Innovative strategies, methods and tools for occupational risks management of manufactured nanomaterials (MNMs) in the construction industry

BEST PRACTICE GUIDE FOR RISK ASSESSMENT OF MANUFACTURED NANOMATERIALS (MNMs) IN THE CONSTRUCTION SECTOR

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Disclaimer

This document was prepared following extensive consultation with a range of stakeholders (via workshops, meetings, surveys, interviews and document reviews):

- Representatives of the construction sector, including:
  - European Construction Industry Federation (FIEC);
  - European Federation of Building and Wood Workers (EFBWW);
  - OHS Managers from several construction companies.
- Manufacturers of construction products;
- European and Spanish agencies for occupational safety;
- Manufacturers of personal protection equipment;
- Experts in nanosafety;
- Policy makers at European and national (Spain) levels.

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The views expressed herein are solely those of the authors.

Presentation

This Best Practice Guide aims to help Occupational Health and Safety managers assess the potential risks derived from the use of nano-objects, and their aggregates and agglomerates NOAAs (ISO 12901-2) in the construction sector. It provides quick advice on methods, examples and good practices to perform the risk assessment when NOAAs are incorporated in the products or the production processes in the sites.

This guide has been developed inside the SCAFFOLD project (Grant agreement Nº 280535, 2011-2015) which address five specific NOAAs that are the focus of this document: nano-TiO_2, nano-SiO_2, nano-clays, carbon nano-fibers and nano-cellulose. Although the Project is focused in the mentioned five NOAAs, the methods proposed in this guide for Risk Assessment can also be applicable to other nano-objects that may be used by the construction industry, with the limitation of the OELs which are specific for the NOAAs in the scope of project. Apart from this guide, three other Best Practice Guides have been developed in the framework of SCAFFOLD, which would complete a set of documents whose main goal is to help the management of risks derived from the use of NOAAs in the construction sector. Additionally, the project has produced a Handbook where the topics of the quick guides are treated more extensively.

This guide is specially addressed to the persons in charge of OHS in companies, OHS consultants providing assistance mainly to SMEs, public authority or any other personal with responsibilities in the safe production of companies.

Knowledge in this area is emerging as research and experience grows. This guide is an initial step to assist the risk assessment in the sector and its practical application jointly with future inputs from the science would lead to new improvements.

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Introduction

Construction in the European Union is a dynamic sector and the biggest industrial employer (3,1 million enterprises - 95% have less than 20 workers - and 14,9 million jobs). The increasing use of NOAA and nano-enabled products in construction might pose new health and safety risks to workers at different stages of the life cycle in construction. Consequently companies need to address the management of these potential occupational emerging risks.

This guide aims to help Occupational Health and Safety managers assess the potential risks derived from the use of NOAAs in the construction sector. This guide has been developed inside the SCAFFOLD project (Grant agreement Nº 280535, 2011-2015),

It is important to highlight that this guide only addresses the potential risks derived from NOAAs by inhalation and other risks that may be relevant for this sector are not considered.

1. Mapping the construction sector & exposure scenarios to NOAAs

NOAA and nano-enabled products are being considered for various uses in the construction industry and related infrastructure industries, not only for enhancing material properties and functions but also in the context of energy conservation.

So far, only a limited number of nano-products make it to today's construction sites, the main ones are based on silicon and titanium oxides. The key areas of application are in: cement based materials, insulation materials, infrastructure coatings and coatings and paints for wood, glass and other materials as well as for self-cleaning purposes.

In Scaffold project we have selected five nano-objects: clay nanoparticles, carbon nanofibers, cellulose nanofibers, nano-SiO2 and nano-TiO2; each of the above mentioned NOAAs are being studied in one particular application, due to the properties that they give to the matrix in which they are added (see table 1).

Table 1. NOAAs and applications selected in the SCAFFOLD project.

NOAA	Application/matrix	Expected benefit
n-SiO_2	Concrete	Improvement of rheology and mechanical properties
n-TiO_2	Mortar	Self-cleaning and decontamination
n-TiO_2	Self-cleaning coating	Self-cleaning and decontamination
Nano-clay	Fire resistance panels	Improvement of creep resistance and thermal stability
Cellulose NFs	Insulations	Improvement of mechanical and thermal properties
Carbon NFs	Coating/paint	Improvement of mechanical, thermal and electrical properties

Cementitious materials such as concrete experience changes in their properties by the incorporation of nano-SiO2; nano-particles of SiO_2 can fill the spaces between particles of gel of C–S–H, acting as a nano-filler and basically improving the strength and durability of the materials. In contrast to the bulk TiO2 (>100 nm) that is considered chemically inert, nano-scale TiO2 can act as a photo-catalyst, and can generate reactive oxygen species upon illumination. A wide range of applications exist, exploiting the various properties of TiO2 nanomaterials. For instance, in coating paints nano-sized TiO2 is used as a photocatalyst producing reactive oxygen that may degrade other organics. The addition of TiO2 to the common mortar implies the improvement of barrier properties of the material. These NOAAs add to the mortar the capacity to maintain the surface of the product clean more time than the common mortar, therefore the maintenance tasks of the product will be reduced during the use of the product. Nanoclays are usually incorporated into polymeric matrixes in order to improve or modify one or more characteristics of the material: improve their mechanical properties, increase their resistance to thermo-oxidative processes, modify their surface properties, increase their crystallinity, improve their creep behavior, reduce the gas permeability, give antibacterial properties, etc. This nano-filler is industrially used in the automotive and packaging sectors as well as in the construction for the preparation of materials and elements with improved fire resistance, since the clay layers reduce the gas permeation and act as protection to the polymeric matrix. Cellulose fibers are extensively used in paper production, cotton textiles, and as insulation and structural strengtheners in construction products. Finally, carbon nanofibers (CNF) are used in construction, for example, in composite materials to improve strength, stiffness, electrical conductivity, or heat resistance.

Although the use of NOAAs in the construction sector is growing, they have found some barriers; the main ones have been identified:

- the expensiveness of NOAAs compared to traditional solutions,
- the conservative profile of the sector and the lack of awareness about emerging technologies,
- the general uncertainty with respect to health and safety risks and how to properly manage them in order to protect the workers and be in compliance with the existing OHS legislation.

Workers exposure to NOAA may occur over the life cycle of nano-enabled products: during the nano-objects manufacturing process, in the manufacturing of products containing NOAAs, their application and installation, during their use (e.g. maintenance tasks) and finally in the products end of the life including demolition/disposal and recycling processes. In all these steps, many enterprises from the sector with different profiles are implied.

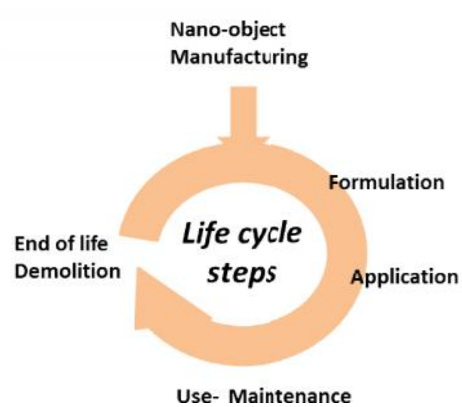


Figure 1. Life cycle steps of nano-enabled products and applications.

Exposure predominantly can occur via inhalation, dermal, oral and ocular routes. The major possible portals of NOAAs entry are lung, skin, gastrointestinal tract, nasal cavity and eyes. Exposure through inhalation of dust is the scenarios most likely to pose health risks. Skin penetration may in theory play a role as well, but most studies have shown little to no transdermal absorption through healthy skin. However, the uptake via damaged skin cannot be ruled out. Oral exposure can occur from intentional ingestion and from unintentional hand-to-mouth transfer. Swallowing inhaled particles that are cleared via the mucociliary escalator, and of drainage from the eye socket via the nasal cavity following ocular exposure are less important ways of exposure.

Critical factors affecting exposure to NOAAs include the amount of material being used, the ability of the material to be dispersed (in the case of a powder) or form airborne sprays or droplets (in the case of suspensions), the degree of containment, and duration of use.

Jobs and operations that may increase the likelihood of exposure to nanoparticles include for example:

- Generating nanoparticles in the gas phase in non-enclosed systems.
- Handling nanostructured powders.
- Working with nanomaterials in liquid media without adequate protection (e.g., gloves).
- Working with nanomaterials in liquid during pouring or mixing operations or where a high degree of agitation is involved.
- Machining, sanding, drilling, or other mechanical disruptions of materials containing nanoparticles (e.g. during the installation of materials, in demolition/recycling processes).
- Conducting maintenance on equipment and processes used to produce or fabricate nanomaterials, or the clean-up of spills or waste material.
- Cleaning of dust collection systems used to capture nanoparticles.

In Scaffold the occupational exposure to the five selected NOAAs has been measured in scenarios covering the life cycle of the six applications; see next matrix summarizing the scope of the scenarios investigated in the project (table 2).

	Nano-object and application					
Life cycle step	**nano-TiO2** depollutant mortar	**nano-TiO2** self-cleaning coating	**nano-SiO2** self-compacting concrete	**nano-Clay**(fire retardant panels	**carbon nano-fibers** coating laminates	**nano-cellulose** insulations
Nano-object manufacturing	X	X	○			
Manufacturing nano-enabled products and application	X	X	○	○	X	X
Use/maintenance: Machining	X	X	X	Ⓧ	X	X
Demolition	X	X	X	Ⓧ	X	X
Accidental fires	X	X	X	X	X	X

Table 2. Scope of the scenarios investigated in Scaffold project.
Note: cells marked with X have been investigated at lab/pilot scale; cells marked with the red circle have been investigated in the case studies.

The results found are encouraging and in general workers performing the tasks measured were not overexposed to NOAAs in the scenarios investigated. Data of occupational exposure were below the limits proposed for the NOAAs by Scaffold (Stockmann-Juvala H. et al, 2014), NIOSH (NIOSH 2011) and the nano-reference values proposed by IFA (IFA, 2014, SER 2012); the limits used are showed later in this document. For that reason, the scenarios in the matrix are showed in green color although some remarks have been marked for some of them.

(1) Considering the metric of mass concentration (mg/m3), the occupational exposure measured in all scenarios was below proposed limits by NIOSH and SCAFFOLD. As expected, the highest mass concentration measured was found in tasks where nano-objects were handled directly and in significant quantities as for example, during cleaning operations in the nano-TiO2 manufacturing process or during the spraying of a self-cleaning coating in a wall.
(2) Considering the metric of particles concentration (particles/cm3), the occupational exposure measured in all scenarios was also below the recommended nano-reference value of 40000 particles/cm3 (IFA, 2014). As expected, common activities in this sector produced a high release of particles. For instance, the highest values measured were during the machining of quite hard materials such as the self-compacting concrete and the laminates filled with CNF. However two issues should be underlined here. On the one hand, the release of particles is intrinsic to the machining process and in fact, no sticking differences have been found for processes performed with control materials (without NOAAs) and materials filled with NOAAs. On the other hand, the machining processes were performed during short times and, consequently, the concentrations averaged to the 8 h-day did not exceed the OELs; however, other working conditions with longer processes may lead to higher exposures.
(3) Fire tests performed with the materials from the six applications did not observe the release of the NOAAs added to the materials with the exception of the fire retardant panels where there may be indications of possible release of nano-clays during the combustion of the materials.

Nowadays there are still very few data available on workers exposure to NOAAs in the construction sector. The data achieved in Scaffold contributes to clarify if the use of new nano-enabled products may increase the risk of workers handling these materials. It should be noted that most of the measurements have been taken at pilot scale, so short times and small quantities have been handled. More data from real scenario would help to incorporate in a safe way these new materials in the sector. Finally, it should be underlined that construction work environments are rather complicated, typically handling different activities and chemicals, and where other hygienic risks may be more relevant than exposure to NOAAs.

2. Risk Assessment

2.1 Introduction: overview

Risk establishes the probability of the adverse effect occurring by considering both the HAZARD and the EXPOSURE together. As for other chemicals, for the NOAA the Risk Assessment may be performed qualitatively or quantitatively mainly depending on the availability of information on both, hazard and exposure.

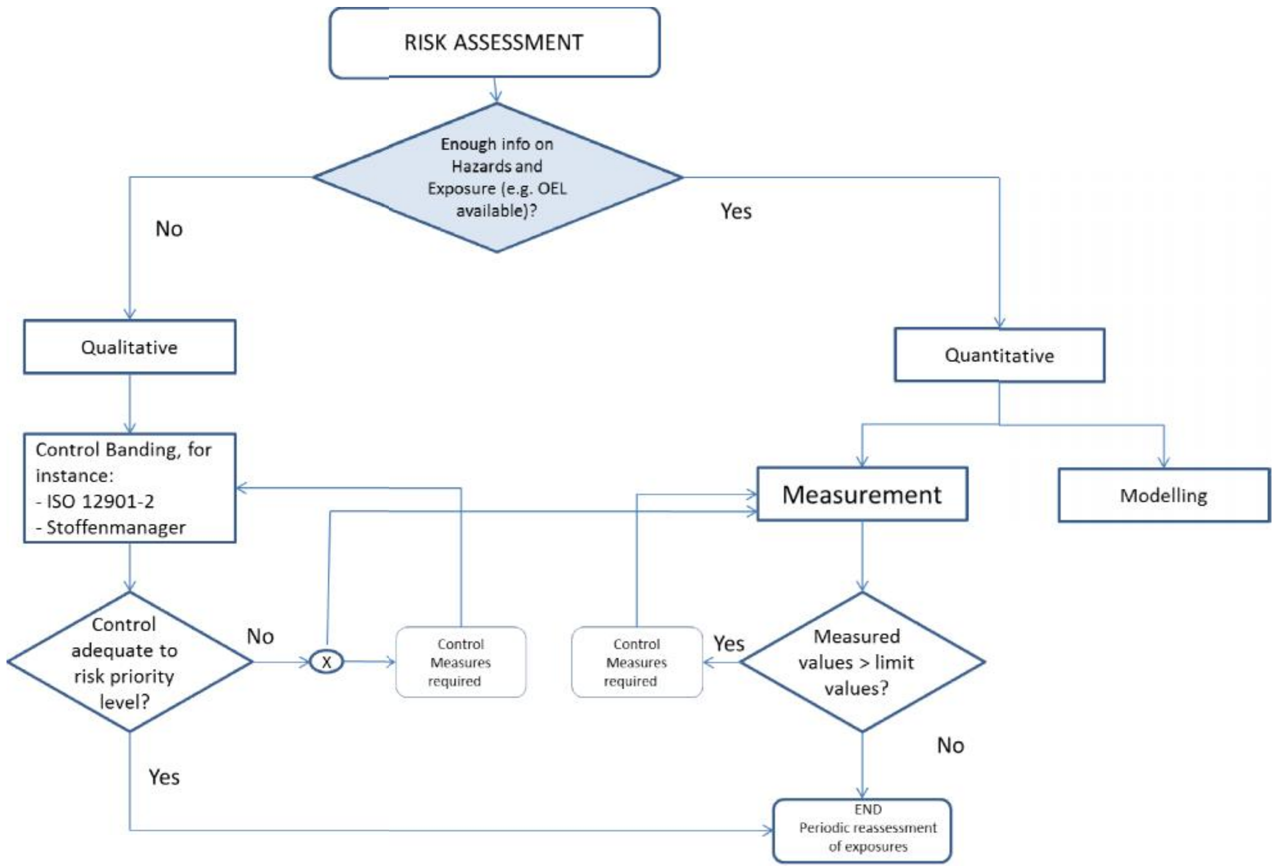
Basically when few data are available on the hazards of the material, for instance, when no exposure limit values are available, then a qualitative approach is typically followed. On the other side, if there are exposure limit values for comparison jointly with methods and resources to measure exposure, then a quantitative approach could be performed.

The qualitative risk assessment is based on professional judgment and follows a similar process than the quantitative approach with the difference that hazards and exposures are estimated generally in terms of bands or categories. Next point 2.2 addresses two recognized methods for NOAA, Stoffenmanager-Nano and ISO/PDTS 12901-2 which provide guidance to use control banding approaches

On the other side, the quantitative approach is more complicated and can be addressed by modelling or by performing measurements in the workplace. Modelling is a complex approach currently developed at a research stage for NOAAs; in the scope of Scaffold models have been used to study occupational exposure in simulated accidental conditions (Pilou et al, in press). Finally, the risk assessment performed through measurement consists on achieving data of occupational exposure which would be compared to a proposed limit value: if the measured value is above the limit, then control measures are required; if not, the process would end indicating the periodic re-assessment of the process. Moreover, following the prevention principles, prevention/control measures would be welcomed to further reduce the exposure. This approach is addressed in chapter 3.3.

In practice, the qualitative and the quantitative approaches are complementary. For instance, if control banding tools indicate that the current controls are not adequate for the risk priority band, then the industry may decide to carry out a quantitative approach with experts or the company may decide to introduce the adequate controls, and the decision would depend mainly on the resources and economic factors.

Next figure 2 shows a flow chart and a simple decision making matrix with the general approach for risk assessment of the five NOAAs in the scope of Scaffold.



NOAA	Risk Assessment		Application in the scope of Scaffold
	Qualitative (a)	Quantitative (b)	
Nano-TiO2	CB	number/mass	Depollutant mortar/self-cleaning coatings
Nano-SiO2	CB	number/mass	Self-compacting concrete
Nano-clay	CB	number/mass	Fire retardant panels
CNF	CB	fibers	Laminate coatings
Nano-cellulose	CB	fibers	Insulations

Figure 2. Flow chart and decision making matrix with the general approach for risk assessment of NOAA
(a) CB: Control Banding (b) The quantitative measurements can address different metrics: number concentration, mass concentration and fibers concentration (see chapter 2.3)..

2.2 Qualitative Risk Assessment: Control Banding

Two different control banding approaches have been investigated in Scaffold for the qualitative risk assessment of NOAAs: the standard ISO 12901-2 and Stoffenmanager-Nano tool Duuren-Stuurman B. et al., 2011).

Both approaches are quite similar. Basically they define five bands of hazard and four bands of exposure which combination defines a matrix with three levels of risks or priority bands (see figure 3). The definition of the hazards and exposure bands is slightly different for each approach but in short the hazard band is based mainly on the toxicity of the material (from A: no significant risk to health, to E: severe hazard) while the exposure band depends on the process performed, physical form of the NOAA and quantities (from exposure band 1: low exposure to exposure band 4: high exposure). The three levels of risks or priority bands score from low risk or low priority band to high risk/priority band.

Exposure band / Hazard band	1	2	3	4
A	Low	Low	Low	Medium
B	Low	Low	Medium	High
C	Low	Medium	Medium	High
D	Medium	Medium	High	High
E	Medium	High	High	High

Figure 3. Risk or priority bands (source: ISO 12901-2).

The main advantage of these tools is that they are simple and easy to use tools which require few resources. However, the main handicap of control banding tools is that generally their results are conservative. One reason for that is that, due to the scarce information on the hazards of the NOAAs, the nanomaterials may be classified in one of the hazard classes C (high), D (very high), or E (extremely high). Once the substance has been classified in a high hazard band, then the risk priority level will be also the highest ones independently of the exposure band, so even though the possible exposure is low, the risk priority level may be the highest one. Here, we should keep in mind that the outcomes of the tool is not risk levels, but risk priority levels, meaning that in these cases one should be very careful with the substances and check that the control measures are working properly and the best practices are applied at the workplace.

As a practical recommendation for the sector, it may be said that the use of control banding tools in the site may be useful for the company because managers and workers have to study the material safety data sheet (MSDS) or get other information about the used product and also consider how they are handling it. Often this has already a positive reaction to the work practices and attitude at the workplace. However, the results that may be achieved with these tools would generally not be enough for the risk assessment in the construction site and may require for example the help of experts or the use of other assessment methods.

Scenario 1. Example of use of Stoffenmanager-Nano tool

A coating process was carried out in an indoor environment in two phases: the first task was high-pressure spraying and the second task was mopping of the sprayed surface.

Figure 4. Stoffenmanager Nano-Tool (source: https://nano.stoffenmanager.nl/default.aspx

The used products were a combination of two different protective materials. A mixture was spread on the floor with a high pressure spraying gun. After drying, another mixture of protective material was spread by mopping. The MSDSs were available. During the project it turned out that the products were made by the application of nanotechnology, but the end-products may not contain any nanosized particles.

In this scenario there were four workers at the site. The worker who used the spraying gun wore a power assisted respirator with the face shield (assigned protection factor (APF) is 20) and chemical protective gloves. The other workers used filter respirators and gloves. The work was done indoors.

Although it was not sure if the used product contained engineered nanoparticles (polymer), we wanted to test the usage of the tool because it might be unclear for downstream users also whether the product contains nanoparticles or not.

For the tasks in this scenario, the Stoffenmanager Nano classified **hazards** of the used products as **very high** (D) when it was assumed that the product contains nanosized polymer. The e**xposure** was considered as **high** both in task weighted and time and frequency weighted exposure in the spraying task. **Risk** score was ***high*** for the task of coating the floor by **spraying**. The **exposure** class was **average** in the mopping task. **Risk** score was ***average*** in the task of coating the floor by **mopping**.

The results of the Stoffenmanager Nano tool were compared with the expert assessment performed in Scaffold project. For this scenario, Stoffenmanager gave similar results as the expert evaluation for the spraying task. However, for the mopping task, the exposure and risk priority classes obtained by Stoffenmanager Nano were higher than the expert judgment.

Scenario 2. Example of use of ISO 12901-2.

A self-cleaning coating based on ano-TiO2 was sprayed on a wall out-doors using a spry gun, in a pilot scale experience.

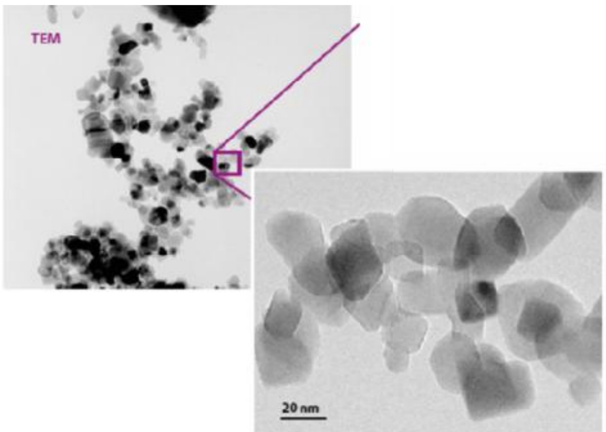


Figure 5. TEM images of Aeroxide P25.
Source: **AEROXIDE, AERODISP and AEROPERL Titanium Dioxide as Photocatalyst. Technical Information 1243. https://www.aerosil.com/product/aerosil/Documents/TI-1243-Titanium-Dioxide-as-Photocatalyst-EN.pdf**

The NOAA was dispersed on a liquid coating. The nano-TiO2 used was commercial Aeroxide P25, Evonik (figure 5). MSDS and product information was available, indicating that it was a powder which primary particles had a mean diameter of 21 nm. Two coatings were sprayed, one with a concentration of 1.7% of nano-TiO2 (product A) and the second with a concentration of 0.7% of nano-TiO2 (product B).

The process was performed outside and the operator wore PPEs including protective clothes, glasses, gloves and respiratory mask FPP3.

The control banding tool ISO 12901-2 was applied to this scenario.

- The hazard band identified was B or C, considering the selected OELs for nano-TiO2, 0.3 or 0.1 mg/m3 respectively.
- The exposure band identified was 4 considering: NOAA in a suspension, deliberate aerosolization or spraying.
- The combination of the above bands reports a band of **high risk or high priority band**.

On the other hand, occupational exposure was quantitatively measured in this scenario to be compared with the selected OELs, 0.1 mg/m3 and 0.3 mg/m3 (recommended by Scaffold and NIOSH respectively). Filters collected at the personal breading zone showed a concentration of TiO2 around 0,1 mg/m3, the level of the selected limits, during the short time sampled (13-15 minutes). Averaging the concentration to the 8 hours-day, in this pilot study the occupational exposure of the worker would be very low due to the short time of the tasks which lasted only some minutes. However, if the task would be performed during longer periods in the working day, occupational exposures in the level of the OELs may be expected.

Comparing the results of the control banding tool ISO 12901-2 and the real measured data it may be a good estimator tool of the risk.

2.3 Quantitative Risk Assessment: Measurements

2.3.1 Steps of the process

The classical steps of a risk assessment process for chemicals can also be applied to NOAA:

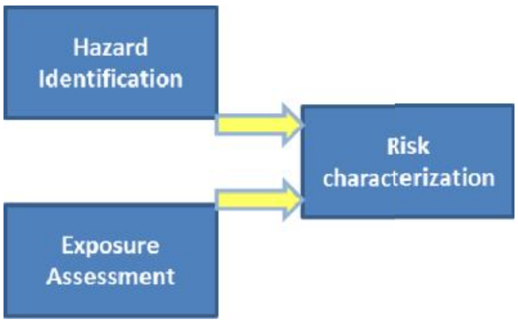


Figure 6. Risk assessment process.

Step 1: Hazard identification

Hazard Identification is the process of determining whether exposure to a specific chemical, in this case the NOAA, can cause an adverse health effects.

In practice at this step the industries will look at the MSDS of the products used in the workplace which may include info on hazards and occupational exposure limits (OEL). However, in some cases the material may not have info on his composition (e.g. if it is filled with NOAA). In this case, if the industry suspect that the materials handled may content NOAA, the OHS responsible should require this data directly to the provider. Also, if OELs are not available on the MSDS, the industry may consider limits proposed for NOAA by recognized organizations as the ones proposed in next chapter 2.3.3 for the 5 NOAA in the scope of the project.

Step 2: Exposure Assessment

At this step the industry will measure the exposure of workers to the specific NOAA. As for conventional chemicals, initially the evaluator will identify the potential sources of particles release jointly with the operators potentially exposed. Then, it should be chosen the metric to measure, the method and the limit to perform the complete risk assessment. In next chapter 2.3.3 it is described the exposure measurement methods proposed for the NOAA in the scope of this project.

Step 3: Risk Characterization

This step consists on the comparison of measured levels with the OEL selected, in order to determine the level of risk and to make decisions about the need of control measures.

2.3.2 Hazard

2.3.2.1 Potential hazardous effects caused by nanomaterials

There are indications that nanomaterials are more biologically active than larger-sized particles of the same chemistry, due to their greater surface area per mass. Additional characteristics that may influence their toxicity include shape, surface functionalization or coating, solubility, surface reactivity, association with biological proteins, binding to receptors, and their tendency to agglomerate.

Soluble or partly soluble nanomaterials may induce hazardous effects mainly due to the toxicological profile of the dissolved ions. However, the majority of nanomaterials being used in the construction sector is consisting of poorly soluble or insoluble nanomaterials, where some of the toxicological effects may be a result of so-called particle effects.

The main concerns regarding occupational exposure to nanomaterials are related to local pulmonary effects. Due to their small size, inhaled nanomaterials can be deposited in the lung cells in high amounts. This may consequently cause a significant local inflammation, as the immunological defense system is not cable of removing all particles. The ability of the particles to travel from the lung to the systemic blood circulation and further to other organs, is in theory possible, as the small particles might pass through membranes.

The potential hazardous effects of many nanomaterials are currently being studied in numerous research projects. A few of the materials have already now been investigated in large numbers of toxicological tests, whereas for other materials there is almost no data available yet. What is clear is that the nanomaterials cannot be considered as one homogenous group, as the hazardous effects are likely to be very different. One of the main concerns at the moment is related to the hazardous effects of fibrous nanomaterials. However, the effects may be very different for different types of fibrous materials. According to the current knowledge, long, rigid fibrous nanomaterials (e.g., certain carbon nanotubes) seem to be significantly more harmful than other types of fibrous materials. The concerns are based on findings of animal studies, indicating a behavior similar to asbestos, meaning that repeated exposure might in the worst case cause carcinogenic effects.

As various nanomaterials may have different toxicological profiles, it is important to identify the nanomaterial in use, in order to be able to make a hazard and risk assessment. Making a risk assessment is complicated as, so far, the majority of nanomaterials has not been classified as harmful, and the safety data sheets seldom contain any nano-specific information on the hazardous effects.

In the hazard assessment it is highly important to consider all chemicals in use, and not only the nanomaterials. In many cases, other components of the products (for example organic solvents) are likely to be much more harmful than the nanomaterials.

2.3.2.2 *Occupational Exposure Limit values and reference values*

So far, no regulatory occupational exposure limit values (OELs) have been given for any nanomaterial by the European Union or any national OEL-setting authority. On the basis of available, published data on hazardous effects, occupational exposure limit values (OELs) were derived for five nanomaterials in the Scaffold project.

Amorphous silicon dioxide (SiO2)

SiO2 has been extensively studied and mild, reversible, local lung effects have been identified as the critical effects in toxicological studies. Based on these findings, the suggested 8 h OEL for the respirable fraction is 0.3 mg/m3.

Titanium dioxide

TiO2 has during the last decade been one of the most studied NMs. Its critical effects are related to local inflammatory effects in the lungs after repeated inhalation. An 8 h OEL of 0.1 mg/m3 is suggested for TiO2 (respirable fraction).

Carbon nanofibres and nanocellulose

The amount of data related to the potential hazards caused by carbon nanofibres and nanocellulose is still very low, and there are no valid studies which could be used for the derivation of an OEL. As there are some indications that biopersistent fibrous NMs (e.g., some types of carbon nanotubes) might be harmful when inhaled, an OEL of 0.01 fibres/cm3 is suggested for these materials, based on the precautionary principle. As it will be described again in point 2.3.3.4, we are aware of the fact that there is currently a lack of quantitative measurement methods for the estimation of exposure to carbon nanofibres or nanocellulose. Thus a minimization of the exposure is recommended as long as reliable methods, allowing comparison of sample concentrations with the suggested OEL, are not available.

Nanoclays

Very limited amounts of data on the hazards related to nanoclays have been published. The term ‘nanoclays’ contains many different materials, which complicates the assessment. No substance-specific OEL can be set for nanoclays at this stage.

General, low-toxicity dust

Within the construction sector, mixed exposure to different kinds of dust is extremely common. In addition to the substance specific OELs, our recommended 8 h OELs for general, inert dust are 0.3 mg/m3 for the respirable fraction, and 4 mg/m3 for the inhalable fraction. These values can also temporally be applied to nanoclays, as long as no valid substance-specific data is available.

Additional reference values

General benchmark exposure levels for nanomaterials have been recommended by different institutes, e.g., the IFA in 2009 (IFA 2014a). The values recommended by the IFA were also adopted as provisional reference values for engineered nanomaterials by the Social and Economic Council (SER) in the Netherlands in 2012 (Table 3) (SER 2012). These values are also recommended as reference values for engineered nanomaterials by the Finnish Institute of Occupational Health (FIOH 2013). These values are mainly based on experiences in exposure measurements and the detection limits of the available measurement methods, and are not substantiated toxicologically.

Table 3 Benchmark exposure levels for nanomaterials recommended by the IFA and the SER (IFA 2014a; SER 2012).

Nanomaterial	Benchmark exposure level	Comments
Rigid, biopersistent nanofibres for which effects similar to those of asbestos are not excluded	0.01 fibres/cm^3	
Biopersistent granular nanomaterial with density of > 6000 kg/m^3	20.000 particles/cm^3	Size range 1–100 nm.
Biopersistent granular nanomaterial with density of < 6000 kg/m^3	40.000 particles/cm^3	Size range 1–100 nm. Includes SiO_2, TiO_2, nanoclays, and nanofibres for which asbestos-like effects are excluded.
Non-biopersistent granular nanomaterials	applicable OEL	

So far, **no regulatory occupational exposure limit values** (OELs) have been given for any OEL-setting authority. Scaffold proposed the following ones for the NOAAs in the scope of Scaffold project:

Nano-object	OEL (mg/m3) or fibers/cm3 (1)	Reference Values particles/cm3 or fibers/cm3(1)
nano-TiO2	0.1	40.000
nano-SiO2	0.3	40.000
nano-clay	(2)	40.000
Low toxicity dust	0.3 (respirable) & 4 (inhalable)	
nano-cellulose	0.01 (1)	0.01 (1)
Carbon nano-fiber	0.01 (1)	0.01 (1)

Table 4 OELs and reference values recommended by Scaffold project.
(1) OELs in fibers/cm3; (2) The OEL for low toxicity dust can be temporarily applied to nanoclays, as long as no valid substance-specific data is available.

2.3.3 Exposure measurement methods

2.3.3.1 Introduction

The assessment methods proposed in this guide are related to the two metrics in which OELs are expressed so, number concentration (particles/cm3) and mass concentration (mg/m3)

In the table 5 it has been summarized the assessment methods proposed for the NOAA in the scope of the project. The table includes the procedure and the equipment/techniques needed to perform measurements based on both metrics, number and mass concentration.

As can be observed in table 5, to measure particle number concentration we propose to follow the procedure described in the flowchart in figure 8 using handle CPC devices (Condensation Particle Counter) for on-line measurement. On the other side, to measure mass concentration the recommendation is to follow the protocol included in the flowchart in figure 11; in this case the equipment/techniques needed include conventional equipment used in hygienic for personal sampling and gravimetric plus SEM analysis, jointly with ICP or other analytical techniques specific for the NOAA. Finally, specific recommendations for fibers are given, which OELs are expressed in fibers/cm3.

NOAA	Assessment method (inhalation)						
	Number (particles/cm3)		**Mass (mg/m3)**				
				Equip. /Technique			
	Procedure	**Equip./technique**	**Procedure**	**Personal sampling + Gravimetric.**	**Electron Microscopy**	**ICP (*)**	**Others**
Nano-TiO2	Fig. 8	CPC	Fig. 11				
Nano-SiO2	Fig. 8	CPC	Fig. 11				
Nano-clay	Fig. 8	CPC	Fig. 11				
CNF	(1)		(1)				
Nano-cellulose	(1)		(1)				

Table 5. Decision taking matrix for the selection of the assessment method for the NOAA.

(*) ICP: inductively coupled plasma

(1) Specific recommendations for fibers are given, which OELs are expressed in fibers/cm3.

2.3.3.2 Method to measure Particle Number concentration

The flowchart in figure 8 describes the procedure recommended to measure NOAAs, related to number concentration (particles/cm3). Basically it consists on measuring particle concentration at the personal breathing zone using handle devices as CPCs; measured data would be corrected with the background concentration and then compared with limit values (NRV or other benchmarks, self-imposed limits): if the measured value is higher than the limit, then the OEL would be exceeded during the sampling time; if not, the processes for Risk Assessment would finish. This procedure can be applied to nano-TiO_2, nano-SiO_2 and nano-clays and consider the NRV 40.000 particles/cm3 (or other if available).

The handicap of this method is the lack of specificity of CPCs, which can no distinguish the NOAAs from the background particles, including other conventional dust particles produced in common processes in the construction sector. In this sense the procedure proposes to measure the particles concentration before the task (background, BG) and during the task (particle concentration, PC); mean total particle concentrations will be calculated during the sampling times for comparison. If measured PC values are higher than BG, then a release of particles has been produced due to the task monitored. Next step is to correct the particle concentration with the BG by subtracting and to compare the corrected particle concentration with the selected OEL (e.g. NRV).

Common tasks in the workplace as mixing powders or machining materials would produce a high release of particles also from conventional materials. In these processes, when working with NOAAs, the measurement of particle concentration will be the sum of conventional particles plus the NOAA added. For these cases, as no discrimination is possible, if the measured value is higher than the NRV our recommendation is to consider that the OEL has been exceeded during the sampling time. In these scenarios, following a precautionary approach, it is considered the global risk of both the conventional nanomaterials produced in the task and the NOAA and it is recommended to reduce the exposure to nanomaterials (conventional or nano-objects) as much as possible.

Figure 7. Picture of portable CPC3007, OPC and DISCmini.

The equipment proposed to run this protocol is basically portable CPCs (e.g. TSI-CPC3007, 10 nm->1 µ) or personal monitors as DISCmini (matter aerosol, 10-700 nm) (see figure 7). Possible this last device is more appropriate because the worker can wear it similar to conventional hygienic personal pumps; the performance of this device is currently being analyzed in NanoIndex[1] project. Additionally, we recommend doing measurements with an Optical Particle Counters (OPC) together with the CPCs. These OPC devices would inform about the presence of particles in the range of big particles (0,3-10 µm), which is the common range for the agglomerates/aggregates of NOAAs. Moreover, when the OPC shows the release of big particles, the mass concentration may be a more relevant metric than the number and we recommend to also measuring this metric.

An important handicap of this approach is that currently there is no an harmonized procedure to measure particle number concentration which would allow, for instance, comparison among

[1] NanoIndex http://www.nanoindex.eu/

different measurements or the calculation of uncertainties in the data. The tiered approach nanoGEM (Asbach et al, 2012) provides guidance on how to do these measurements; also the OECD is currently developing a document in this sense.

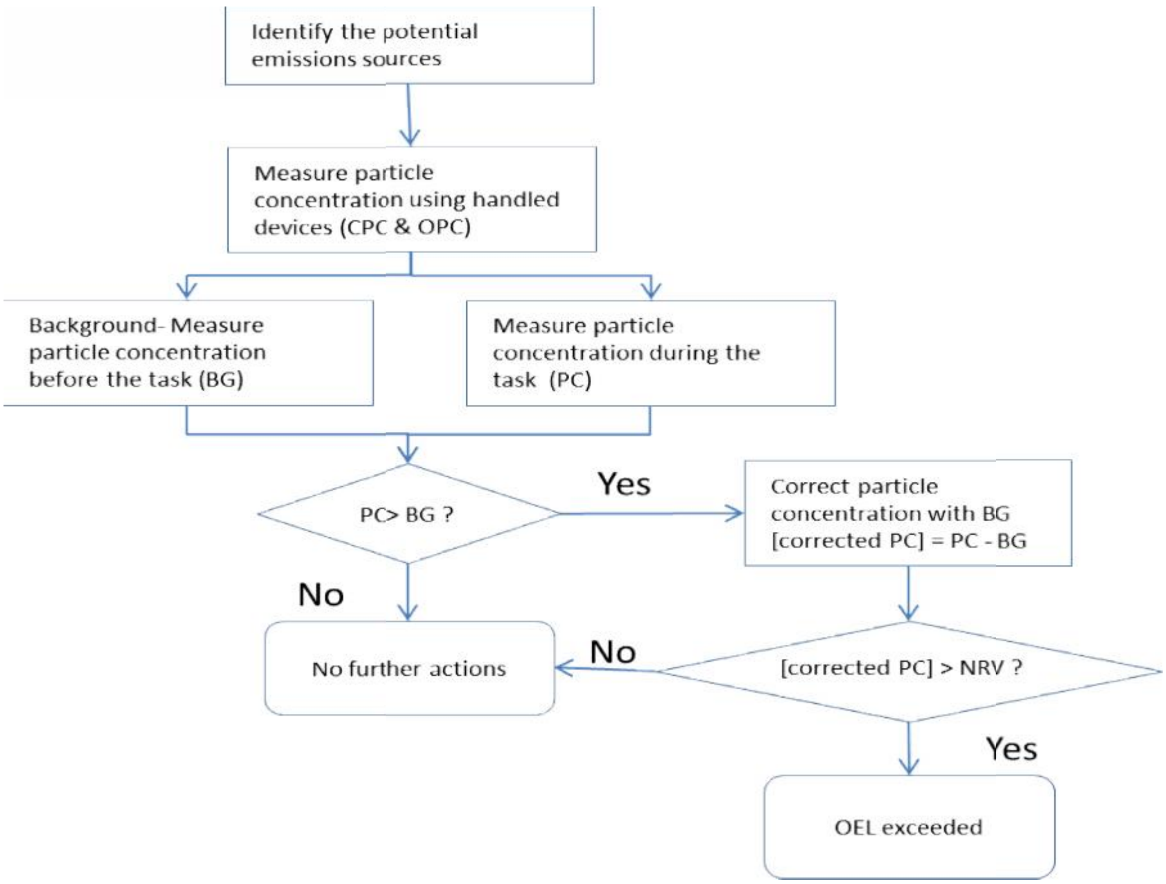


Figure 8. Flowchart describing the procedure to measure particle concentration (particles/cm3).

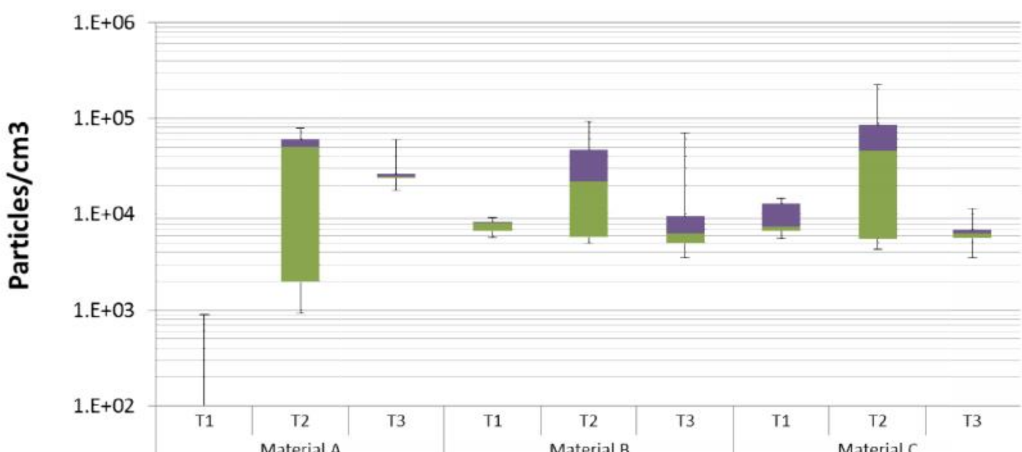
Scenario 3: An example of the measurement of particle concentration

Depollutant mortar filled with nano-TiO2 was manufactured at an industrial site.
Three mortars were manufactured:

- mortar A: control, conventional mortar,
- mortar B: filled with 0.8 % of nano-TiO2 supported on sepiolite[2] and,
- mortar C: filled with 0.4% of nano-TiO2 (Evonik P25).

Figure 9. Pictures of the process

Three batches were produced (1 Ton each); the quantities added of nano-TiO2 to Materials B and C was the same (4,1 kg).
The process included three tasks: weighing of additive (T1), adding additives to the hopper (T2) and bagging final product (T3). All these tasks took about 60 minutes per material. The industrial site had natural ventilation. One person was working at time, and the worker used PPEs (FFP3 mask and gloves). The process was monitored using on-line devices (portable and complex devices, including a portable CPC3007) to measure the particle concentration during the tasks performed. The main results are showed in next figure 11. This boxplot graph indicates the average number concentration (particles/cm3) during the three tasks for the three mortars manufactured (data from portable CPC3007, background-corrected). The data showed that the highest particle concentration is produced during the adding of additives to the hopper (T2) for the three materials. The highest value measured was 5.7E+4 particles/cm3 for T2, material C, measured during a quite short time of 4 minutes, which is the only one that is above the reference value of 40.000 particles/cm3 (NRV proposed by IFA). Moreover, the measured values should be averaged to the 8 hours-day to be compared with the reference values; so the concentrations measured during the performance of T2 (lasting 4 minutes) should be averaged to the hole working day leading to values clearly below the reference value.



	T1	T2	T3	T1	T2	T3	T1	T2	T3
	Material A			Material B			Material C		
Sampling time (min)	1	1	10	2	4	11	2	4	10
Mean (particles/cm3)	8	35010	25447	7660	30719	8493	9510	56864	6334

Figure 10. Summary of results

[2] This additive has been created by TOLSA (http://www.tolsa.com) to achieve better dispersions of nano-TiO2.

2.3.3.3 Method to measure Mass concentration

The flowchart showed in figure 11 describes the procedure recommended to measure the mass concentration of NOAAs, which is quite similar to conventional procedures followed in hygienic for other chemical substances.

The procedure consists on taking two samples at the Personal Breathing Zone (PBZ) of the respirable fraction; one will be used for gravimetric plus chemical analysis of filters and the duplicate for SEM analysis (if necessary). If the gravimetric analysis (or the specific chemical analysis of the NOAA, if available) shows that mass concentration is below the OEL, then, no further actions are required. On the other side, if mass concentration is higher than the OEL, then it should be analyzed the duplicate in SEM/TEM microscopy. If there is evidence of NOAA in the filter, then it is assumed that the OEL has been exceeded. On the other side, if no NOAA is observed on the filters, then other limit values could be considered, as those for the fine material or other limits proposed for low toxicity dust. This procedure can be applied to nano-TiO2 (OEL recommended in Scaffold is 0.1 mg/m3, respirable fraction), nano-SiO2 (0.3 mg/m3, respirable fraction) and nanoclays (0.3 mg/m3 for respirable and 4 mg/m3 for inhalable fraction). Finally, Scaffold also recommends for general, low toxicity dust a limit of 0.3 mg/m (respirable fraction) and 4 mg/m3 (for inhalable fraction)..

The equipment and techniques necessary to run this protocol are basically the same than used in hygienic to evaluate exposure to particulate material, with the exception of the SEM/TEM analysis that would be performed when required. For instance, it can be followed methods NIOSH 0600 or CEN/TR 15230:200 to evaluate the respirable fraction of the samples or more specifically, the exposure to nano-TiO2 can be analyzed following method NIOSH 7300.

It should be highlight that in these measurements the sampling time may be a key factor that will be related to the detection limit of the analytic technique; for instance, when gravimetric analysis is going to be performed, long periods of sampling may be required.

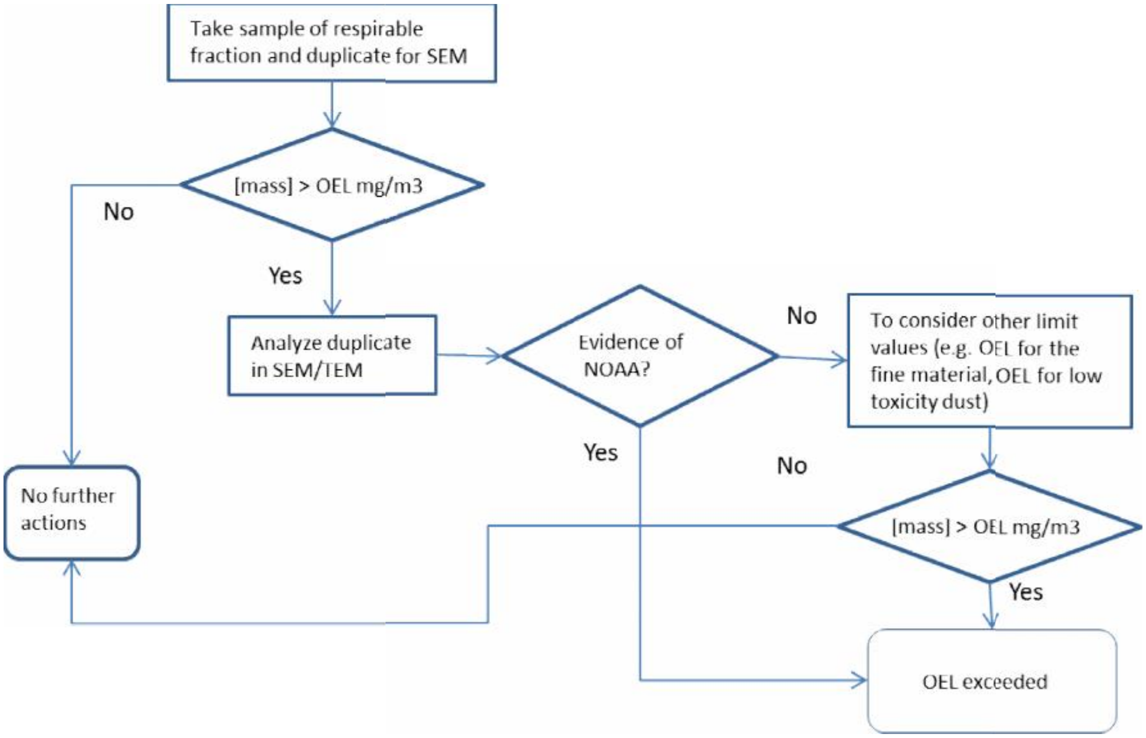


Figure 11. Flowchart describing the procedure to measure mass concentration (mg/m3).

Scenario 4. An example of the measurement of mass concentration

Depollutant mortar filled with nano-TiO2 was applied in a construction site. The three mortars previously developed and described in Scenario 2 were applied in a wall: mortar A (control), mortar B (0.8% of nano-TiO2 supported on sepiolite) and mortar C (0.4% of nano-TIO2)

Figure 12. Pictures of the process

The process includes three tasks: (T1) adding mortar and mixing with water, (T2) mortar application and (T3) scrapping; T1 and T2 are performed sequentially, while T3 is performed after some hours, when the mortar is partially dried. The work was performed outdoors by two operators who wear respiratory masks, gloves and work ropes.

One of the operators wore personal pumps to collect two samples of the respirable fraction; one of the samples for mass analysis of TiO2 following NIOSH7300, so using ICP-MS analysis of TiO2; the duplicate sample was for SEM analysis: Samples were taken during the performance of T1 and T2 for the three materials during a sampling time between 24-44 minutes for each one.

The main results are showed in next table 6. As can be observed, the TiO2 concentration during the sampling time was between 0.003 mg/m3 (for the control material) and 0.043 mg/m3 (for material C). Occupational exposure was calculated assuming the worst case, so the workers performed the tasks the 8 hours-day. As showed in the table, all measured values are below the OEL proposed by Scaffold (0.1 mg/m3). The duplicates were not analyzed by SEM due to the low concentration of TiO2.

Material	Tasks	Sampling time (min)	TiO2 conct. (mg/m3)	Occupational Exposure (mg/m3)
Mortar A	T1 & T2	41	0.003	0.003
Mortar B	T1 & T2	44	0.016	0.016
Mortar C	T1 & T2	24	0.043	0.043

Table 6. Results of occupational exposure to n-TiO2

2.3.3.4 Method to measure Fibers concentration

As other recognized organizations, Scaffold has proposed a limit value for the fibers of 0.01 fibers/cm3 (CNF and nano-cellulose in the scope of the project). However, currently there is a lack of consensus on the methods to quantitatively measure the fibers in a filter to be compared with this limit. Due to this, unfortunately it cannot be proposed a method to measure fibers to be compared with the OEL proposed to complete the risk assessment.

Following a cautionary approach, for scenarios related to the handling of CNF, in this guide it is proposed to collect samples at the PBZ of the operators for electron microscopy analysis and, if there is evidence of the presence of fibers, then the recommendation is that controls should be taken in order to avoid exposure to fibers. Alternatively it has been suggested that methods to measure asbestos by TEM (e.g. ASTM D6281, NIOSH 7402) could be followed for carbon nanotubes. In this sense, Dahm 2012 used a modified NIOSH 7402 to count structures of CNT in filters collected in several primary and secondary industries handling CNT.

Moreover, in construction, raw fibers materials would not normally be handled, but the common scenario would be the machining of polymeric matrix doped with the fibers (e.g. the insulations and laminates in the scope of Scaffold). Again, unfortunately for these scenarios no clear recommendations about the measurement method can be made at this moment apart from taking samples for microscopy analysis. In these tasks a high release of particles is expected. However, although SEM analysis does not observe the presence of fibers, there may be uncertainties about the release of free fibers and moreover, about the toxicity of the dust resulting from these machining tasks. Consequently, following a precautionary approach, the only recommendation that could be made at this moment is to control the exposure to this dust as much as possible.

It can be mentioned that other organizations have proposed an OEL for CNF based on mass concentration. For instance, NIOSH has recommended an OEL of 1 µg/m3 for CNF (NIOSH 2013, bulletin 65) and proposes the measurement of mass of Elemental Carbon to get data to compare with this OEL (following NIOSH 5040). In this sense, it can be cited the work performed by Dahm et al (2012, bis) which follows this method. However this approach is suitable when raw material of CNF are handled. But, for dust originated from polymeric matrixes, which would be the common scenario in construction, this method presents several limitations. For instance, it would not distinguish unbounded CNFs from those embedded in the matrix. Also, if the filter sample is overloaded with organic carbon from the polymer, there is a risk of being unable to quantify the elemental carbon content. In addition, this method may be inappropriate for sites where other sources of elemental carbon may be present, as combustion products from diesel.

The equipment and techniques suggested to run this protocol basically would be conventional hygienic devices to take samples at the PBZ (e.g. following methods NIOSH 0500 or CEN/TR 15230) which would be analyzed in electronic microscopy. Alternatively, as previously suggested, the mass concentration of CNF could be measured following the method NIOSH 5040 (NIOSH, 2013 bulletin 65).

Scenario 5. An example of the measurement of fibers concentration

Figure 13. Picture of the process

The manufacturing process of laminates coatings filled with CNF has been monitored (resin doped with 0,67% of CNF, PR-24-LHT from Pyrograf Inc). The process is performed at lab scale and it includes three tasks: (T1) the weighing of CNF, (T2) dispersing the CNF in polymer and (T3) the manufacturing of the laminate with the glass matts. The quantities of CNF used are at the level of grams.

Task T1 is performed inside a fume-hood by an operator who weights the powders; (T2) is performed in the lab using a dispersion rotor and covering the container to avoid spills; finally T3 is performed manually by the operator that wets the matts of fiber glass with the dispersion filled with CNF.

Three samples of total particulate were taken at the personal breathing zone of the operator during the process. Two samples were for SEM analysis and they were taken during the performance of T1&T2 (sample 1) and during the realization of T3 (sample 2). The third sample was an integrated sample taken during all the process for elemental carbon analysis. The main results of the measurements are showed in next table:

sample	Tasks	SEM analysis Evidence of CNF?	Sampling Time (min)	Elemental Carbon (µg/m3)
Sample1	T1 & T2	No (1)		
Sample 2	T3	No		
Sample 3	T1, T2 & T3		86	n.d.

Table 7. Results.

(1)There was no evidence of CNF at the PBZ; however, samples taken at source during the weighting task showed the evidence of agglomerates of CNF (see figure 16) ; n.d.: no detected; below the limit of detection of the technique.

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The samples collected at the PBZ have been analyzed in the electron microscopy and no CNF were identified; however, big aggregates of CNF were observed in samples taken at the source during the weighting task (inside the fume hood, see next figure 14). The elemental carbon analysis showed that the mass of carbon was below the limit of detection. (1 µg/cm2)

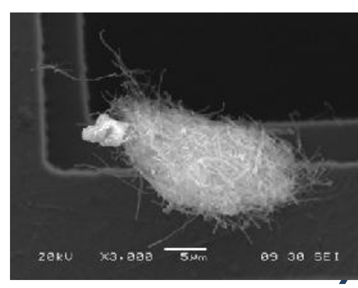

Figure 14. Picture of aa aggregate of CNF (sample taken at source)

2.3.3.5 Combination of measurement methods

In this document, the two approaches to measure occupational exposure (based on number or mass concentration) have been separated for simplification. However, combination of these approaches is an alternative. For instance, the strategies NEAT (NIOSH, 2009) or nanoGEM (Asbach, 2012) propose a tier approach which merge both approaches. Basically these methods propose a first level where portable on-line devices (particle counters) would be used to identify potential releases from processes. If significant releases are identified, the methods propose a second level of measurement to better characterize the aerosol using expert on-line devices (SMPS, ELPI, etc) plus sampling collection for the off-line chemical/morphology characterization of the particles. It should be highlighted that the OECD is currently developing a document in this sense, proposing a harmonized tiered approach to measure the occupational exposure to NOAA.

A practical approach for the sector may be to measure particle concentration using portable devices (e.g. CPCs or DISCmini) to identify potential sources, or when gravimetric analysis is not possible due to short time duration of tasks and considerations about particle release are desired. However, occupational exposure to the MNMs can be better assessed measuring the mass concentration at the PBZ, moreover considering that nano-objects in the construction sites will be mainly present as aggregates or agglomerates jointly with the high interferences of conventional dust particles occurring in these environments.

2.3.4 Risk Characterization

Risk Characterization is the final step in the risk assessment process: it combines the results of both the hazard characterization and the exposure assessment in order to estimate a potential risk from a chemical substance, in this case the NOAA.

In practice, the data of concentration measured as explained in previous chapter, either in number concentration or mass concentration, should be normalized to the 8 h-day, 40 h-week to be compared with OELs. Additionally, the industry may define their internal Risk characterization Ratios to express if risk calculated is high or if it is controlled.

3. Best Practice

In the following paragraphs we have collected some good practice for the sector when addressing the risk assessment derived from the use of NOAAs. Although most of the recommendations are addressed to the exposure measurement of NOAAs, some basic principles for risk assessment are also added:

- Gather contextual information for the risk assessment e.g. the used products, processes, work tasks and workers.

- For the evaluation of hazards, look at the MSDS of the products and look for info on NOAA, hazards and OELs. If this info is not available, ask the provider. Alternatively, consider OELs from recognized organizations including OELs proposed in Scaffold.

- Don't forget to evaluate the risks of other chemicals and emissions from the processes.

- For the evaluation of the exposure, find out the source for emissions, check the processes and tasks, used amounts, frequency and duration of the activities and implemented risk management measures.

- For the qualitative risk assessment the control banding approaches can be used. With the control banding tool it is possible to prioritize the work tasks, which one need actions for reducing risk.

- Check that all the needed and used technical control measures are working properly.

- When measuring particles concentration (particles/cm3) use portable devices. It is also recommended to use OPC to identify the presence of agglomerates/aggregates. When big particles are released, then mass concentration may be a more appropriate metric to monitor, which is a typical situation in construction sector.

- When measuring particle concentration (particles/cm3) in particle-generated processes (e.g. machining tasks) the measurement would be the sum of both, particles generated on the processes plus the NOAA; for these cases the recommendation is to consider the global risk of both the conventional nanomaterials produced in the task and the NOAA

- When measuring mass concentration, if available try to use specific chemical analysis for the NOAA. This recommendation is suitable mainly for scenarios where nano-TiO_2 is involved.

- When measuring mass concentration and no specific analytical technique is available, then gravimetric method is the alternative. In this case, the mass measured will be the sum of the mass of conventional dust (quite habitual in construction) plus the mass of the NOAA. In this case, if the NOAA is not evidenced in SEM analysis, we recommend comparing the mass concentration with the OEL for Low Toxicity Dust proposed by Scaffold, 0.3 mg/m3.

- The measurement of mass concentration may be limited by the detection limit of the analytic technique, specially the gravimetric analysis, which would require long time of sampling.
- For fibers, unfortunately there is a lack of agreement on the measurement methods for these materials, either when manipulating the raw material, or during the use of matrices filled with fibers (e.g. in machining tasks). Following a precautionary approach, the recommendation is to control exposure to these materials using engineering controls or PPEs for specific tasks.

- The measurement of different metrics is a recommendation, e.g. combining the measurement of number concentration, mass concentration plus off line analysis of samples in order to have as much info as possible on the exposure scenario.

- Finally, as stated at the beginning of this guide, the presence of other contaminants in the workplace should not be forgotten; for instance, the potential exposure to substances as solvents, crystalline silica or asbestos may be quite more important in construction sites than the exposure to NOAAs.

Annex 1. Definitions

Agglomerate

Collection of weakly bound particles or aggregates or mixtures of the two where the resulting external surface area is similar to the sum of the surface areas of the individual components [ISO/TS 27687:2008, 3.2]

Aggregate

Particle 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. [ISO/TS 27687:2008, 3.3]

Bulk material

Material of the same chemical nature as the NOAA, at a non-nano scale. (ISO/TS 12901-2)

Exposure

Contact with a chemical, physical or biological agent by swallowing, breathing, or touching the skin or eyes. (ISO 12901-1:2011).

Health hazard

Potential source of harm to health [ISO 10993-17:2002, 3.7]

Health risk

Combination of the likelihood of occurrence of harm to health and the severity of that harm [ISO 10993-17:2002, 3.8]

Nanomaterial

material with any external dimension in the nanoscale (2.1) or having internal or surface structure in the nanoscale (ISO/TS 80004-1).

Nano-object

Material with one, two or three external dimensions in the nano-scale [ISO/TS 27687:2008]

NOAA

Nano-objects, and their aggregates and agglomerates greater than 100 nm (ISO/TS 12901-2

nanoscale

Size range from approximately 1 nm to 100 nm. [ISO/TS 27687:2008]

Particle

Minute piece of matter with defined physical boundaries [ISO/TS 27687:2008, 3.1]

Annex 2. References

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ASTM D7439 Standard Test Method for Determination of Elements in Airborne Particulate Matter by Inductively Coupled Plasma–Mass Spectrometry

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ISO/PDTS 12901-2 Nanotechnologies — Guidelines for occupational risk management applied to engineered nanomaterials — Part 2: The use of the Control Banding approach in occupational risk management

NIOSH (2009) Approaches to Safe Nanotechnology

Asbach et al (2012). NanoGEM Tiered approach for the assessment of exposure to airborne nanoojects in work-places.

NIOSH (2013) Bulletin 65. Occupational Exposure to Carbon Nanotubes and Nanofibers)

NIOSH 0500 Particulates not otherwise regulated, total

NIOSH 0600. Particulates not otherwise regulated, respirable

NIOSH 5040. Elemental Carbon

NIOSH 7300 Elements by ICP

NIOSH 7402 Asbestos by TEM

NIOSH 7501. Silica, amorphous

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Annex 3. Guide for a training program for operators

Next paragraphs provides an example of a training course on NOAAs risk assessment

Training on Risk Assessment

Objective

This document aims to provide guide on the contents for a training course in Risk Assessment to operators working with NOAAs in construction. It provides two levels of training, basic and advanced, depending on the responsibilities on occupational health and safety (OHS) of the operators.

Contents

The contents of a training course are summarized in the next table, indicating the level (basic/advanced) and if the material would be theoretical and/or practical.

Contents	Basic level	Advanced level	Theory (T) / Practice(P)
Exposure Scenarios	X	X	T
Hazards	X	X	T
Exposure Assessment			
Measurement methods		X	T
Measurement devices (simples)	X	X	T/P
Measurement devices (advanced)		X	T/P
Risk characterization		X	

Addressed to

Basic level may be addressed to operators working with NOAAs who could made limited measurement of OHS in specific processes.

Advance method may be addressed to operators with responsibilities on OHS, who could perform the risk assessment of the processes performed.

Delivered by

OHS experts with knowledge on Management of risks derived from NOAAs.