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Nanotechnologies — Considerations for the measurement of nano-objects and their aggregates and agglomerates (NOAA) in environmental matrices

Nanotechnologies — Considérations pour la mesure des nano-objets, et leurs agrégats et agglomérats (NOAA) dans les matrices environnementales

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Foreword

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This document was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

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

Introduction

There is an interest in determining the concentration of nano-objects and their aggregates and agglomerates (NOAA) in environmental matrices. Manufactured nanomaterials (NM) enter the environment via release from the manufacturing process and its waste streams, as well as via the use of commercial products and their recycle and disposal streams. Such measurement efforts require an understanding of the occurrence of natural materials that can interfere with the analysis or skew the results, knowledge of how the environment can interact with NM, and insights that require unique collection and analytical techniques specific to the composition of the particle. This document provides a review of published studies that report levels of NOAA in the environment and aspects of collection and sample preparation. The reader is also directed to the Further Reading section of this document for information regarding ISO guidance on sampling of air, water, and sediment, as well as a matrix of measurement techniques.

Not all manufactured NM are discussed here because there might not yet be published studies that examined them in the environment. On the other hand, collection methods and pre-analytical procedures might be similar for some or all NOAA in a given environmental matrix. Furthermore, NOAA isolated from the environment can be characterized using the same instruments and analytical techniques used for pristine NOAA. Thus, the lack of published studies does not preclude the ability to collect a specific NM from any environmental matrix and measure the NOAA present.

Although it is recognized that biota (i.e. living organisms) also can interact with NM by sequestering and/or transforming them, analysis of biota is intentionally excluded so that the scope of this Document does not become too broad. However, the impact of biota should not be overlooked. Such considerations could be part of a subsequent Technical Report.

Furthermore, when NM are used for environmental remediation, and there is interest in measuring residual levels of remediating NM after the environmental medium has been processed. It is anticipated that the considerations described here would be applicable to those investigations.

The audience for this document is expected to be scientists from the regulatory, academic, or industrial communities who wish to answer the question of how much manufactured NM is present in a specific environmental medium. The results could be used for environmental stewardship, for risk assessment, or to calibrate modelled exposure estimates, although these applications are not discussed here.

NOTE The term NM refers to the identity of the nanomaterial, whereas NOAA is a more inclusive term encompassing NM and aggregates that are the focus of the analyses described here.

Nanotechnologies — Considerations for the measurement of nano-objects and their aggregates and agglomerates (NOAA) in environmental matrices

1 Scope

This document provides some considerations for the collection of environmental samples to be analysed for manufactured NOAA, considerations to distinguish manufactured NOAA from background levels of naturally occurring nanoscale particles of the same composition, and preparation procedures to aid in the quantification of manufactured NM in environmental matrices.

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

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

3 Terms and definitions

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

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

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

3.1
environmental matrices
ambient air, surface water, sediment, soil, estuarine and marine waters and sediments

3.2
ambient air
outdoor air to which people, plants, animals or material may be exposed

Note 1 to entry: Workplace is excluded.

[SOURCE: ISO 4225:1994, 3.6]

3.3
surface water
water in overland flow and storage, such as rivers and lakes, excluding seawater

[SOURCE: ISO 14046:2014, 3.1.3]

3.4
sediment
bottom sediment
naturally-occurring solid material deposited by settling from suspension onto the bottom of bodies of water, both moving and static

[SOURCE: ISO 6107-2:2006, 13]

3.5
soil
upper layer of the Earth's crust composed of mineral particles, organic matter, water, air and living organisms

[SOURCE: ISO 18589-1:2005, 3.2.1]

3.6
estuarine water
water in the lower reaches of a river that is freely connected with the sea, subject to the influence of the tides and receiving an influx of salt water and fresh water supplies from upland drainage area

[SOURCE: ISO 772:2011, 1.20]

3.7
seawater
marine water
water in a sea or an ocean

[SOURCE: ISO 14046:2014, 3.1.4]

3.8
pore water
water occupying space between sediment particles in freshwater (including soil), brackish and marine environments

[SOURCE: ISO 11348-1:2007, D.2.4]

3.9
coastal lagoon
shallow body of water, such as a pond or lake, close to the sea and usually with a shallow, restricted inlet from the sea

[SOURCE: ISO 6107-8:1993, 29]

3.10
nano-object
discrete piece of material with one, two or three external dimensions in the nanoscale

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]

3.11
nanomaterial
NM
material with any external dimension in the nanoscale [as defined in 2.1 of ISO/TS 80004-1] or having internal structure or surface structure in the nanoscale

Note 1 to entry: This generic term is inclusive of *nano-object* [as defined in 2.5 of ISO/TS 80004-1] and *nanostructured material* [as defined in 2.7 of ISO/TS 80004-1].

Note 2 to entry: See also definitions 2.8 to 2.10 of ISO/TS 80004-1.

[SOURCE: ISO/TS 80004-1:2015, 2.4]

3.12
euphotic zone
upper layer of a body of water where light penetration is sufficient to support effective photosynthesis

[SOURCE: ISO 6107-3:1993, 29]

4 Symbols and abbreviated terms

AAS	atomic absorption spectroscopy
CNT	carbon nanotube
ICP-MS	inductively coupled plasma mass spectroscopy
HDC	hydrodynamic chromatography
HPLC	high-performance liquid chromatography
HRMS	high-resolution mass spectrometry
NOAA	nano-objects, their aggregates, and agglomerates
NOM	natural organic matter
PM2.5	particulate matter with a diameter of 2,5 μm and smaller
SWCNT	single-walled carbon nanotube
TEM	transmission electron microscopy
TEM-EDX	transmission electron miscroscopy equipped with energy dispersive X-ray detector
UHPLC	ultra-high performance liquid chromatography
UV-vis	ultraviolet-visible spectrometry

5 General considerations

5.1 General

As the use of NM becomes more widespread, questions about what concentrations exist in the environment from their use are likely to be raised. Nowack et al.[1], Mueller and Nowack[2], Liu and Cohen[3], and Keller et al.[4] have suggested potential pathways into the environment from manufacturing waste streams, end-of-use waste streams (e.g. NM in sunscreens that enter the waste stream), and release from products. In order to determine the concentrations of NM present in the environment, several issues/questions need to be addressed:

- What are the background levels of naturally occurring materials of the same or similar composition?
- How do concentrations of naturally occurring materials change over time/geography?
- Can the manufactured NOAA be distinguished from naturally occurring nano-objects?
- What are the instruments that have been used to quantify and characterize NOAA in the environment?
- What are the proper sample preparation methods? Do they vary with the NM of interest, or do they vary with the medium?

These questions are considered in the following document.

5.2 Considerations for determining background levels of NM

Many NM of the same chemical composition as manufactured NM can already occur naturally in the environment, for example substances such as TiO_2, SiO_2, and fullerenes, just to name a few. For manufactured NM, processes such as top-down manufacturing reduces the size of a large particle to a smaller one, while bottom-up manufacturing creates larger particles from smaller ones. Naturally-occurring NOAA can also be produced by top-down processes like erosion of mineral particles via wind or via weathering (e.g. UV irradiation and rain). Metals (e.g. gold and silver), oxides of iron, silicon, aluminium, and manganese, and sulphides (e.g. iron sulphide) occur via a bottom-up process from dissolved metal ions. The bottom-up processes may be abiotic or bio-assisted. In addition, NOAA can be produced from combustion of biological matter or from chemical precipitation. (Figure 1). Nanoscale particles can also be part of cosmic dust or be produced from volcanic activity[5].

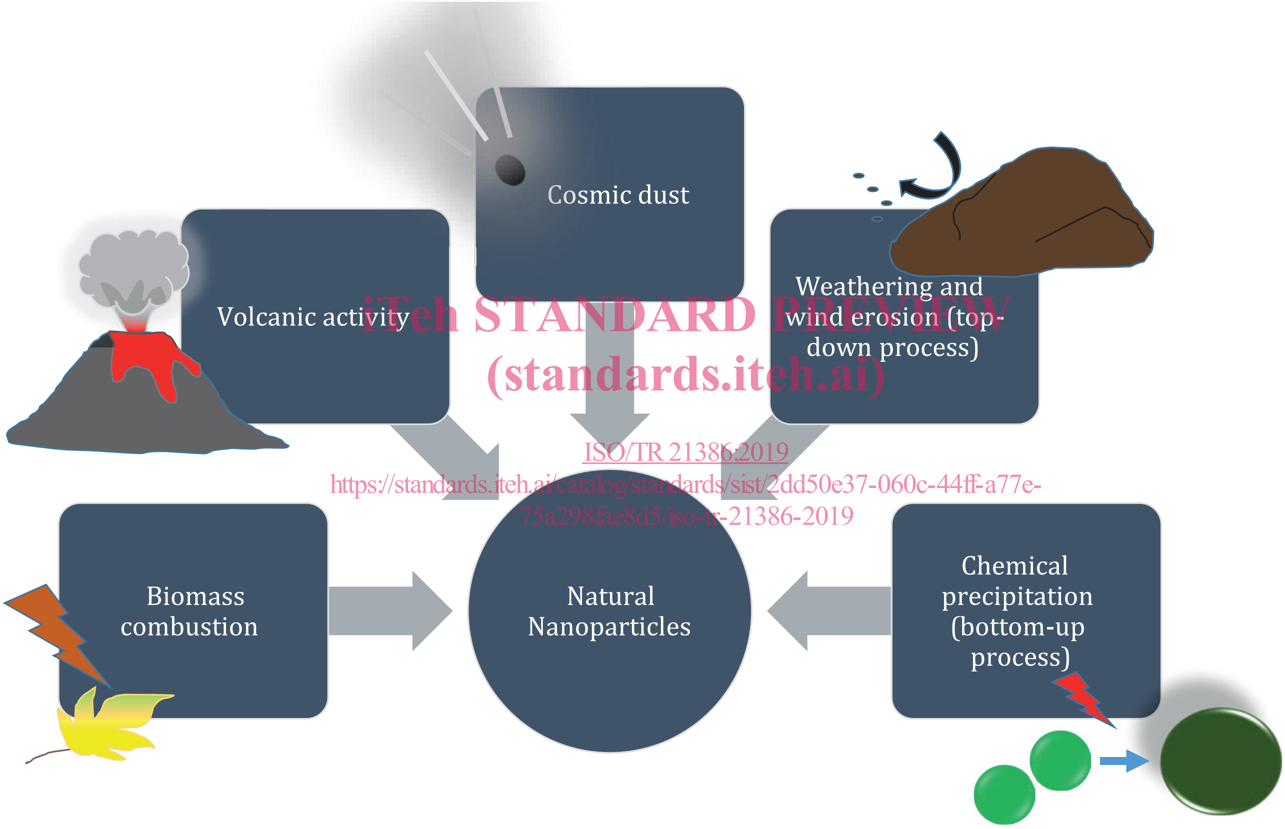

Figure 1 — Processes that create nano-objects in the environment. Adapted from Sharma et al.[5]

Therefore, some manufactured NM can be indistinguishable from naturally occurring nano-objects, making it impossible to assess the environmental exposure to these manufactured NM.

5.3 Distribution of NM in the environment

Where, in the environment, naturally occurring nano-objects or manufactured NM exist can depend on several factors, such as proximity to road surfaces, climate extremes, salinity of water, and the presence of objects onto which particles can adsorb. Liu and Cohen[3] predicted concentrations of various metal oxides in the environment based on global manufacturing, releases from production, and releases from disposal. Using the "MendNano" modelling program developed by Liu and Cohen (http://nanoinfo.org/mendnano), the concentrations of Ag, Al_2O_3, CeO_2, carbon nanotubes (CNTs), Cu-based NM (metal and metal oxides), Fe-based NM (metal and metal oxides), nanoclays, SiO_2, TiO_2, and ZnO were predicted for air, water, soil, and sediment in the Los Angeles (LA) region (USA) for a period of one year. The concentrations for any one matrix ranged more than 3 to fourfold, with TiO_2 at the highest concentration and silver or copper (as oxide) at the lowest concentration, depending on the matrix. Concentrations in air were predicted to be between 10^{-3} and 1 ng/m^3 for all substances, with the concentration of TiO2 predicted to be the highest (~1 ng/m^3) and copper oxide the lowest (~10^{-3} ng/m^3). The order of substances from highest concentration to lowest was $TiO_2 > SiO_2 >$ Fe oxide = ZnO = $Al_2O_3 >$ nanoclay = $CeO_2 >$ CNT > Ag > Cu oxide. For water, concentrations ranged from 10^{-2} to 10^2 ng/L, with TiO_2 predicted at the highest concentration and ZnO at the lowest (Ag was predicted as 0 because it is insoluble in water). The ranking of substance by concentration in water was roughly the same as that in air, with $TiO_2 > Al_2O_3 > SiO_2 =$ Fe oxide > nanoclay > $CeO_2 >$ CNT > Cu oxide > ZnO > Ag. For soil, concentrations ranged from 10^{-3} to 1 µg/kg soil with the same relative ranking as that for air. Concentrations in sediment were several-fold greater than those for soil, ranging from 10^{-1} to 10^4 µg/kg sediment (Cu oxide was predicted to have undetectable concentrations in sediment). The ranking of substances by concentration was similar to that for water, with $TiO_2 >$ Fe oxide > $Al_2O_3 = SiO_2 >$ nanoclay > $CeO_2 >$ CNT > Cu oxide > ZnO > Ag. Although these initial predictions represent the mass concentration of manufactured NM, it is not known if relative levels of naturally-occurring nano-objects might distribute in the same amounts or size distributions.

Furthermore, the levels of NOAA vary with time, season, and weather conditions. Liu and Cohen[3] predicted the daily and monthly variation in TiO_2 levels in various environmental media in LA County in California. The levels in air and water fluctuated by a factor of 10 over the course of the month and even during the course of a day in response to weather conditions. Concentrations in sediment and soil were predicted to be stable over a one-year time period. Daher et al.[6] showed that measured total particulate concentration in LA County varied depending on the season and location of sampling. In some locations, the total particulate in air was double that in winter compared to the concentration in the spring (16,1 ± 2,8 µg/m^3 [mean and standard error] in winter versus 7,9 ± 0,8 µg/m^3 in spring for Long Beach). These variations suggest that samples should be collected over extended weather conditions in order to eliminate seasonal fluctuations as a confounder in interpreting data.

5.4 Interaction with materials in environmental matrices

NOAA can be chemically transformed or adsorbed onto naturally occurring materials in the environment. The degree to which these phenomena happen and the extent of their impact differ based on the chemical properties of the NM and the matrix. A report from Denmark by Hartmann et al.[7] summarized the potential transformation processes in the four major environmental compartments and the relevance of such transformations for modelling. They describe how photochemical degradation, oxidation, reduction, dissolution, precipitation, speciation/complexation, sedimentation, adsorption, and biotransformation can impact or modify several different NM (metal oxides, metals, and carbon-based NOAA) in the environment[7]. The extent to which the concentration or sequestration of NOAA occurs in a matrix is dependent on the physical/chemical nature of the NM and the chemical nature of the environmental matrix. This report focuses on the impact of these processes on modelling of life cycle and fate, but they are also applicable to measurement of NOAA and, perhaps more importantly, to the metric used to describe concentration.

According to the report by Hartmann et al.[7], photochemically induced reactions (i.e. oxidation, reduction, or transformation) occur to the greatest extent in air, to a lesser extent in water, and not at all in soil or sediment (Table 1). NM with a particular molecular composition might be more subject to modification than others; thus, metals (e.g. silver and iron) or metal oxides (e.g. TiO_2 and perhaps CeO_2) that have bound to organic matter can be modified by oxidation. In addition, carbon-based NOAA (e.g. CNTs and carbon black) can be oxidized in air. The results of these changes can alter the surface properties (if not the chemical identity, such as for silver and iron), thereby leading to changes in adsorption or agglomeration. Hartmann and coworkers assessed the impact of photochemical reaction in air on modelling as “high” for these NM (metals such as silver and iron, metal oxides such as TiO_2 and to some extent CeO_2, and carbon-based NOAA), but non-existent for other NM that are not prone to such photo-induced reactions.

Several physical phenomena with NM can occur in the environment, including dissolution, aggregation, agglomeration, sedimentation, and adsorption. Dissolution occurs primarily in water and sediment, and to some extent soil depending on the presence of pore water. The impact of dissolution on the concentration of the NOAA can vary from low to high depending on the NM; thus, dissolution is a key transformation process of ZnO, Ag, and CuO and plays a significant role in their binding to natural organic matter (NOM) or larger particles. Therefore, for these metals and metal oxides dissolution in the presence of water could have a high impact on modelling and measurement. Of course, the ionic strength, pH, and presence of other materials also play roles in the extent of dissolution. Aggregation and agglomeration also occur primarily in water, but have an impact on NM in air, soil, and sediment as well. Thus, aggregation and agglomeration in water tends to have a high impact on the ability to quantify NM, and a medium impact in air, soil and sediment. Surface charges can change in water with ionic strength and pH playing a role. The nature of the NM, whether metal, metal oxide, or carbon-based NM, seems to have little impact on the importance of this physical process, given all types of NM are subject to the phenomenon. Sedimentation, according to Hartmann et al.[7], occurs primarily in water and to some extent in air. The end result of sedimentation can be to transfer NM from one matrix to another, such as from air or water to sediment or soil. Thus, the impact on quantitation is high for NMs in water, and medium for NMs in air. As with aggregation and agglomeration, the nature of the NM has little impact on the extent of sedimentation, which is most influenced by particle or agglomerate size. Adsorption onto other particles or NOM, like agglomeration, is dependent on surface properties, which in turn can be influenced by the ionic character of the matrix (pH, etc.). Adsorption not only impacts the concentration of NM in soil and sediment, but also in water. The nature of the NM seems to have little impact on the adsorption, as is the case for agglomeration.

Biodegradation of so-called organic compounds, which are based on carbon chemistry, frequently plays a role when substances enter the environment and often leads to lowering of the concentration of the substance, whereas metals and metal oxides do not biodegrade. Hartmann et al.[7] reported that biodegradation is not likely to have a great impact on NM, with the exception of carbon-based NM, such as CNTs. However, biomodification of the surface of NM can occur, which can lead to dissolution, complexation, or agglomeration. Similar processes are described by Sharma et al.[5] for naturally occurring nano-objects. As a result, transformations of the manufactured NM should be considered and the final concentrations of NM should be adjusted to reflect masking by transformed particles.

Table 1 — Predicted environmental transformation processes. Adapted from Hartmann et al.[7]

Process		**Impact on particle concentration or likelihood of occurrence**	**Matrix**			
			Air	**Water**	**Sediment**	**Soil**
Reaction	Photochemical oxidation, etc.	H	sMe, sMeO	sMe, sMeO		
		M				
		L				

Impact: H = high, M = medium, L = Low

s = some of the NM in this class

Me = metal such as silver or iron

MeO = metal oxide such as ZnO, TiO_2, or CeO_2

All = generally applies to all NM.

NOTE A ‘high’ impact is critical to accurately determine or model the fate and behaviour, and thus the concentration, of the NM. A ‘low’ significance is considered to have a low impact on the fate modelling or measurement of that specific NM and omitting the process will therefore not result in a large error.