Mass distribution	Optical transmission as a function of position settling rate	Centrifugal liquid sedimentation (isopycnic method)	10 <sup>-18</sup> g to 10 <sup>-11</sup> g (1 ag to 10 pg)	Mass fraction of ±4 %	Still in development stage	[14],[29]
	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	Mass fraction of 5 %	The sample dispersion should be transparent and not absorb light of the wavelength used. Typically, a large sample volume (1 ml) is required.	[55]
Mass distribution Density distribution	Individual particle mass	Resonant mass measurement	350 ag 50 µm to 5 µm	Mass fraction of ±3 % 0,002 g cm <sup>-3</sup>		[56]

### 8.4.2 Relevant standards

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

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

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

ISO 16014-5, *Plastics — Determination of average molecular weight and molecular weight distribution of polymers using size-exclusion chromatography — Part 5: Light-scattering method*

ISO 18747-1, *Determination of particle density by sedimentation methods — Part 1: Isopycnic interpolation approach*

ISO 18747-2, *Determination of particle density by sedimentation methods — Part 2: Multi-velocity approach*

### 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

In SLS, 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 nanoparticle size for

of radii above 1 % to 2 % the incident wavelength. Depending on the orientation of the detector angles relative to the direction of incident light, LALS, RALS, MALS are the various implementations of SLS.

#### 8.4.5 Resonant mass measurement

The 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 the same density as the solute are not detected. The density value is required for size or volume evaluation. Hence, the minimum size of a particle detected depends on the minimum detectable mass.

### 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. Zeta potential is not an intrinsic nano-object property, as it depends on both the particles and the medium in which they are dispersed. The measurands are given in [Table 11](#) and described in more detail along with the methods in the subsequent subclauses.

**Table 11 — Measurands related to charge**

Overarching measurand	Measurand specific to the method	Method	Range	Resolution	Limitations	References
Charge, zeta potential	Electrophoretic mobility (particle velocity/applied field strength)	Electrophoretic light scattering	-500 mV to 500 mV	0,1 mV	Some materials subject to degradation in applied electric field. Concentrations should be appropriate for light scattering detection.	[57],[58]
Charge, zeta potential	Dynamic electrophoretic mobility	Electroacoustic measurements	-500 mV to 500 mV	0,1 mV	Requires calibration. Response is particle mass dependent for larger particles (>300 nm).	[59]

#### 9.2 Relevant standards

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

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

ISO 13099-3, *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 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 anemometry. 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 zeta potential by considering the dispersant viscosity and dielectric permittivity and applying the appropriate theory.

#### 9.4 Electroacoustic phenomena measurements

There are two electroacoustic effects used for determining zeta potential: CVC and ESA. These instruments measure the dynamic electrophoretic mobility, which depends on zeta potential.

CVC arises when ultrasonic waves propagate through a fluid containing charged nanoparticles. 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.

ESA 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 of 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 required to correct for size-dependent damping of the electroacoustic motion.

### 10 Measurands related to crystallinity

#### 10.1 Measurands

The main measurands related to crystallinity are:

- 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](#). In this table, 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 specific to the method	Method	Range	Resolution (at best point in range)	Limitations	References
Lattice system Lattice constant	X-ray scattering angle and intensity	SAXS	1 nm to 150 nm	0,5 nm	Qualitative	[60],[61]
Lattice system Lattice constant	X-ray scattering angle and intensity	USAXS	1 nm to 2,5 µm	0,1 nm	Qualitative; not ideal for two component or amorphous systems	[62]
Lattice system Lattice constant	X-ray scattering angle and intensity	WAXS	<1 nm	<0,1 nm	Qualitative	[62]
Lattice system Lattice constant Crystallinity Crystalline index	X-ray scattering angle and intensity	X-ray diffraction	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.	[63]
Lattice system Crystallinity Crystalline index	Electron scattering angle, amplitude and phase	TEM	50 µm to 0,5 nm	0,05 nm	Resolution scales inversely with scan area (magnification). UHV techniques. Electron beam induced damage.	[64]
Lattice system Crystallinity Crystalline index	Electron scattering angle, amplitude and phase	EBSD, RHEED, LEED	1 nm to 1 000 µm	EBSD 0,5 nm RHEED 0,5 nm LEED <0,0 1 nm	Normally requires an electrically conductive sample or conductive coating sample in vacuum.	[65],[66]
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 <sup>3</sup>	[67]
Crystallinity Melting point Glass transition temperature Crystalline index	Heat flow	DSC	-180 °C to 1750 °C	0,02 °C		[68],[69]
Crystallinity Crystalline index	Resonance frequency as a function of magnetic field	NMR crystallography	Up to 100 kDa	< 0,1 nm	Slow, expensive can require isotope labelling	[70],[71]
Crystallinity Chirality (of carbon nanotubes)	Raman scattering frequency shift	Raman crystallography				[72]

## 10.2 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 1 nm and 150 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

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 High-resolution transmission electron microscopy

HRTEM 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 Å. 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.

#### 10.5 Electron backscattered 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. 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. 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 3D crystals required for XRD. Unlike XRD, crystallographic structure factor phase information can be experimentally determined in electron diffraction. Experimentally EBSD is conducted using an SEM equipped with an EBSD detector.

#### 10.6 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<sup>3</sup>) 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 is 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.

#### 10.7 Reflection high-energy electron diffraction and low-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. 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.

#### 10.8 Differential scanning calorimetry

DSC is a technique of thermal analysis in which the difference in the amount of heat flow required to change 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  $-180\text{ }^{\circ}\text{C}$  to  $700\text{ }^{\circ}\text{C}$  or from room temperature to  $1\ 600\text{ }^{\circ}\text{C}$  is possible.

This method provides information about phase transition, glass transition temperature, fusion of nano-objects and crystallization.

### 10.9 Relevant standards

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

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

### 10.10 Solid state nuclear magnetic resonance 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.

### 10.11 Raman crystallography

Raman spectroscopy (see also [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.

### 10.12 Relevant standards

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

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

ISO 13067, *Microbeam analysis — Electron backscatter diffraction — Measurement of average grain size*

ISO 24173, *Microbeam analysis — Guidelines for orientation measurement using electron backscatter diffraction*

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

## 11 Optical properties measurands

### 11.1 General

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

Optical properties of nano-objects, nanomaterials and nanostructures originate from the fundamental interaction of light with the material. The measurands are summarized in [Table 13](#).

**Table 13 — Measurands for optical properties**

Overarching measurand	Measurand specific to the method	Method	Range	Resolution	References
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	[73]
Optical absorption	Wavelength absorbed	Absorption spectroscopy	175 nm to 3 330 nm	0,05 nm (UV) to 0,2 nm (IR)	[74]
Optical emission	Wavelength emitted	Photoluminescence spectroscopy	400 nm to 2 700 nm	0,05 nm (UV) to 0,2 nm (IR)	[75]
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)	[73]
Fluorescence	Intensity	Spectrofluorometer	200 nm to 850 nm in wavelength	50 femtomolar fluorescein	[75]

## 11.3 Spectroscopy techniques

A number of standardized optical spectroscopies can 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 components 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 can 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. 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).

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 photoexcitation can occur. The photoexcitation causes the material to jump to a higher energy electronic state and then releases energy (photons) as it relaxes and returns back to a lower energy level. The emission of light, or luminescence through this process is PL.

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 10868, *Nanotechnologies — Characterization of single-wall carbon nanotubes using ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopy*

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

## 12 Electrical and electronic measurands

### 12.1 Measurands

The important measurands associated with electrical and electronic measurements of nano-objects are:

- 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.
- In plane sheet resistance: used especially for 2D nanomaterials, such as graphene. It is defined as resistance of a square area of the material.
- Bandgap: the energy gap between the valence and the conduction band of a semiconductor nano-object. Band gap of metallic nano-objects is defined as zero. Bandgap 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 change 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 specific to the method	Method	Range	Resolution	Limitation	References
Specific conductance/resistance (conductivity/resistivity)	Conductance/resistance (together with particle dimensions)	2-probe or 4-probe electrical measurement	Resistivity $0 \Omega \cdot m$ to $10^{16} \Omega \cdot m$	$0,1 \mu\Omega \cdot m$		[76],[77]
In plane sheet resistance	Resistance (together with thickness)	4-point probe, e.g. Van der Pauw method	Zero (superconductor) to infinity (insulator)	$0,1 \mu\Omega$		[76],[77]
Band gap	Photoemission intensity as a function of angle	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	[74]
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	[75]

Table 14 (continued)

Overarching measurand	Measurand specific to the method	Method	Range	Resolution	Limitation	References
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.	[78]
Nanoscale conductivity	Current	Conducting atomic force microscopy	10 $\mu\text{m}$ $\times$ 10 $\mu\text{m}$ scan field; currents of a few pA up to 500 nA	0,1 nm to approximately 10 nm	Limited to conducting samples. Also limited by the range of the scanner.	[79]
Piezoelectric coefficient	Surface charge and displacement	Piezoforce microscopy	10 $\mu\text{m}$ $\times$ 10 $\mu\text{m}$ scan field; currents of a few pA up to 500 nA	0,1 nm to approximately 10 nm	Limited by scan range of the scanner	[80]

## 12.2 Techniques

### 12.2.1 2- or 4-point conductance measurements

The conductance measurement can 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 bandgap of a nanomaterial 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

The band gap can also be measured using photoemission spectroscopy techniques such as 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

The band gap can also be measured using STS, which is an extension of 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 the 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 can 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 AFM (see 6.6.3) that records local electrical conductivity as well as a topographic image of the sample. To achieve nanoscale conductivity measurements, a conducting probe tip is required, for example, a silicon or silicon nitride 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  $10^{-12}$  A to  $10^{-6}$  A 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 to V curves can be measured in a spectroscopic mode.

### 12.2.5 Piezoforce microscopy

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 PFM. It can 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 General

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, such as probe microscopy 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 magnetization, 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 specific to the method	Method	Range	Resolution	Limitation	References
Saturation Magnetization	Inductive impedance	RLC circuit measurement of an inductive circuit component. VSM and AGFM can be used for this measurement.	1,2 $MA/m < H_{max} < 4 MA/m$ $m_{max}: 1 Am^2$	$H: 0,1 kA/m$ $M: 10^{-9} Am^2$	Volume of the sample needs to be known.	[81],[82], [83]
Curie temperature	Change of magnetic susceptibility or magnetization or emitted energy	MOKE with a temperature control VSM with a temperature control DSC	$2,2 K < T < 500 K$	From $\pm 0,1 K$ to $\pm 1 K$ based on stability of temperature control.	Magnetometry measurements require slow temperature change. DSC is limited by a very small change in heat	[81],[82], [83],[84]
Curie temperature	Hyperfine field	Mössbauer spectroscopy	$2,2 K < T < 500 K$	From $\pm 0,1 K$ to $\pm 1 K$ based on stability of temperature control.	Can only be used for very specific isotopes. It can also be used to determine Néel temperature (temperature above which an antiferromagnetic material becomes paramagnetic).	[85],[86]
Magnetic susceptibility	Slope of the magnetism versus magnetic field strength (M-H)	RLC measurement of an inductive circuit component. VSM and AGFM can 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.	[81],[82], [83]
Surface magnetization	Force Kerr rotation and ellipticity Hall effect emf related directly to stray magnetic field	MFM MOKE Scanning Hall effect magnetometer	Typically, low magnetic field strengths ( $H$ ). $H$ up to $0,3 T$ .	Limited by the tip. Limited by the optical resolution. $\pm 3\%$ to $5\%$ .	The tip field can alter the sample and only gives information on stray fields. Only probes sample depth comparable to laser (light) skin depth. Gives information of stray fields.	[79],[80], [83],[87]
Coercive field	Inductive signal, Kerr rotation (for MOKE)	Inductive magnetometry or optical magnetometry that allow full saturation of the material	1,2 $MA/m < H_{max} < 4 MA/m$ $m_{max}: 1 Am^2$	$H: 0,1 kA/m$ $M: 10^{-9} Am^2$		[79],[80]
Magnetic phase composition	Isomer shift	Mössbauer spectroscopy	0 % to 100 % (relative)	$\approx 1\%$	Limited to very specific isotopes of specific elements, e.g. iron	[85],[86]

### 13.3 Techniques

#### 13.3.1 Superconducting quantum interference device

A SQUID is a very sensitive magnetometer used to measure extremely small magnetic fields, based on Josephson junctions. There are two main types of SQUID: DC and 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  $5 \times 10^{-18} T$ .

### 13.3.2 Vibrating sample magnetometer

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 Mössbauer spectroscopy: an isomer shift, also known as a chemical shift; a quadrupole splitting; and a 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. Only specific isotopes of certain elements are suitable for Mössbauer spectroscopy these include  $^{57}\text{Fe}$ ,  $^{129}\text{I}$ ,  $^{119}\text{Sn}$  and  $^{121}\text{Sb}$ .

### 13.3.4 Electron paramagnetic resonance spectroscopy

EPR or 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

The 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 smaller than  $0,005^\circ$ .

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 a scanning capability can increase that resolution. A typical scanning range of  $10\ \mu\text{m} \times 10\ \mu\text{m}$  is often used. Spatial resolution of approximately 50 nm is achievable.

### 13.3.6 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 can be converted into the surface magnetization using a number of micromagnetic assumptions. The range of scanning is approximately  $10\ \mu\text{m} \times 10\ \mu\text{m}$  with special resolution of approximately 10 nm. Limitations are linked to the tip to sample interaction where the sample magnetization may be altered by the presence of the tip. Measurements are often performed in air and at 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

### 13.3.8 Spin-polarized scanning tunnelling microscopy

SP-STM is a variation of STM (see 12.2.3) where the STM tip has a net magnetic polarization at the atomically sharp apex. This results in a spin-polarized tunnelling current flowing between tip and the sample. If the sample magnetization is in the same orientation the tunnelling probability is higher than if it is antiparallel. In addition to topography the localized magnetic polarization (or in fact the spin-polarized tunnelling probability) is mapped with STM special resolution. For most systems the SP-STM is operated under ultrahigh vacuum [lower than  $10^{-5}$  Pa ( $10^{-7}$  mbar)] and under low temperature (below 66 K).

### 13.3.9 Relevant standards

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

ASTM A342/A342M-14, *Standard Test Methods for Permeability of Weakly Magnetic Materials* [88]

## 14 Thermal measurands

### 14.1 Measurands

Materials containing nano-objects and their agglomerates and aggregates can 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 can be enhanced by the addition of carbon nanotubes or thermal capacity can be enhanced through the 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 specific to the method	Method	Range	Resolution	Limitations	References
Heat capacity	Specific heat capacity [J/(K kg)]	Calorimetry and DSC	From room temperature to 1 500 °C	>1 µm depending on heating rate	Large scale samples needed	
Spatially resolved thermal conductivity	Thermal conductivity [W/(m K)]	SThM	Scanning range: 100 µm × 100 µm	50 nm to 100 nm for lateral resolution, probe T resolution <0,1 °C	Tip-sample contact (heating) volume difficult to determine	[89]

NOTE 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 [85].

### 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 of bulk material such as calorimetry and DSC (see 7.3.2).

#### 14.2.2 Scanning thermal microscopy

Scanning thermal probe microscopy offers the combination of spatial resolution, imaging and localized measurement of temperature and thermal conductivity. The SThM uses the methodology of the scanning probe microscopy to achieve high special resolution down to single particle 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.

### 14.3 Relevant standard

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

## 15 Other performance related measurands

### 15.1 General

Other performance related measurands for characterizing nano-objects in different forms have been detailed in [Clause 15](#). This covers dustiness, solubility and dispersibility and mechanical properties.

### 15.2 Powders — Dustiness

#### 15.2.1 Measurands

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”<sup>[86]</sup>. 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 specific to the method	Method	Range	Resolution	Limitations	References
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 nanometres to ≈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 instruments.	Biologically relevant mass methods are standardized based on EN 15051-1, EN 15051-2 and EN 15051-3. Nongravimetric methods, standardization under development.	EN 481, EN 15051-1, EN 15051-2, EN 15051-3

#### 15.2.2 Relevant standards

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

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

EN 15051-2:2016, *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*

## 15.3 Liquid dispersions

### 15.3.1 Measurands

This class of materials is also known as a suspension of solid nano-objects in liquids. The presence of nano-objects can change mechanical, thermal, electrical or optical properties of this liquid. In 15.3, the state and stability of the dispersion is important and is the temporal nature of the dispersion. The measurands are summarised in Table 18.

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

Overarching measurand	Measurand specific to the method	Method	Range	Resolution	Limitations	References
Viscosity	Viscosity (Pa s)	Viscometer	0,1 Pa s < $\eta$ < 10 000 Pa s	Accuracy $\pm 1$ % of full range	Rotating disk viscometer requires large sample sizes	ISO 3219-1, ISO 3219-2
Viscosity	Viscosity (Pa s) Viscoelastic behaviour: storage modulus and loss modulus (Pa)	Rheometer	0,01 Pa s < $\eta$ < 10 000 Pa s	Accuracy $\pm 1$ % of the current measured value		ISO 3219-1, ISO 3219-2
Dispersibility	Transmitted and reflected intensity	SMLS	10 nm to 1 000 $\mu$ m in size. A volume fraction of 0,01 % to a volume fraction of 95 % in concentration.	5 % of mean particle size	Requires some independent calibration and yields only mean particle size or particle concentration.	ISO/TS 21357 <sup>a</sup>

<sup>a</sup> Under preparation. Stage at the time of publication: ISO/PRF TS 21357:2021.

### 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 example, if a fine powder of magnetic material (such as Fe or Fe<sub>2</sub>O<sub>3</sub>) 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, gravimetric capillary principle, rolling ball method and rheometer. 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). ISO 3219-1 and ISO 3219-2 can be applied to suspensions containing NOAA even though they are written for use for all 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 miniaturizable to nano-litre sample sizes. With tubes as small as 30  $\mu\text{m}$  to 300  $\mu\text{m}$  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 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  $^{\circ}\text{C}$  and 100  $^{\circ}\text{C}$  and can be applied to samples from 5 mPa s up to 10 000 mPa s with volumes of the order of 100  $\mu\text{l}$ . 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 (e.g. complex suspensions, slurry). The liquids with viscosity values from 1 mPa s to 100 Pa s may be studied. Some rheometers use microfluidic technology requiring sample volumes as low as 100  $\mu\text{l}$  with an accuracy of  $\pm 2\%$  and repeatability of  $\pm 0,5\%$  of the current measured value. Temperature range for such measurements is approximately  $-20\text{ }^{\circ}\text{C}$  to  $65\text{ }^{\circ}\text{C}$ . Larger temperature ranges up to  $500\text{ }^{\circ}\text{C}$  under conditions of either high force (or pressure) or high shear rate, or both, are commercially available.

### 15.3.2.6 Relevant standards

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

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

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

ISO 3219-1, *Rheology — Part 1: Vocabulary and symbols for rotational and oscillatory rheometry*

ISO 3219-2, *Rheology — Part 2: General principles of rotational and oscillatory rheometry*

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

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

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

ISO 12058-1, *Plastics — Determination of viscosity using a falling-ball viscometer — Part 1: Inclined-tube method*

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

ISO 16790, *Plastics — Determination of drawing characteristics of thermoplastics in the molten state*

ISO/TS 21357, *Nanotechnologies — Evaluation of the mean size of nano-objects in liquid dispersions by static multiple light scattering (SMLS)*

### 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 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 (a volume fraction of 0,01 % to a volume fraction of 95 %). 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 standard

ISO/TR 13097, *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. In the former, particles lose their particulate character and change form to become smaller molecules and ions. Dispersibility involves the distribution of the particles into a liquid to form a suspension. This difference is important to stress as the distinction can be difficult to determine in the case of nano-objects.

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. However, 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 biopersistence 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<sup>3</sup>], 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 can 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. Dissolution of metal and metal oxide nanoparticles is often measured by ICP-MS or ICP-OES.

### 15.3.6 Relevant standards

ISO 7579, *Dyestuffs — Determination of solubility in organic solvents — Gravimetric and photometric methods*

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

## 15.4 Mechanical properties

### 15.4.1 General

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 nanoscale. 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. A summary of the measurands is given in [Table 19](#).

NOTE A good compendium of test methods is given in Reference [\[90\]](#).