



**University of
South Australia**

Working Safely with Engineered Nanoparticles

Work Health and Safety Manual

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1. INTRODUCTION

Nanoscale materials are of significant scientific interest because some material properties can change at this scale. Such changes are challenging our understanding of hazards and our ability to anticipate, recognise, evaluate and control potential occupational health, safety and environmental risks.

Exposures to these materials may occur through inhalation, dermal contact or ingestion. Animal studies have indicated that low-solubility ultra fine particles might be more toxic than ones on a mass-for-mass basis. Because of their tiny size they can penetrate deep into the lungs and may translate to other organs following pathways not yet demonstrated in studies with larger particles.

Nanoparticulate forms of some materials show unusually high reactivity, especially for fire, explosion and in catalytic reactions.

Although there is limited specific guidance on evaluation and control of risks posed by nanomaterials, early research suggests that some controls used in conventional laboratory settings will work effectively for them.

2. PURPOSE AND SCOPE

The purpose of this document is to outline health and safety management requirements for the safe handling and disposal of nanoparticles utilised or generated during research projects. This document is primarily intended to provide guidance for small scale laboratory projects where there is a requirement to manage the safety concerns associated with the following:

- Engineered nanomaterials, that is intentionally created in contrast with natural or incidentally formed with dimensions of less than 100nm. This definition excludes biomolecules and nanoscale forms of radiological materials
- Nanoparticles, that is dispersible particles having two or three dimensions greater than 1nm and less than 100nm and which may or may not exhibit a size related property
- Unbound engineered nanoparticles (UNP) which are engineered nanoparticles that are not contained within a matrix that would be expected to prevent the nanoparticles from being separately mobile and therefore a potential source of exposure. An engineered nanoparticle dispersed and fixed within a polymer matrix, and incapable of becoming airborne would be 'bound', while such a particle suspended as an aerosol or in a liquid would be 'unbound'
- Precursors, intermediates and wastes used during, or resulting from synthesising such nanomaterials.

The requirements of this document apply wherever the above materials are used.

Note that information regarding the adverse effects caused by nanomaterials, particle measurement and control effectiveness is still evolving. This document will be updated and modified as necessary.

3. BACKGROUND

The ASTM International (Formerly American Society for Testing and Materials) Committee on Nanotechnology has defined a nanoparticle as a particle with lengths in two or three dimensions between 1 and 100 nanometers (nm). Nanoparticles can be composed of many different base materials and may be of different shapes including: nanotubes; nanowires; and crystalline structures such as fullerenes and quantum dots. Nanoparticles present a unique challenge from an occupational health perspective as there is a limited amount of toxicological data currently available for review. While the properties of engineered

nanoparticles can vary widely, existing studies are relevant to understanding the potential toxicity of nanoparticles. For example, it is known that a greater proportion of nanoparticles will deposit in the lungs compared with larger particles. It should also be recognised that some nanoparticles have the potential to agglomerate or aggregate which means in some cases deposition might either be in other areas of the respiratory tract or may not be inhaled at all. Further studies have also shown that some nanoparticles after initial exposure can be translocated to other areas of the body, although it is not well known how this might be influenced by the chemical and physical properties of the nanoparticles. Additional uncertainties are introduced by the difficulties in predicting human health effects based upon animal studies. There might also be the potential for greater dermal and gastro-intestinal uptake of nanoparticles compared to larger sized particles.

Animal studies have also indicated that some nanoparticles are more biologically active due to their greater surface area per mass compared with larger sized particles of the same chemistry when dose response relationships are expressed as mass. This greater surface area is a fundamental contributor to the greater chemical reactivity and utility of nanoparticles for industrial, commercial and medical applications, but it also raises concern about the potential for adverse health effects in staff exposed to nanoparticles. Other studies (see page 19 for references) have shown that existing exposure control technologies have been effective in reducing exposure to nanoparticles. As such, the accepted exposure control hierarchy was utilised in the development of this document.

4. REGULATIONS

At the present time there are no regulations that specifically address the safety implications of nanotechnology, although there is a growing body of literature which may inform the development of them in the future. In addition, there are no national or international consensus standards on measurement techniques for nanomaterials in the workplace. As with conventional chemicals, research with nanomaterials should be conducted in a manner that is safe and responsible with controls in place to minimise exposure to levels which are as low as possible. Therefore, all chemicals including nanomaterials must be transported, stored, used and disposed of in accordance with existing legislative requirements.

The SA WHS Act, 2012, requires the University to ensure, so far as is reasonably practicable, the health and safety of workers and provide a safe work environment, safe systems of work, and plant and substances in a safe condition. Also, the University must provide adequate facilities for the welfare of employees, provide information, instruction, training and supervision as necessary for health and safety, and monitor workplace conditions and health of workers.

The SA Dangerous Substances Act, 1979, and associated Regulations may have some applicability with respect to storage and transport requirements. Storage of all hazardous chemicals will be addressed by the SA WHS Regulations 2012 from 1 January 2014.

The South Australian EPA through the Environment Protection Act, 1993 and associated Regulations regulates the transportation, treatment, disposal and clean-up of hazardous waste. Nanomaterials that meet the definition of a hazardous waste may be subject to this legislation.

Currently, all legislative requirements applicable to conventional chemicals also apply to their nanoforms. However, the National Industrial Chemicals Notification Assessment Scheme in Australia (NICNAS) is actively addressing issues relating to the regulation of industrial nanomaterials in pace with widespread national and international activities. For further information regarding current legislative issues go to:
http://www.nicnas.gov.au/Current_Issues/Nanotechnology/Stakeholder_Consultation_2009_10/Nanotechnology_Discussion_Paper_2009.asp

5. GLOSSARY OF TERMS

Term	Definition
Agglomerate	Group of particles held together by relatively weak forces, including van der Waals, electrostatic and surface tension forces.
Aggregate	Heterogeneous particle in which various components are not easily broken apart.
Control Banding	A strategy that groups workplace risks into control categories based upon combinations of hazard and exposure information.
Hazard	A situation or thing that has the potential to harm people, property or the environment.
Health monitoring or surveillance	The monitoring of a person to identify changes in the person's health status because of a significant risk from ongoing exposure to a hazardous chemical.
High Efficiency Particulate Filter	Is a type of air filter that satisfies certain standards of efficiency such as those set by the United States Department of Energy (DOE).
Nanoparticle	In nanotechnology, a particle is defined as a small object that behaves as a whole unit in terms of its transport and properties. Nanoparticles are sized between 1 and 100 nanometres.
Nanotechnology	Areas of technology where dimensions and tolerances in the range of 0.1nm to 100nm play a critical role
Personal Protective Equipment	Equipment designed and usually worn to protect from harm.
Risk	The probability of harm occurring.
Safety Data Sheet (formerly known as a Material Safety Data Sheet)	contains information on the identity of a product and any hazardous ingredients, potential health effects, toxicological properties, physical hazards, safe use, handling and storage, emergency procedures, and disposal requirements specific to the chemical.

6. ENGINEERED NANOMATERIALS (AN OVERVIEW)

Engineered nanomaterials are designed with specific properties in mind. Engineered nanomaterials encompass nano-objects and nanostructured materials. The former are defined as materials with one (nanoplate), two (nanorod) or three external dimensions (nanoparticle) in the nanoscale. Examples of nanostructured materials are nanocomposites composed of nano-objects embedded in a solid matrix or nano-objects bonded together in simple random assemblies as in aggregates or agglomerates or ordered as in crystals of fullerenes or carbon nano-tubes.

Relatively simple nanomaterials presently in use or under active development can be classified in terms of dimensionality and the primary chemical composition. However, even simple nanomaterials are often coated and have complex chemical and physical structure. Any attempt to classify nanomaterials is highly artificial with many materials falling into several classification categories.

Carbon containing nanomaterials

- **Fullerenes**
Fullerenes are chemical entities which can be envisioned as a spherical cage built from carbon atoms chemically bonded to three nearest neighbours. The best known example is the soccer ball shaped C₆₀ fullerene. Multi-shell fullerene like nanoparticles referred to as carbon nano-onions, can range in size from 4-36 nm. Fullerenes are actively investigated for a wide range of potential applications including lithium-ion batteries, solar cells, fuel cells, methane storage materials, additives to plastics, oil and rubber, cancer and AIDS treatments.
- **Carbon black**
Carbon black consists of partially amorphous material, organised into spherical or non-spherical particles fused together to give aggregates, weakly interacting to form agglomerates and usually further organised into macroscopic pellets.
- **Carbon nanofibres**
Carbon nanofibres (CNFs) are cylindrical or conical structures that have diameters ranging from a few to 100 nm and lengths ranging from under micrometer to several millimetres. These materials are used as polymer additives, gas storage materials and catalysts supports.
- **Carbon nanotubes**
Carbon nanotubes (CNTs) represent a diverse family of carbon-based materials based upon a grapheme sheet rolled up in the form of a tube. CNTs can be made up of one sheet (single - walled) or several sheets (multi - walled). SWCNTs display metallic or semi-conductive properties depending on how the grapheme sheet is rolled up.
- **Graphene nanosheet**
Grapheme sheet is a single layer of graphite structure which can be described as a hexagonal network of carbon atoms bonded to its three nearest neighbours. Micromechanical cleavage is presently the main method of preparing this material.
- **Oxides**
Metal oxide nanostructured materials in the form of agglomerated and aggregated nanoparticles are used mostly as paint or sunscreen additives and often coated to achieve desired properties. Main production methods are spray pyrolysis, laser ablation and soluble phase synthesis.
- **Metals**
Gold nanoparticles are one of the most extensively studied. They are used in a number of applications such as optical markers and as thermal targeted cancer treatment agents in medicine. Silver nanoparticles are produced in largest volumes and are used in numerous applications ranging from wound dressings to washing machine disinfectant for its anti-microbial properties.
- **Quantum Dots**
Spherical nanocrystals from 1 – 10 nm in diameter composed of semi conductor materials often possess unique optical properties due to quantum effects, hence the name quantum dots. The number of atoms in quantum dots makes them neither an extended solid structure nor a molecular entity. The light emitted can be adjusted to the desired wavelength by changing the overall dimension.

Quantum dots are used, among other purposes, as fluorescent probes in diagnostic medical imaging and in therapeutics. They are used for these purposes due to their

optical properties and our ability to coat and modify their surfaces with peptides, antibodies, nucleic acids and other biologically important molecules.

- Organic polymeric nanomaterials
 - Dendrimers
These are a new class of controlled structure multi-branched polymers with nanoscale dimensions. They allow precise, atomic level control of the synthesis of nanostructures according to the desired dimensions, shape and surface chemistry.
 - Fibres
Nanofibres can be made of a wide variety of polymeric materials.
- Bio-inspired nanomaterials
These nanomaterials are generally those in which a biological substance is trapped, encapsulated or adsorbed onto the surface. They include a wide range of engineered assemblies of biological building blocks such as lipids, peptides and polysaccharides utilised as carriers for drugs, receptors, nucleic acids and imaging agents.

7. EXPOSURE PATHWAYS AND COMMON TASKS THAT COULD RESULT IN EXPOSURE

The potential routes of exposure for nanoparticles are inhalation, ingestion and dermal absorption. As with most particles in the workplace, inhalation is considered to be the primary route by which nanomaterials in the form of free, unbound, airborne particles could enter the bodies of staff. Ingestion could occur by swallowing the mucous that traps and clears particles deposited in the airways, by swallowing contaminated food or water, or by oral contact with contaminated surfaces or hand. Dermal absorption could occur when skin is exposed to nanomaterials during manufacture or use or by contact with contaminated surfaces. It is still under discussion if and to what extent nanoparticles in general are able to penetrate the intact skin and cause adverse effects. The effect of flexing the skin has yet to be fully explored as has the role of solvents in skin uptake. Nanoparticles or nanomaterials used in laboratory experiments will likely be in one of three forms: a powder, in suspension, or in a solid matrix. The form of the nanoparticles or nanomaterial will play a large role in the exposure potential.

For example, a nanoparticle in powdered form will present a larger inhalation hazard potential than a nanoparticle in suspension.

Some common tasks that present some potential for exposure include:

- Working with nanoparticles in suspension without gloves;
- Working with nanoparticles in suspension during pouring or mixing where agitation is involved;
- Generating nanoparticles in the gas-phase;
- Handling nanoparticle powders;
- Maintenance on equipment used to produce nanoparticles;
- Cleaning up spills or waste material;
- Cleaning dust collection systems; and
- Machining, sanding, grinding, or mechanically disturbing nanomaterial which can generate an aerosol.

In addition, Table 1 below outlines potential sources of exposure from specific nanoparticle synthesis methodologies.

Table 1: Potential Sources of Exposure for various Synthesis Methods

Process Synthesis	Particle Formation	Exposure Source	Exposure Route
Gas Phase	In Air	Leakage from reactor, especially if operated at positive pressure	Inhalation
		Product recovery from bag filters in reactors	Inhalation/Dermal
		Processing and packaging of dry powder	Inhalation/Dermal
		Equipment cleaning/maintenance (including reactor evacuation and spent filters)	Dermal (and inhalation during reactor evacuation)
Vapour Deposition	On Substrate	Product recovery from reactor/dry contamination of workplace	Inhalation
		Processing and packaging of dry powder	Inhalation/Dermal
		Equipment cleaning/maintenance (including reactor evacuation)	Dermal (and inhalation during reactor evacuation)
Colloidal	Liquid Suspension	If suspension is processed into a powder, potential exposure during spray drying to create a powder, and processing and packaging of the dry powder	Inhalation/Dermal
		Equipment cleaning/maintenance	Dermal
Attrition	Liquid Suspension	If suspension is processed into a powder, potential exposure during spray drying to create a powder, and processing and packaging of the dry powder	Dermal
		Equipment cleaning/maintenance	Dermal
Note: Ingestion would be a secondary route of exposure from all sources/activities from deposition of nanomaterials on food or mucous that is subsequently swallowed (primary exposure route inhalation) and from hand to mouth contact (primary exposure route dermal)			

8. METHODS OF EXPOSURE CONTROL

Exposure control measures and appropriate work practices are essential in work health and safety and the production and use of nanomaterials might involve various kinds of risks. Any exposure control program should take into consideration the material form (powder, in suspension/solution or embedded in a matrix). Also known hazards (such as flammability, toxicity, carcinogenicity or high reactivity) should be taken into account.

Elements of an exposure control program might include:

- Monitoring and recording the performance and effectiveness of control measures
- Monitoring workplace exposures to nanoparticles
- Developing the criteria and procedures for installing engineering controls (e.g. equipment enclosure, handling procedures, or guideline documents)
- Obtaining SDSs (where available) from manufacturers or suppliers of nanomaterials
- Describing the types of personal protective equipment that should be used;

- Developing procedures that include the frequency of changing or washing personal protective equipment (e.g. gloves, overalls)
- Maintenance of respirator/face mask, including storage, cleaning, records maintenance etc.
- Developing procedures for the cleaning and decontamination of equipment and enclosures etc.
- Seeking expert advice to help guarantee a safe working environment
- Undertaking research projects focused on nanotechnology-based health and safety issues
- Benchmarking and sharing practice know-how with other organisations using nanomaterials.

The established hierarchy of exposure controls for nanoparticles is consistent with existing exposure control options for hazardous chemicals. The exposure control methods are summarized in Table 2.

Table 2: Exposure Control Methods

Control Method Process,	Equipment, or Job Task
Elimination	Change of experimental design to eliminate the hazard
Substitution	Substitution of a high hazard with a lower hazard (chemical)
Engineering, Isolation, Enclosure	Ventilation (fume hood)
Administrative work practice procedures	Chemical hygiene plan policies
Personal Protective Equipment (PPE)	Gloves, goggles, clothing, respirators

**Table adopted from NIOSH document entitled, "Approaches to Safe Nanotechnology"*

The ideal control method involves the elimination of the hazard (i.e. automated process which eliminates occupational exposure potential), or the substitution of a less hazardous material. If the hazards associated with a specific nanoparticle research project cannot be controlled with elimination or substitution other control options should be considered. In practice, an appropriate combination of these strategies will provide the best approach to workplace exposure control.

In order to determine the best risk controls use the following university forms:

- **WHS12 - Chemical Process Risk Assessment and Control**

For a more detailed description of risk control options see below

Elimination

Effective process design can make a major contribution to preventing workplace exposures.

Substitution

Substitution is generally a very effective way to reduce risks to health and safety. While the unique chemical and physical properties/characteristics of nanoparticles are likely to limit possibilities for straightforward substitution of one nanoparticle type for another, it is this uniqueness which will likely determine their application and research and/or commercial usefulness.

Engineering Controls

The physical form of the nanoparticle will greatly influence the exposure potential. The inhalation exposure risk increases from nanoparticles in a solid matrix to nanoparticles in suspension to aerosolised nanoparticles. Additional factors that will influence the exposure risk include the quantity of material used or generated and the frequency and duration of exposure. Engineering controls that should be considered for use in laboratory scale nanoparticle research projects include source enclosure/isolation and local exhaust ventilation systems. Projects or processes involving the generation of nanoparticle aerosols and nanoparticles in suspension should be performed in a chemical fume hood, externally ducted biological safety cabinet, or glove box to limit the inhalation exposure potential. Maximum protection for the environment and the staff member will be achieved through using a Class III Biological Safety Cabinet (BSC) designed for work with highly infectious microbiological agents and for the conduct of hazardous operations.

In general source enclosure, should be effective for capturing airborne engineered nanomaterials, based upon what is known about nanoscale particle motion and behaviour in air.

In case of a leak from enclosed processes, primary nanoparticles can escape and disperse through the room. How much nanoparticle aerodynamic properties resemble those of gases is yet to be determined. But from known relationships, a 10nm particle is expected to have a diffusion coefficient considerably lower than a nitrogen or oxygen molecule of around 0.3 nm size.

In general terms, the choice of this control approach should include consideration of the level of risk involved for example:

- Lowest risk – Use general ventilation
- Less risk – Use local engineering control e.g. local exhaust ventilation (LEV)
- High risk – Use process containment
- Highest risk – Seek specialist advice

Figure 1 below shows how a process known as control banding can be applied when considering engineering risk controls for working with nanomaterials. This approach is useful for materials where there are no established Workplace Exposure Standards (WES) which is currently the situation with respect to all nanomaterials except Titanium Dioxide (TiO₂). Control banding is a qualitative strategy for assessing and managing hazards associated with chemical exposures in the workplace. In relation to nanomaterials a key component of control banding is the ability to categorise easily the toxicity of substances using information that is readily available, in this case material safety datasheet information for bulk size particles. This information links hazard groupings (A, B, C, D), hazard classification (e.g. whether a material is toxic, corrosive etc), risk phrases and guideline control level (8 hour Time Weighted Average) and control recommendations for each group. In the case of nanomaterials the variables that are considered are hazard group, level of dustiness of material used and amount used.

Figure 1: Application of Control Banding to Control Risk

Parameters		Amount Used	Low Dustiness	Medium Dustiness	High Dustiness
		Hazard Group	Hazard Group A		
Dustiness	Small	1	1	1	1
Amount Used	Medium	1	1	2	2
	Large	1	2	2	2
		Hazard Group B			
	Small	1	1	1	1
	Medium	1	2	2	2
	Large	1	3	3	3
		Hazard Group C			
	Small	1	1	2	2
	Medium	2	3	3	3
	Large	2	4	4	4
		Hazard Group D			
	Small	2	2	3	3
	Medium	3	4	4	4
	Large	3	4	4	4
		Hazard Group E			
		For all hazard group E substances, choose control approach 4			

Control Approach	
1. General Ventilation	■
2. Engineering Control	■
3. Containment	■
4. Specialist Advice	■

www.ilo.org

Source: www.ilo.org

Currently, for engineered nanoparticles and most particles of nanostructured materials there is limited understanding of the level of risk involved therefore in this environment where there is risk uncertainty, a precautionary risk management approach should apply based upon the As Low As Reasonably Achievable (ALARA) principle. For specific examples of engineering controls see Table 3 below.

Table 3: Examples of Enclosure Methods Used In the Nanotechnology Industry

Control	Details
Airlock & sealed containers for collecting nanomaterials from reactor.	Reactors operated in a vacuum. Collection done automatically in an airlock. Built in house.
Synthesis of nanomaterials in an enclosed environment.	Vented automatically before opening with a self cleaning burn cycle to eliminate residue. Fitted in fume hood.
Clean rooms with positive pressure differentials.	Positive pressure differentials that could be exhausted with immediate spaces of lower pressure between labs.
Portable peristaltic pumps to transfer liquid to waste containers.	Aim to prevent potential spills and reduce aerosolisation of material.
Use of distillation system for evaporating solvent from a colloidal dispersion within an explosion proof enclosure.	Enclosure designed with concern for the potential for nanomaterials to be explosive.
Using an in-line disperser device, which would open a bag of fine particulate feed stock and transfer the material to a chemical reactor.	Minimises handling of dry powder form. Mechanical disposal of used bag into a drum. Use in a HEPA filtered enclosure for an exposure and emission free process.
Remote control set up for the nanomaterial production equipment.	Allowed equipment to be operated in an isolated environment within a ventilation enclosure. Only trained and respirator equipped individuals would be allowed access to the room for cleaning or maintenance.
Use of safety alarms for nanomaterial production.	Within the close system were 2 sensors for changes in oxygen and pressure. If either sensor activated, the equipment shuts down which prevents the unintentional release of nanomaterials due to malfunction or accident.

If the use of closed containment options is not possible, then it is best to avoid the formation of dusts or aerosols. However, in some processes, it is impossible to avoid airborne release of dusts and aerosols. Source capture of these pollutants (e.g. by using local exhaust ventilation, (LEV) is then the method of choice to prevent airborne propagation of these products in the work environment.

Fume hoods are the most frequently used engineering control for the handling of nanomaterials. Where such hoods are used consideration should also be given to the use of exhaust filtration systems e.g. HEPA filters, non HEPA filters, wet scrubbers and sub-micrometre rated cartridge filters that block nanoparticles to less than 10 nm.

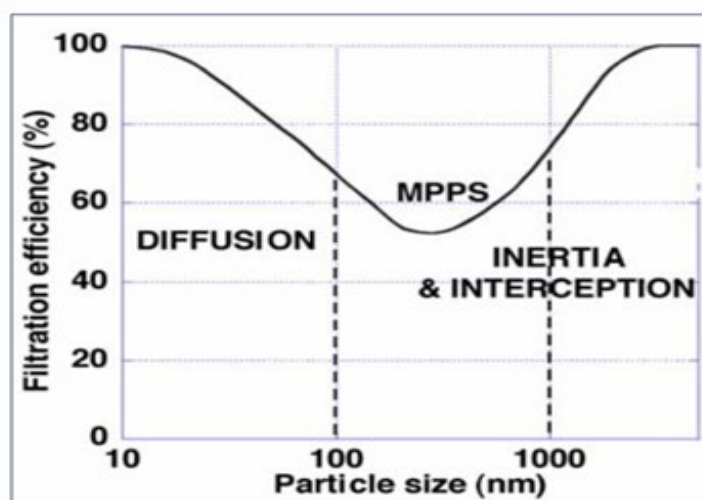
General ventilation by dilution in the work environment can draw contaminants outward, and if it is the only engineering control utilised, might allow significant exposure of staff to nanoparticles. If the use of LEV for open processes is not practicable, then it might be preferable to use displacement ventilation to reduce background levels, where fume is extracted at roof or ceiling level.

Filtration also plays an important role in the control of exposure to airborne particles. HEPA filters could be used in engineering control systems to clean air before returning it to the workplace, or before discharge to the atmosphere. Such filters are usually classified as mechanical filters. Current knowledge indicates that a well designed exhaust ventilation system with a HEPA filter should effectively remove nanoparticles. It should be noted however, that only a limited amount of work has been done to quantify the performance of filters against particles in the nanometre size range.

Filtration involves a number of mechanisms by which particles might be captured by filter fibres. Mechanical capture of particles can occur by (see Figure 2):

- Direct interception, where a particle follows the streamline and is captured if it comes into contact with a fibre;
- Inertial impaction, where capture is effected by deviation of a particle from the streamline by its own inertia;
- Diffusional deposition, where the combined effect of airflow and Brownian motion brings a particle into contact with a fibre;
- Gravitational settling.

Figure 2: Fractional Collection Efficiency versus Particle Diameter for a Mechanical Filter



(Source: Nanosafe2, 2008).

Current methods for certification of HEPA filters do not routinely require testing at particle sizes below 100 nm. The US Department of Energy's standard, DOE HEPA Filter Test Program, an internationally recognised standard, requires that each filter is tested at an aerosol diameter of 300 nm aerodynamic diameter and that the particle collection efficiency is greater than 99.97%. Given the dimensions and physical properties of nanoparticles, an approved HEPA filter should have a filtration efficiency greater than 99.97% for most nanoparticles.

Administrative Controls

Administrative controls that should be considered and/or implemented during a laboratory scale nanoparticle research project focus on employee training and proper work procedures. Such controls constitute an additional approach to supplement engineering approaches but are not a substitute for engineering approaches. Some administrative controls that should be considered include:

- Providing known information to workers and students on the hazardous properties of the nonmaterial precursors or products;
- Education/training of staff and students on the safe handling of nanomaterials;
- Restricting access to areas by using signs or placards to identify areas of nanoparticle research;
- Transport dry nanomaterials in closed containers;
- Handle nanoparticles in suspension on disposable bench covers;
- Always perform nanoparticle aerosol generating activities in a fume hood, externally ducted biological safety cabinet, or glove box; and
- Clean the nanomaterial work area daily at a minimum with a HEPA-vacuum or wet wiping method.
- Modification of work practices.
- Minimising the number of exposed staff.
- Ensure effective personal hygiene measures.
- Use of preventive maintenance, which minimises the risk of unscheduled interruption of production while assuring safer operations.
- Good housekeeping.

PPE and Laboratory Protection

Monitoring the work environment will determine the effectiveness of control approaches described above. Evaluation findings will inform about whether personal protective equipment (PPE) is required.

General PPE recommendations for working with nanomaterials are consistent with PPE recommendations for working with chemicals in the laboratory. PPE recommendations include:

- Wear latex or nitrile gloves when handling nanoparticle powders and nanoparticles in suspension (double gloving is preferred and glove changes should be performed frequently);
- Wear chemical splash goggles when working with nanomaterials in suspension or dry powdered form;
- Wear lab coats. Lab coats should be laundered on a periodic basis. Do not take lab coats home for laundering;
- Wear commercially available arm sleeves in situations where dermal contact with nanoparticles in powder or in suspension are expected;
- Wear closed-toe shoes (if necessary cover shoes with commercially available booties); and
- Consult with your Divisional safety consultant or the Safety & Wellbeing team regarding the use of respiratory protection if an inhalation exposure hazard exists.

9. EXPOSURE MONITORING

Traditional methods of air sampling that measure mass are not appropriate for nanomaterials. Measurement methods that count nanoparticles or measure surface area are being developed for nanomaterials. If you have concerns about particle release in your laboratory, please contact the Safety & Wellbeing team for an evaluation and possible air monitoring.

10. FIRE, EXPLOSION AND CATALYSIS PREVENTION AND CONTROL

The same principles applying to the management of fine powders, dusts or dusty materials should be considered for nanomaterials, with particular care taken in the case of easily oxidisable metallic dust. However, the effectiveness of methods for nanoparticle fire, explosion and catalysis prevention and control is yet to be evaluated.

Explosion protection measures have been described for dust dispersions and for hazardous quantities of larger sized materials and can be potentially applied to the handling of potentially explosive nanoparticles. For the handling of flammable nanoparticles, following these types of measures is also recommended. For reactive or catalytically active nanoparticles, contact with incompatible substances should be prevented.

Fire prevention should also take into account existing regulations, especially electrical requirements regarding intrinsic safety.

The selection of an extinguishing agent should consider the compatibility or incompatibility of the material with water. Some metallic dusts react with water to form, among other things hydrogen. Chemical powder extinguishers should be made available to extinguish burning metallic dust powders.

When extinguishing these types of fires care should be taken to avoid significant air movement since this can have the effect of putting the metallic dust in suspension, thereby increasing the risk of deflagration (subsonic combustion that usually propagates through thermal conductivity) (hot burning material heats the next layer of cold material and ignites it). Most "fire" found in daily life, from flames to explosions, is technically deflagration. Deflagration is different from detonation (which is supersonic and propagates through shock).

When working with potentially explosive nanomaterials there are reports of:

- Anti-static shoes and mats being used in areas where the materials are handled. Such shoes reduce the build-up of static charge, which could potentially ignite the materials.
- A distillation system for evaporating solvent from a colloidal dispersion being housed within an explosion-proof enclosure. This enclosure was designed with concern for the potential for those particular nanomaterials to be explosive.

11. STORAGE and TRANSPORT

Consideration should be given to special protective measures to conserve the products and to ensure workplace health and safety. Suitable records should be kept of all material kept on site using *Chemgold3*.

Storage containers for nanomaterials and particles of nanostructured materials should accommodate the different granulometric characteristics and reactivity of the particles. The fine granulometry of the materials might result in long settling times and re-dispersion. Any containers should be tightly sealed to avoid leakage or contamination of the workplace during transport or transfer.

The small size of nanoparticles (which often tend to agglomerate), provides a very large surface area in contact with the surrounding air, thereby facilitating chemical reactivity of the

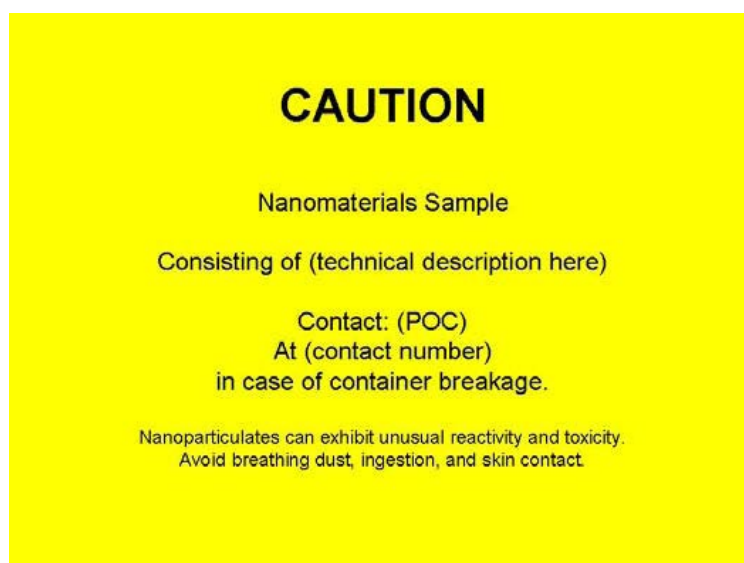
particles. Depending on the product that is being stored a variety of procedures can be used to prevent deterioration of the product and the risk of fire or explosion. Possible storage solutions include storage in inert gas or in anhydrous conditions. To avoid the potential for oxidation or even explosion in the case of certain metals, nanoparticles often need to be protected from the air. In other conditions it might be possible to surround the nanoparticles in a protective layer of salts or various polymers. Such layers can be removed before using the product.

Nanomaterials removed from furnaces, reactors, or other enclosures within laboratories should be put in sealed containers for transport to other locations. If nanomaterial product from a reactor is bound or adhered to a substrate, the substrate may be removed and put in a transport container. If the nanomaterials product is unbound and easily dispersible (such as in CNT synthesis using aerosolised catalyst), the removal from a reactor should be done with supplementary exhaust ventilation or a glove bag connected to a HEPA vacuum.

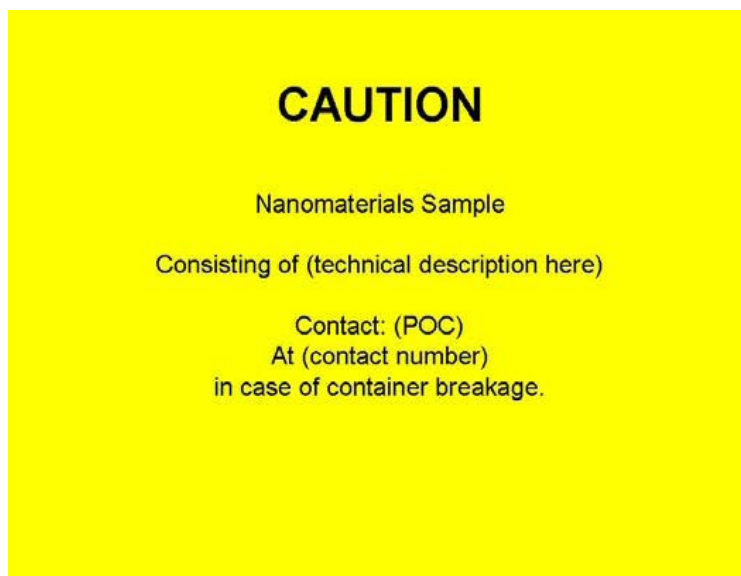
Transportation of nanomaterials to off-site locations and other universities or laboratories outside of UniSA may be covered by EPA regulations. Improper packaging and/or transportation could lead to regulatory action and fines.

Any nanomaterial that is required to be transported off-site that meets the definition of a dangerous good or hazardous chemical should be packaged using an inner and outer container. The inner container should be tightly sealed to prevent leakage. It should have a secondary seal, such as tape or wire to prevent leakage. The outer package should be filled with a shock absorbing material that can protect the inner container from damage and absorb liquids that might leak from the inner container.

Any inner package containing dry particulates should be labelled as follow:



Any inner package containing non-particulates should be labelled as follows:



Contact your WHS consultant or the Safety & Wellbeing team for procedures to follow for shipping or transporting materials.

For materials being transported on-site:

- Assess and record the hazards posed by the materials following an approach that takes into account the form of the materials e.g. free particles versus fixed on substrate.
- Use packaging and labelling that is consistent for off-site shipment or packaging that affords an equivalent level of safety.
- Include the following in the transportation package:
 - The results of any risk assessment.
 - An SDS if available. If not available the researcher should supply material specific knowledge.
 - Notify the receiving area of the incoming package.

12. WASTE DISPOSAL, DECONTAMINATION, AND SPILL PROCEDURES

Waste Disposal Procedures

There are no specific EPA regulations that apply to nanomaterial waste. It is important to take a cautious approach when handling nanomaterial waste that is defined as hazardous however. The following waste management guidance applies to nanomaterial-bearing waste streams consisting of:

- Pure nanomaterials (e.g. carbon nanotubes)
- Items contaminated with nanomaterials (e.g. wipes/PPE)
- Liquid suspensions containing nanomaterials
- Solid matrices with nanomaterials that are friable or have a nanostructure loosely attached to the surface such that they can reasonably be expected to break free or leach out when in contact with air or water, or when subjected to reasonably foreseeable mechanical forces.

The guidance does not apply to nanomaterials embedded in a solid matrix that cannot reasonably be expected to break free or leach out when they contact air or water, but would apply to dusts and fines generated when cutting or milling such materials.

Nanomaterial – bearing waste streams should not be placed into the regular rubbish or down the drain.

Since the toxicology and environmental fate of nanoparticles is still largely unknown, all nanoparticle waste (solid material and liquids) should be conservatively managed as hazardous waste. This also includes any debris (i.e. PPE, plastic) that has become heavily contaminated with nanoparticles.

- Do not put material from nanomaterial-bearing waste streams into the regular waste or down the drain.
- Do not permit nanomaterial-bearing wastes to be transferred off-site to researchers' home institutions for disposal.
- Characterise and manage nanomaterial-bearing waste streams as hazardous or non-hazardous waste.
- Package nanomaterial – bearing wastes in containers that are compatible with the contents, in good condition, and that afford adequate containment to prevent the escape of nanomaterials.
- Where possible, segregate nanomaterial waste from other waste during management and disposition.
- Label the waste container with a description of the waste and the words '**contains nanomaterials**'. Include available information characterising known and suspected properties.
- Collect paper, wipes, PPE and other items with loose contamination in a plastic bag or other sealable container and store in a fume hood. When the bag is full, remove from the hood and place into a second plastic bag or other sealed container. Label the outer bag with a waste label.
- Keep an inventory of all nanomaterial waste that is transferred off-site. This should contain a description of the waste, quantity and means and location of final disposition.

Refer to the university procedure [Safe Management of Chemicals](#) for more information regarding the management of hazardous waste.

If there are further questions, call your WHS consultant or the Safety & Wellbeing team for a waste determination.

Decontamination and Spill Cleanup Procedures

Fume hood or enclosure surfaces should be wet-wiped after each use or at the end of the day. Alternatively use of bench liners would also prevent contamination. Bench liners, if contaminated, must be disposed of as hazardous waste. Do not dry sweep or use compressed air for cleanup.

Depending upon the quantity of nanomaterials in use in the lab, each lab should consider having the following items in a nanoparticle spill kit: barricade tape, nitrile gloves, disposable P100 respirators, adsorbent material, wipes, sealable plastic bags, walk-off mat (e.g. Tacki-Mat™). Minor spills or small quantities of nanomaterial can be wiped up using wet wiping for solid material and absorbent wipes for suspensions. Larger spills can be cleaned using a vacuum cleaner specially fitted with a HEPA filter on the exhaust to prevent dispersion into lab air. A reliable model of HEPA vacuum is the Nilfisk GM80CR. A log of HEPA vacuum use should be maintained so that incompatible materials are not collected on the HEPA filter. HEPA filter change-out should be done in a fume hood.

All spills involving nanoparticles should be treated like a hazardous material spill and cleaned up immediately. If the spill presents an emergency situation, evacuate the area and dial 88888 (FM Assist) or 000 for Emergency Services. If the spill does not present an emergency situation but assistance is needed with clean-up, contact your local laboratory supervisor/technician.

For more detailed information regarding spill response procedures please refer to the university procedure **Safe Management of Chemicals**.

13. HEALTH MONITORING

Health monitoring/surveillance should be considered where there is risk of exposure to nanoparticles and where it has been demonstrated that there is a relationship between exposure to the substance and a measurable biological indicator.

If the work with nanoparticles is associated with the use, handling, generating or storage of a hazardous chemical, and ongoing exposure to that chemical represents a significant risk to health, then health monitoring must be considered. In such circumstances health monitoring is mandatory if the hazardous chemical is listed in the table shown in Appendix E of the SA Approved WHS Code of Practice, *Managing the Risks of Hazardous Chemicals in the Workplace*.

Given that exposure to very low concentrations of nanoparticles might be widespread, measurable changes in biological indicators from baseline levels, rather than a comparison of body burden with the Biological Exposure Index (BEI), might be the most appropriate parameter to examine. The use of health surveillance in this context is an indicator of whether exposure is occurring, rather than determining that levels of exposure are safe. Due to the currently limited capability for measuring airborne concentrations of nanoparticles, the use of biological indicators might be a useful approach in evaluating the effectiveness of control measures.

The problem at the moment is that the current body of knowledge about the possible health effects of occupational exposures to engineered nanoparticles is not sufficient to support the determination of specific health surveillance to determine preclinical changes associated with exposure to them. At this time only a few types of engineered nanoparticles have been studied and a clear and consistent picture of the relevant endpoints has yet to emerge.

14. CLASSIFICATION OF LABORATORIES

Every effort should be made to classify laboratories using or producing engineered nanoparticles on the basis of the Decision Tree for Laboratory Type Determination (Appendix 1). This classification tool has been designed to assist researchers implement appropriate risk controls based upon the type of materials used or produced and the processes in place for using or producing them (Appendix 2).

In applying this decision tree, laboratories can be classified as **Nano 1 – low hazard**, **Nano 2 - medium hazard** or **Nano 3 – high hazard**. This classification process is similar to the process applied to laboratories using radio isotopes or hazardous biological materials.

15. FURTHER INFORMATION

Please contact the Safety & Wellbeing team on 8302 2459. Other sources of information are listed below:

Websites that post current information about nanotoxicology

International Council on Nanotechnology at: <http://icon.rice.edu>. Up-to-date postings on nanotoxicology worldwide.

National Institute for Occupational Safety and Health (NIOSH) Nanotechnology Topic Page at www.cdc.gov/niosh/topics/nanotech

National Nanotechnology Infrastructure Network (NNIN) at: <http://www.nnin.org/>

National Centre for Biotechnology Information (NCBI) Pub Med. Can search for articles on nanoparticle toxicity.]

Safe Nano (UK) [excellent regularly updated site on health and safety risks of nanotechnology with comments by toxicologists and regulators]

<https://www.iom-world.org/research/our-work/exposure-to-nanomaterials/>

[Safe Work Australia](#) Nanotechnology

Websites that can be searched for current information on nanomaterials

International Council on Nanotechnology at: <http://icon.rice.edu>. Up-to-date postings on nanotoxicology worldwide. Can search for nanoparticle toxicity by type and time period.

National Centre for Biotechnology Information (NCBI) Pub Med. Can search for articles on nanoparticle toxicity.

National Institute for Occupational Safety and Health (NIOSH) Nanotechnology Page at <http://www.cdc.gov/niosh/>. [Click on Nanotechnology Home Page – see particularly Progress Toward Safe Nanotechnology in the Workplace, Publication No. 2007-123.]

University websites with guidelines for working with nanomaterials

DOE Nanoscale Science Researcher Centres. Approach to Nanomaterial ES&H (June 2007). <http://science.energy.gov/>

University of Massachusetts-Lowell, Department of Work Environment, Centre for High Rate Nanomanufacturing. Interim Best Practices for Working with Nanoparticles. November 2007. MIT. Potential Risks of Nanomaterials and How to Safely Handle Materials of Uncertain Toxicity.

Review articles or reports about nanotoxicology

Borm P JA, Robbins D, Haubold S et al. The potential risks of nanomaterials: a review carried out for ECETOC. Part Fibre Toxicol 3:11-35 2006.

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- f. SA WHS Regulations 2012
- g. Current Intelligence Bulletin 60, Interim Guidance for Medical Screening and Hazard Surveillance for Workers Potentially Exposed to Engineered Nanoparticles, NIOSH, 2009
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17. RELEVANT LEGISLATION, PROCEDURES AND FORMS

[SafeWork SA Resources](#)—WHS legislation and Approved Codes of Practice:

- Work Health and Safety Act 2012
- Work Health and Safety Regulations 2012
- How to Manage Work Health and Safety Risks
- Managing Risks of Hazardous Chemicals in the Workplace.

Safe Work Australia [Nanotechnology Publications](#)

University Documents/Forms

For further advice on managing risks in university workplaces, including procedures, guidance, forms and training courses, please visit the Safety & Wellbeing website.

[Safety & Wellbeing website](#)

- Managing Workplace Health and Safety Risks
- Safe Chemicals Management
- WHS2 – General Risk Assessment
- WHS12 – Chemical Process Risk Assessment and Control
- WHS60 – Chemical Spills Guides

[Online Hazard/Incident Reporting & Investigation System](#)

18. DOCUMENT CONTROL

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APPENDIX 1: DECISION TREE FOR LABORATORY TYPE DETERMINATION

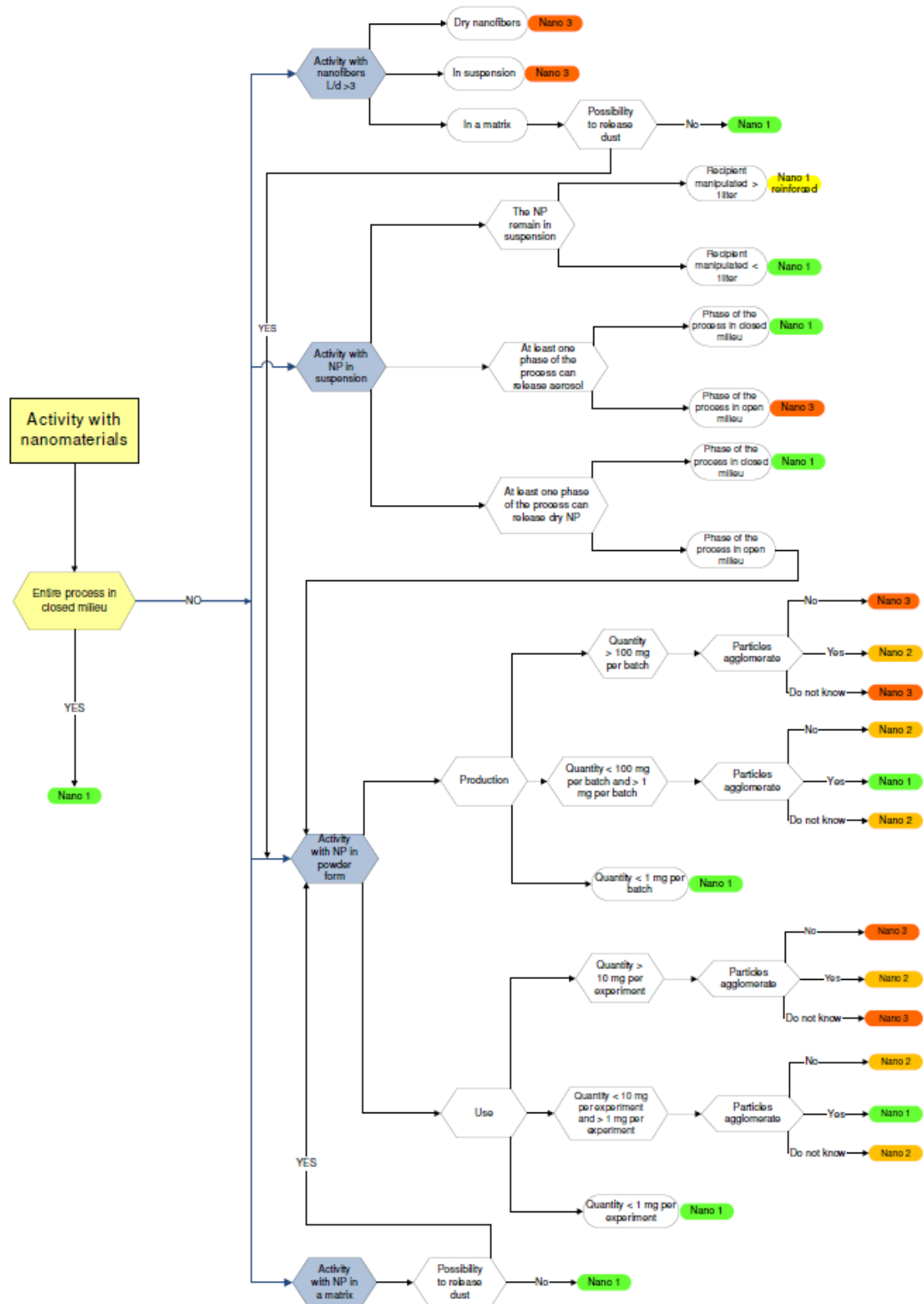


Figure 2

Source

Management of nanomaterials safety in research environment

Particle and Fibre Toxicology 2010, 7:40 doi:10.1186/1743-8977-7-40

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APPENDIX 2: RISK CONTROL OPTIONS FOR NANOSAFE LABORATORY CLASSIFICATIONS

Measures			Laboratory		
			Nano 1	Nano 2	Nano 3
Technical	Ventilation	Chemistry lab type (renewal without recycling 5-10 X/h)	x	x	x
		With at least sealed F7 filter (maintenance!) for exiting air			x
		Low pressure in the room	x	x	> 20 mPa
		Capture at source		x	x
	Floor	Flooring	Tiling or linoleum		Resin
	Manipulation under fume hood	Optional	x (1)		
		Compulsory		x	x
	Access restriction	Restricted (magnetic card access control system)		x	x
		Regular lab access control (laboratory key)	x		
		Evidence about exposed people + board to record presence			x
	SAS entrance and exit	Double SAS (if > 100 g ultrafine particles)			x
		Simple SAS (if < 100 g ultrafine particles)		Light SAS	x
		Safety shower			x
Use of vacuum cleaners	Asbestos type	x	x	x	
Figure 1	Housekeeping type	Forbidden			

Measures			Laboratory		
			Nano 1	Nano 2	Nano 3
Organizational	Restricted access	Authorized persons only		x	x
		Only activities nano in the laboratory			x
	Training	Written working procedures	x	x	x
		Basic training	x	x	x
		Continuous training		x	x
	City/laboratory clothes separation			x	
	Conditioning of material contaminated by nano	Toxic (trash bin for toxic)	x	x	x
		Double bag for toxic waste (100 microns thickness)	x	x	x
		Storage of bags in a sealed container	x	x	x
	Elimination of nano substances and products	Liquid waste	Double packaging		
		Solid waste	Double packaging		
Waste and PPE evacuation	Domestic waste treatment channel	Forbidden			
	Special waste treatment channel	x	x	x	
Transports of "nano-objects"	Simple packaging	Forbidden			
	Double packaging	x	x	x	

Measures			Laboratory		
			Nano 1	Nano 2	Nano 3
Personal	Eyes protection	Safety glasses	x		
		Laboratory mask or close fitting safety goggles		x	x
	Respiratory organs protection	Mask with assisted ventilation			x
		FFP3 mask		x	if < 2 h
	Body protection	Overall with hood - Tyvek style			x
		Non-woven lab coat		x	
		Simple lab coat	x		
		Overshoes		x	x
	Hands protection	2 pairs of adapted gloves		x	x
		1 pair of adapted gloves	x		

Measures			Laboratory		
			Nano 1	Nano 2	Nano 3
Cleaning	Who ?	External personnel	x		
		Specially trained external personnel		x	
		Only laboratory personnel			x
	How ?	Wet cleaning only	x	x	x
		Broom	Forbidden		
		Housekeeping type vacuum cleaner	Forbidden		
	Protective equipment	Regular	x		
		The same as for laboratory personnel		x	x
	Supervision	Laboratory responsible		x	x
		Without supervision	x		

Source

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APPENDIX 3: ILLUSTRATION OF PPE FOR A NANO 3 LABORATORY



SOURCE

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