Working with nano particles

Working with nano particles

At this moment there exists no legislation for nano materials (yet). General obligations laid down in the Working Conditions Act and the Working Conditions Hazardous Substances Decree are however applicable. This guideline provides the starting points that need to be met in working with nano particles within the UT.

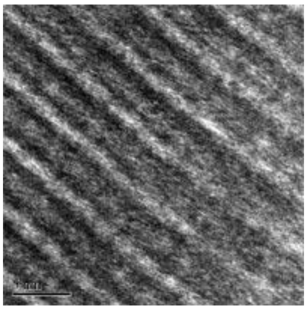
1. Classification nano particles

1.1 Classification into classes

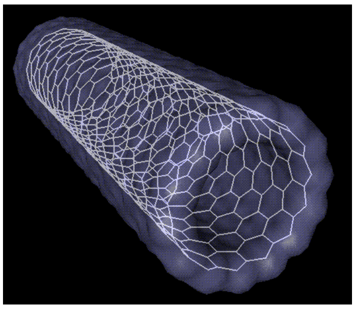
Whilst there may not exist an international definition for nano particles, the generally accepted description is: particles which in one or more dimensions are smaller than or equal to 100 nm. Also, nano particles generally have a strong tendency to agglomerate mutually, and therefore separate nano particles are rare. A further classification into nano particles is arbitrary, but classifications commonly used are based on their spatial appearance and their chemical properties (NEN 2008).

1.2 Spatial classification

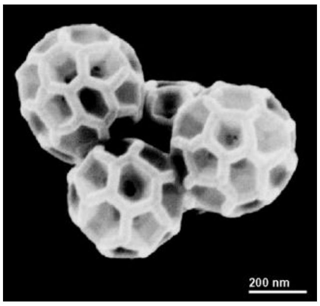
The spatial manifestation indicates the dimension in which the particle shows its nano size: in 1, 2 and 3 dimensions.



1 dimension (coating, film, multi-layer)



2 dimensions (carbon tubes)



3 dimensions (bucky balls).

1.3 Chemical classification

Chemically, nano particles are to be classified into the following categories: carbon structures, metal oxides, metals, quantum dots, organic polymers, and biological nano particles. Annexe 1 contains a detailed overview of these categories including applications.

1.4 Other terms

Term	Explanation
Ultrafine particles	This term is sometimes used for substances on a nano scale that occur for example in welding smoke and with diesel exhaust.
Nano aerosols	Nano particles contained in a gas. The particles can occur as nano particles but also as aggregates or agglomerates of nano particles. If in the latter two forms the size is more than 100 nm but the physical properties sufficiently correspond with those of nano particles, they are still referred to as nano aerosols.
Nano-structured material	These refer to aggregates of nano particles.

2. Risks

2.1 Health effects

Micro particles and nano particles have always occurred in nature, but over the centuries their concentration in the air has increased strongly as a result of the combustion of fossil fuels. Small dust particles can penetrate deeply into the lungs and if they cannot solve or disintegrate, they can accumulate in the body and inflict damage (Kalusa 2010). Due to their penetrating nature, nano particles can even reach the brain via the mucous membrane of the nose. Because of their very small size, nano particles can even penetrate cells and influence cellular processes. Because of their special shape and high level of reactivity, the effect of nano particles on the metabolism of humans and animals cannot be predicted easily.
Within the body, nano particles can stimulate the formation of hazardous substances such as reactive oxygen compounds. In addition, they can stimulate inflammatory reactions that may lead to dangerous concentrations of reactive substances in the blood, originating from the immune system. Little is known about the power of nano particles to penetrate into the skin or the digestive tract. Until more research is conducted in this area, caution is called for. Nevertheless TiO_2 nano particles, for example, are widely used in sun creams.

Research into the hazardous effects of nano particles focuses in particular on three effects: oxidative stress, inflammatory effects, and genotoxicity (Aitken 2009).
Inflammatory effects are in particular seen in fibrous nano particles such as carbon nano tubes, and are expected to have asbestos-like health effects; the inflammatory effect is however strongly dependent on the build of the nano tube (multiple-sided; open or closed ends). Specific information is however still lacking. Oxidative stress is an effect of nano particles often seen, but – as with inflammatory effects – varies strongly per type and the effect is to be judged on a case by case basis. Little is known about the genotoxic effects of nano particles.

2.2 Safety effects

Safety effects of nano materials other than toxic effects are mainly limited to combustibility and explosiveness. Due to their high surface/weight ratio, nano materials can show a considerably higher reactivity with oxygen than the conventional manifestation of the same material. It is therefore important to examine the pyrophoric properties of the nano material to be used in advance and to be cautious in particular when using larger amounts.
In addition to combustibility and explosion, the power of nano materials to easily penetrate equipment can constitute a risk if conductive nano materials are involved. It is a known fact that nano carbon can cause a short circuit in print circuits.

3. Limiting values

Under the Working Conditions Act, the employer is held to assess the industrial risk of its staff via an RI&E. By taking measures the risk subsequently is to be kept as low as possible and at an acceptable level. The government provides limiting values for a number of dangerous substances. For substances for which no official limiting values are given, the employer itself must establish the values within the range of which the staff member is sufficiently protected.

For nano materials, however, there is still too little scientific knowledge at hand to establish substantiated limiting values. In expectation of the formulation of limiting values in the area of health and safety, the advice is to work with **'temporary nano reference values'** (see Table 3.1).
However, it remains necessary to always keep the concentration as low as possible and to pursue the "As Low As Reasonably Achievable" principle (ALARA).

Table 3.1: Temporary limiting values, as advised to the minister in the RIVM report (RIVM 2010)

Category	Description category	Proposal benchmark exposure limits (BELs)*
1	Ultra fine liquid particles (fats, hydrocarbons, siloxans)	Current limiting values from a health and safety perspective of the non-nano form
2A	Metals, metal oxides and other bio-persistent granular nanomaterials with density > 6000 kg/m^3 and a particle size in the range of 1 to 100 nm e.g: Ag, Fe, Au, Pb, La, TiO_2, CeO_2, ZnO, SiO_2, Al_2O_3, Fe_xO_y, SnO_2, CoO and nanoclay.	20.000 particles/cm^3**
2B	Bio-persistent granular nanomaterials with density < 6000 kg/m^3 and a particle size in the range of 1 to 100 nm e.g.:C60, carbon black, TiN, Sb_2O_5, polymers, polystyrene, dendrimers and carbon nanotubes for which asbestos like health effects have been excluded.	40.000 particles/cm^3**
3	Carbon nanotubes for which asbestos like health effects have not been excluded.	0.01 fibres/cm^3 (10.000 fibres/m^3) *** based on asbestos exposure risk ratio.

* The proposed benchmark exposure limits are issued in order to minimize workplace exposure according to present knowledge and are not based on toxicological data. Health risks of workers exposed to these levels cannot be excluded. These benchmark limits may not be confused in any case with health based exposure limits on the workplace.

** 8 hours time weighed average increase with regards to background level.

*** measured with a phase contrast microscope (PCM) or 20.000 fibres/m^3 when measured with a transmission electron microscope (TEM).

4. RI&E Nano UT

In working with nano particles in the workplace, the UT employs the precaution principle. In working with nano particles, the risks relating to which are still largely unknown, the precaution principle implies that an effort is made to prevent exposure and – in cases in which exposure is unavoidable – to keep the period and extent of the exposure as limited as possible. For this an RI&E is to be performed; Annexe 2 contains a format for this. The different steps in this are explained in more detail in this chapter.

4.1 Information nano material

Collect as much information available as possible about the toxic properties of the material used (both of the starting material and of the material in nano form in so far as information is available).

a. Avoid the use of nano materials which (or the starting material of these) are known to have highly toxic properties;
b. If little information is known or can be retrieved about the toxic properties of a substance, treat the nano material as a highly toxic substance. As the lack of knowledge increases and consequently also the uncertainty about the risks, a greater safety margin is to be built in and more measures need to be taken to avoid exposure.

4.2 Health hazard nano material

As starting point for the risk assessment a classification into three groups is made. The higher on the list, the more measures need to be taken to prevent exposure:

1= (Water) soluble nano particles. These are nano particles with a solubility > 100 mg/l
Examples: particles of lipids, sucrose, soloxanes ranging from 1-100 nm.

2= Synthetic, persistent nano materials (non fibrous)
Examples: metals (e.g. Ag, Au, Pb, La), metal oxides (e.g. TiO_2, ZnO, CeO_2, CoO), carbon black, fullerenes, nanoclay, polymers, dendrimers ranging from 1-100nm.

3= fibrous, insoluble nano materials regarding which asbestos-like effects cannot be excluded.
Example: SWCNT (=one-sided carbon nano tubes) and MWCNT (=multi-sided carbon nano tubes).

4.3 Inventory of activities

Identify and rate all the tasks and activities which involve potential exposure and classify these on the basis of the level of possible exposure (based on duration, frequency and numbers of staff members exposed).

a. Collect as much information as possible about the steps of the process that may lead to exposure.
b. Also identify all tasks and activities that can cause exposure to nano particles outside of the normal processes (draw up exposure scenarios).
c. Evaluate the risks identified and take measures, if necessary.

Based on the risk of exposure and the danger category a control class is determined (see the decision matrix in Annexe 2) for any measures that may need to be taken.

Examples of activities with nano materials that may cause exposure:

- preparatory activities such as weighing, solving, mixing, pouring, spilling, atomizing;
- manipulating such as preparing coatings, applying coating, examining coatings for specific properties;
- synthetising nano material in a non-closed system;
- maintenance of equipment whereby nano material may be released.

4.4 Measures: plan of action

The nature of the measures to reduce exposure for nano particles are generally comparable to measures to be taken for other toxic substances. In fact, the package of measures for nano particles should be stricter than for larger particles, in view of the uncertainties about the toxic effects of nano particles. The basis to prevent exposure to nano particles is the classic order:

1. avoiding the use of hazardous nano particles;
2. replacing nano material by particles creating less hazard;
3. encasing nano materials when processing in a space;
4. technical and organisational control measures;
5. personal protective measures.

ad 1. **Avoiding**
Avoid the use of dangerous substances or processes that create or involve exposure. For example, activities involving the formation of aerosol (such as spraying) are to be avoided. This is of course difficult if nano material has already been selected for its specific properties. Naturally, it is to be taken into account whether the superior properties of the nano material outweigh the larger risks that are involved in its use.

ad 2. **Replacing**
Replace the nano material or process by material or a process involving less risk. If this is not possible, try to reduce the exposure by, where possible, using nano particles in a matrix (dispersions, pastes, encapsulated in pallet form) instead of as a powder or in the gas phase.

ad 3. **Encasing**
Work as much as possible in a closed space and in closed systems (closed fume cupboard, glove box). This applies in particular to nano materials such as powder or in the gas phase. Ensure there is directed extraction if activities using the material are required. Frequently clean workplaces where nano materials are used; preferably use wet cleaning.

ad 4. **Technical and organisational measures**
If a closed system is not feasible, use local/directed ventilation to capture the exposure at the source:

a. A properly designed ventilation system will capture nano particles effectively (ventilation systems must meet the same quality criteria as other toxic substances);
b. Nano particles will largely behave like gas and can therefore easily escape from leaks;
c. Ventilation systems must be properly kept and regularly checked for effectiveness (see also § 4.5);
d. Avoid recirculation of air.

Organisational measures can be taken in addition to the technical control measures:

a. Limit the number of exposed staff members. Limit (for example) the access to spaces with potential exposure;
b. Limit the duration of the exposure;
c. Limit the access to spaces with potential exposure.

ad 5. **Personal measures**

If the exposure cannot be avoided adequately, by way of a last resource use personal protection gear for a limited number of tasks or activities:

a. Limit the time that your wear the personal protection gear;
b. As regards respiratory protection the information now available indicates that the existing filter media can effectively capture the nano particles. The minimum protection to be used is a P3-filter. The largest risk comes from leakage resulting from respiratory protection that does not fit properly (because nano particles will behave like a gas).
c. For skin protection the information available so far indicates that woven cotton clothing offers less adequate protection than airtight clothing (e.g. Tyvek/Tychem) .
d. Use disposable gloves (nitrile, latex, neoprene).

4.5 Measurements

The effectiveness of measures can be determined by measuring the exposure to nano particles. A suitable instrument for this is the Philips nano tracer. The Philips nano tracer measures between 10 and 300 nm and in addition to the concentration, also indicates the size of the particles. Measuring equipment is not standard equipment at the UT but must be hired.

4.6 Information and training

Provide staff with information and give them training. Give all staff involved instructions about the properties of the nano particles and the necessity of special measures and give staff adequate training.

4.7 Health monitoring

Currently there is no specific, measureable health effect for exposure to nano particles, which suggests that medical surveillance cannot be performed at the moment. From a viewpoint of due care, also because of the uncertainties about the effects, at any rate the available information about the materials used and the duration of exposure is to be collected in case any later health effects are found. An exposure register can be maintained on the basis of the information collected in step 3 of the RI&E Nano (see § 4.3). This register can then be used as soon as a relevant health aspect is known.

4.8 Transport and removal of nano materials

Sealed containers must be used for the transport of nano materials within laboratories.
Amounts of nano materials (powders, colloids) above the milligram range are to be treated as chemical waste when the solubility in water is very low (e.g. inorganic materials such as metals, oxides, etc.). If the solubility is higher, the rules according to the toxicity class of the macroscopic material can be used.
Contaminated materials that cannot be cleaned must be disposed of as chemical waste.
Contaminated materials and surfaces can be cleaned by wiping materials and surfaces with a wet cloth (water or solvent) and disposing of these as chemical waste.

5. Literature

- Aitken, R. e. a. (2009) EMERGNANO: A review of completed and near completed environment, health and safety research on nano materials and nano technology. **Volume**, 198 DOI:
- Kalusa, S. e. a. (2010). workplace exposure to nanoparticles. Bilbao, OSHA EU**:** 89.
- NEN (2008). nanotechnologies **-** Health and safety practices in occupational settings relevant to nanotechnolies. NPR-ISO/TR 12885. NEN. Delft, NEN**:** 79.
- RIVM (2010), Tijdelijke nano-referentiewaarden, Report 601044001/2010, S. Dekkers **|** C. de Heer

Annexe I: Classification nano particles and applications

Classifications	Applications
Carbon structures	
• Carbon fullerenes (diameter 4-36 nm) are spherical cage structures of carbon atoms.	Many applications, including in batteries, fuel cells, plastic additives and medicines.
• Carbon black (80-500 nm) is amorphous carbon powder on a nano scale.	In particular used as pigment and in the tyre industry.
• Carbon nano fibres (diameter: 2-100 nm; length micro metres-millimetres) are built from bent, overlapping graphite layers. The nano fibres can be massive or concave.	Polymer additives and catalysts.
• Carbon nano tubes (diameter 0,4-100 nm; length up to several centimetres) are concave carbon nano fibres the graphite layers of which are parallel to the axis of the tube. Carbon nano tubes can be concave, or covered by half a fullerene at the ends. Carbon nano tubes can be one-sided or multiple sided.	e.g. polymer additives, electronics, batteries, composite structures
• Carbon nano sheet: (1 nm thickness) is a 1-layer network of carbon atoms.	Electronics and coatings
Metal oxides	
• Nano metal oxides (5-10 nm) can be produced in various forms, such as amorphous, sticks, tubes, slices, and more complex structures.	(Opto)electronics, sensors, transducers, medicines, paint and sun cream.
• Nano silicon oxides (5-10 nm) are not found free as particles, but shortly after their creation bundle together to form larger agglomerates.	Strengthening elastomers, additions to powders and heat insulation.
Metals	
• Nano gold particles	Medicines, conductors and optical markers
• Nano silver particles	Wound covering, disinfectants, socks.
• Nano cobalt and copper	Interconnectors in (nano)electronic circuits.
Quantum dots	
• Quantum dots (1-10 nm) are spherical nano crystals of semiconductor material with special optical properties as a result of quantum effects.	Fluorescence, diagnostics
Organic polymers	
• Dendrimers are polymers at nano scale the polymer chains of which can be checked at atomic level.	Medicines
• Nano fibres are polymers the properties of which can be checked more generally.	E.g. ultrafiltration, bio degradable fibres, tissue culture, medicine dosage, wound covering.
Biological nano particles	
• Biological nano particles are used to absorb, bear or insulate biological material. They consist of biological building stones such as fats, proteins and polysaccharides.	Medicines and biochemical research

Annexe 2: RI&E Nano

Based upon: Guidance working safely with nanomaterials and naoproducts. The guide for employers and employees; FNV, VNO NCW, CNW, version 1.0 – May 2011.

RI&E Nano particles*)

Carried out by:
Faculty: CTW/EWI/TNW
Department:

1. Information Nano material

Product name:	
Chemical name:	
CAS-reg. no.:	
Size distribution of particles of primary particles in product	nm
Are fibrous particles involved:	Yes/No length fibres = nm, diameter fibres = nm.
CMR characteristics of nano material (or parent material) **)	Carcinogenic Mutagenic Reprotoxic
Density (kg/dm^3)	kg/dm^3
State of aggregation of the nano material	Liquid Solid

2. Health hazard nano material

Danger category	1, 2, 3
1= (Water) soluble nano particles. These are nano particles with a solubility > 100 mg/l *Examples: particles of lipids, sucrose, soloxanes ranging from 1-100 nm.* 2= Synthetic, persistent nano materials (non fibrous) *Examples: metals (e.g. Ag, Au, Pb, La), metal oxides (e.g. TiO_2, ZnO, CeO_2, CoO), carbon black, fullerenes, nanoclay, polymers, dendrimers ranging from 1-100nm.* 3= fibrous, insoluble nano materials regarding which asbestos-like effects cannot be excluded. *Example: SWCNT (=one-sided carbon nano tubes) and MWCNT (=multi-sided carbon nano tubes).*	

*) *If you are asked to choose between options, delete where not applicable.*

**) *This information is used to assess whether in addition to the control measures described in this manual, extra measures need to be taken to meet the statutory requirements for working with substances with CMR-characteristics: see UT guideline* working with carcinogenic, mutagenic and reprotoxic substances.

3. Activity, risk of exposure in the activity and control category

No.	Activity/purpose activity	Space no.	Exposure category [1]			Control category [2]			Amount mg ml	Release of dust/aerosol possible (yes/no)	Length of time activity (minutes)	Frequency number of times per day (d), week (w) or month (m)	Number of (exposed) staff
			I	II	III	A	B	C					
1													
2													
3													
4													
5													
6													

[1] **Exposure category:**
I: No free nano particles are released by using a closed system *(e.g. use of glove boxes or fully contained process).*
II: Release of <u>bound</u> nano particles is possible (*e.g. when weighing nano material, when grinding, spraying and polishing nano products)*
III: Release of <u>free</u> nano particles is possible *(e.g. when producing nano particles or research activities)*

[2] **Control category: From danger category (see previous page point 2) and exposure category the control category can be determined via the decision matrix on the next page:**
A: Use what is already accepted to limit risks on workplace and what is required by law.
This means: applying sufficient ventilation of space, possibly exhaust at source and/or protection, supplemented by suitable personal protective gear.
B: Check what extra measures can reasonably be used. *Measures are to be in conformity with the occupational health strategy; all measures that are technically and organisationally feasible are further assessed on their economic feasibility.*
C: Apply the precaution principle. *All steps of the occupational health strategy are successively checked and all solutions that are technically and organisationally feasible are implemented.*

Decision matrix to determine the control category of an activity involving nano materials

	Description danger category of nano material or nano product			
Risk of exposure to nano particles materials during an activity		***Danger category 1:*** (water) soluble nano particles	***Danger category 2:*** Synthetic, persistent nano materials (non-fibrous)	***Danger category 3:*** Fibrous, insoluble nano materials for which asbestos-like effects cannot be ruled out
	Exposure category I: Release of nano particles is minimised by using 100% closed system	A	A	B
	Exposure category II: Release of nano particles (1-100 nm) bound in larger solid or liquid particles up to 100 µm during activity is possible	A	B	**C**
	Exposure category III: Release of primary nano particles (1-100 nm during activity is possible	A	**C**	**C**

4. Plan of action

No.	Activity	Space no	Control category			Measure	Action by	Date completed
			A	B	C			
1								
2								
3								
4								
5								
6								
7								

In selecting specific control measures the occupational health strategy is conformed to (1. Source measures, 2. Technical measures, 3. Organisational measures and 4. Personal protection gear)

Working out a plan of action with specific control measures requires a creative approach. The next page contains an overview of possible control measures, classified in conformity with the occupational health strategy. This can be a useful tool.

Overview of possible control measures to make activities involving the use of nano materials safer; classified in accordance with the occupational health strategy

Measures at source:
o B1. Check whether the nano material can be replaced by non-nano material or by nano material in a lower danger category;
o B2. Use nano materials if in powder form or in the gas phase in a closed system as much as possible;
o B3. Transport nano material in sealed packaging;
o B4. Do no use more material than required;
o B5. Try looking for applications that can be supplied ready-made and do not require mixing on the workplace;
o B6. Use the particles where possible in a matrix (e.g. dispersion, suspension, paste, pallet form or contained);
o B7. Choose processing methods that produce little dust or aerosol: cutting instead of sawing; brushing/rolling instead of spraying.

Technical measures
o T1. Nano particles distribute like a gas. Try to work in a closed system as much as possible;
o T2. If possible work in a fume cupboard, glove-box to avoid spreading nano materials to surrounding spaces;
o T3. Use an effective exhaust at source when using nano materials. Exhaust at source is effective if the distance from the exhaust opening to the source of nano particles does not exceed the diameter of the exhaust opening;
o T4. Avoid recirculation of air that is possibly contaminated with nano materials and make sure that the exhaust air is not brought into another space;
o T5. Provide the ventilation systems with HEPA filters to capture the nano particles;
o T6. Nano particles can easily escape from any leaks in ventilation systems. Repair leaks and poor sealing immediately;
o T7. Prevent unwanted spreading of particles after use and fixate them in a resin, liquid, etc. Discharge the particles as chemical waste;
o T8. Clean spaces where nano materials are used frequently by using wet cleaning only (scrubbing machine) or use an industrial vacuum cleaner with a special HEPA filter.

Organisational measures

o O1. Consult with the manufacturer/supplier of nano materials about the possibilities for supplying the nano materials in a packaging that is suitable for the activities to be carried out (e.g. a water soluble packaging);

o O2. Ask the supplier to stick a warning on the packaging such as for example: to be opened in a controlled environment by addressee/user of this package only;

o O3. Limit the number of actions to be performed with the product (weighing, pouring over, mixing, etc.);

o O4. Screen off the workplaces where nano materials are processed;

o O5. Limit the access to workplaces where materials are processed;

o O6. Use disposable tools as much as possible and discharge these as chemical waste. Also any remainders are to be discharged as chemical waste. Even better: include them in a matrix before discharge (e.g. in a resin).

o O7.Provide staff with adequate information and instructions about the safe use of nano materials.

The information to be provided should involve:

- possible risks of working with nano materials;
- recognising the nano materials used;
- the safe use, storage and discharge of the materials used;
- any limiting values for nano materials;
- the correct use and maintenance of the personal protection gear prescribed;
- the correct use and maintenance of the technical facilities prescribed;
- what to do in the event of spillage and other incidents.

o O8. Arrange for adequate periodical maintenance of the exhaust system.

Personal protection gear

o P1. Give staff proper user instructions about the safe and correct use of the personal protection gear prescribed.

o P2. Use disposable gloves. Preferably no woven cotton gloves. Gloves considered suitable are for example nitrile, latex and neoprene.

o P3. Use safety goggles when activities involve substances that may spread.

o P4. Working clothes should preferably not be woven, but Tyvek, for example.

o P5. Use at least FFP3- respiration protection (with a protection factor (NPF) of 30 or higher).

RI&E Nano Particles

Seen and approved Head of department

Name:

Date:

Signature: