northumbria UNIVERSITY NEWCASTLE

Guidance on Safe Use of Nanomaterials

Reviews and Revisions

Action	Date	Reason	Reviewer
Draft Document	01/10/15		Lesley Salkeld
Link to HSE guidance added. Waste disposal clarification.	07/10/15	http://www.hse.gov.uk/pubns/books/hsg272.pdf	Ange Ferguson
Updated to include specific University requirements	23/3/16	Ready for issue	LRounds

Contents

1. Introduction

This guidance is intended to assist Principle Investigators/ Academics in the creation or manipulation of nanomaterials in undertaking risk assessments and developing control strategies that will ensure, so far as reasonably practicable, that staff and students are not exposed to any unnecessary risk in relation to the use of nanomaterials.

2. Guidance

The **UK Nanosafety Partnership Group** has recently published a document that summarises the current understanding and guidelines for working safely with nanomaterials **'Working Safely with Nanomaterials in Research and Development'**.

The **Control of Substances Hazardous to Health Regulations 2002** (as amended) (**COSHH**) apply to workplace activity involving particulate nanomaterials and require that employees are protected from harmful substances in the workplace. The **University COSHH code of practice** can be found here.

The **Dangerous Substances and Explosive Atmospheres Regulations 2002** (**DSEAR**) also apply to nanomaterials as the chemical and physical properties of some particulate nanomaterials means that they can give rise to the risk of a fire or explosion. **DSEAR** requires that risks from dangerous substances are assessed and eliminated or reduced so far as reasonably practicable. The **University DSEAR code of practice** can be found here.

The **Registration, Evaluation, Authorisation & Chemicals Regulation** (**REACH**) are the key European legislation which regulates chemical substances, including nanomaterials.

3. Exposure Risk and Hazardous Properties of Nanomaterials

Exposure to some particulate nanomaterials can occur by ingestion, skin penetration or inhalation, with the resultant adverse effects depending upon the size, dose and toxicity of the nanoparticle. Toxicity investigations indicate that the effects appear to be related to the total surface area of the particles. The exposure potential will be directly related to the structure and form of the nanomaterial. The exposure risk to particles encapsulated in a matrix or strongly adhered to a substrate will be lower than that from 'free' aerosolised, particulate nanomaterials.

Some particulate nanomaterials may have inherent hazardous properties and may be classified as carcinogens or mutagens. They may also have other hazardous properties such as toxic, harmful etc., as classified in the Chemicals (Hazard Information and Packaging for Supply) Regulations 2002. It is generally agreed that the current knowledge regarding the toxicity of particulate nanomaterials is incomplete and current safety data sheets may not adequately contain all the required safety information.

Fire and explosions from dust clouds of organic, inorganic and metallic substances are well known. The potentially higher surface area and reactivity of particulate nanomaterial powders means that this safety hazard should be seriously considered and addressed in risk assessments.

In general, the potential risks to health from particulate nanomaterials can be reduced by safe handling and control of exposure. Whilst no single piece of guidance can provide a definitive, step-by-step approach to safe handling of all nanomaterials in all circumstances, there are a number of general and specific best practice guides that can be used in most applications.

The general approach for safe handling and control of particulate nanomaterials is similar to that for other types of chemical substances and seeks to:

- Identify the hazards and assess the risks.
- Decide what precautions are needed.
- Prevent or adequately control exposure.
- Ensure that control measures are used and maintained.
- Monitor the exposure.
- Carry out appropriate health surveillance.
- Prepare plans and procedures to deal with accidents, incidents and emergencies; and
- Ensure employees are properly informed, trained and supervised.

There are currently no Workplace Exposure Limits specifically for nanoparticles. The information contained within the Material Safety Data Sheet [MSDS] for a substance in conventional micron size, cannot be regarded as relevant for the same substance in the nano range. The supplier of nanoparticles should supply the information required for a risk assessment.

The exposure risk to particles encapsulated in a matrix or strongly adhered to a substrate will be lower than that of free aerosolised particulate nanomaterials.

4. Definitions

Nanomaterial: as defined by the European Commission (EC, 2011): a natural, incidental or manufactured material containing particles (nanomaterials), in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm. In specific cases and where warranted by concerns for the environment, health, safety or competitiveness, the number size distribution threshold of 50% may be replaced by a threshold between 1 and 50%." By derogation, fullerenes, graphene flakes and single wall carbon nanotubes with one or more external dimensions below 1 nm should be considered as nanomaterials.

Within this definition of nanomaterials, the terms "particle", "agglomerate" and "aggregate" are defined as follows:

"Particle" means a minute piece of matter with defined physical boundaries;
"Agglomerate" means a collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components;
"Aggregate" means a particle comprising strongly bound or fused particles.
Nanofibre: Nano-object with two similar external dimensions in the nanoscale and the third dimension being significantly larger [ISO/TS 27687, def. 4.3].
Nano-object: material with one, two or three external dimensions in the nanoscale [ISO/TS 27687, def.2.2].
Nanoparticle: Nano-object with all three dimensions in the nanoscale [ISO/TS 27687, def. 4.1].

Nanoplate: Nano-object with one external dimension in the nanoscale and the two other external dimensions significantly larger [ISO/TS 27687, def. 4.2].
Nanoscale: size range from approximately 1 nm to 100 nm [ISO/TS 27687, def. 2.1].
Nanotube: hollow nanofibre [ISO/TS 27687, def. 4.4].
Particulate nanomaterial(s): nanomaterials that consist of nano-objects such as nanoparticles, nanopowders, nanofibres, nanotubes, nanowires, as well as aggregates and agglomerates of these materials either in their original form or incorporated in materials or preparations, from which they could be released.

5. Assessing the risks of working with Nanomaterials

As required with any research procedure, a risk assessment must be carried out prior to working with nanomaterials. The principal investigator will complete appendix 1 with as much information as possible and send to the Central Health & Safety Section who will assign the Risk level.

The use of any nano particle or Carbon Nano Tube (CNT) must be approved in writing by the Central Health & Safety Section who will specify the risk level (1-4) (see appendix 2) and the expected control measures. These will be documented in a COSHH risk assessment by the Principal Investigator/Academic responsible for the work.

The subsequent COSHH risk assessment must be a suitable and sufficient assessment of the risk to health caused by the work and should follow the University risk assessment strategy taking into account:

- ***Where*** are nanomaterials likely to be ***generated/synthesised*** etc.?
- Is ***exposure*** likely?
- ***Who*** is likely to be exposed?
- Can the exposure be ***prevented***?

If the exposure cannot be prevented, estimate the ***potential level of exposure***.

- *Is the particulate classified as a carcinogens, mutagens, teratogens and reproductive toxicants (CMTR) or skin/respiratory sensitizer?*

If the bulk or parent version (if it exists) of a nanomaterial is already classified as a CMTR or skin/respiratory sensitizer, there is a high likelihood that the nanoparticulate form will also demonstrate this toxic potential. Indeed due to their characteristically large surface area, the nanoparticulate form may exhibit comparatively greater activity than that of the bulk compound and should therefore be considered as potentially hazardous.

- *Is the nanomaterial composed of reactive metal(s)? Is the nanomaterial photo reactive? Does the nanomaterial have a highly charged surface?*

The presence of reactive metals is known to drive the toxicity of various complex particulate mixtures such as welding fumes. Therefore a nanomaterial possessing a significant proportion of such metals (e.g. large amounts of catalyst remaining within unrefined carbon nanotubes) could be regarded as having a potentially hazardous component.

When exposed to light, photocatalytic nanomaterials (e.g. certain forms of TiO2) can release free radicals that may generate toxicity by causing inflammation, oxidative damage and genetic damage

The surface charge of a nanomaterial is known to influence its propensity to agglomerate/aggregate, but it can also play a prominent role during cellular uptake or interactions with charged molecules such as proteins.

These attributes, singly or collectively, can contribute to the surface activity of a nanoparticle and are potential drivers of toxicity. The combination of high surface area and high reactivity may lead to the formation of a "double hazard"

- *Is the nanomaterial highly acidic/basic?*

If contact with a nanomaterial leads to a substantial pH change away from the normal range of the biological environment at a point of contact (e.g. skin or site of deposition within the lungs), this could cause adverse effects. These could include local effects such as skin irritation/corrosion or, for example, cell death within the lungs leading to inflammation/oedema/fibrosis.

- *Is the nanomaterial soluble?*

The solubility of a nanoparticle can have a positive and/or negative influence on its propensity to cause harm. Specifically if a particle is soluble in an aqueous environment but *does not* release toxic components, a progressive reduction/removal of dose will occur as the particle dissolves. However if the particle releases reactive or cytotoxic components such as toxic ions as it dissolves, its toxicity could increase.

An attribute of nanoscale materials is the potential for changes in physico-chemical characteristics, including solubility, compared to the bulk material; e.g. bulk silver is insoluble, but nano-silver releases free silver ions in aqueous solutions by dissolution. Therefore the contention that since the bulk material is insoluble, the nanomaterial is also insoluble is not necessarily correct. As such when considering the hazardous nature of a material, it is pertinent to consider both the insoluble (particle) and soluble components in the hazard assessment.

- *Is the nanomaterial fibrous (i.e. possess a high aspect ratio)?*

There is concern that fibrous nanomaterials such as carbon nanotubes or nanowires may represent a similar danger to health as hazardous fibres such as asbestos, refractory ceramic fibres or certain man-made vitreous fibres (MMVFs). The basis for this is the morphological similarity between these fibres and newly developed High Aspect Ratio (fibrous) Nanomaterials (HARN).

- *Does the nanomaterial possess a low aerodynamic diameter yet one or more high aspects?*

As the basis for respiratory toxicity from fibres requires a low aerodynamic diameter for penetration into the distal airways yet a large physical aspect (e.g. fibre length or particle diameter), it is worth bearing in mind that other shapes, not just fibres, can possess these properties. Plate-like structures such as grapheme/graphite platelets can have a very large (>15 µm) diameter yet be very thin (<100 nm) and as such possess a low aerodynamic diameter, allowing them to be respirable. In addition, low density 'fluffy' bundles of fibres, often seen with carbon nanotubes, may also, due to their very low density, possess the potentially hazardous mix of low aerodynamic diameter with one or more high aspects, making clearance from the distal lung difficult.

Work activities involving nanomaterials which require special attention when assessing exposure include:

- Weighing and handling of particulate nanomaterials.
- Manufacturing of nanoparticles (especially production of nanoparticles in a gas phase) and associated maintenance of equipment.
- Machining of materials containing nanoparticles (e.g. sawing, polishing, grinding).
- Tensile testing of nanoparticles.
- Spraying of liquids containing nanoparticles, causing aerosols.
- Processing nanoparticles in a liquid where a high energy output is involved.
- Waste disposal of all types of nanomaterials.

In making the assessment, careful attention should be paid if there is a possibility of inhalation of the particulate nanomaterials.

In all cases, the assessment should be recorded on the COSHH Assessment form and reviewed if circumstances change or new information becomes available on the hazard of the nanomaterials being used.

Where information or previous experience is lacking particular efforts should be made to search for and collect as much information as possible on the materials and similar applications. The starting point for this will usually be the suppliers Material Safety Data Sheet or technical specification.
The risk assessments should be regularly reviewed, at least annually to ensure they remain suitable and sufficient.

6. Control of exposure to particulate Nanomaterials

When carrying out the risk assessment and identifying the appropriate risk control strategies the following hierarchy of controls must be applied:

- Consider first if there is any way of avoiding manipulation of nanomaterials, particularly in powder form.
- Consider the form which the nanomaterial is in and any manipulations within the process which will generate free nano powders or aerosols of solutions containing nanomaterials.
- In the case where the nanomaterial is in solution avoid aerosol production and where this is not possible; contain the process in a HEPA filtered fume cupboard/MSC (HP14).
- Seek to minimise the quantities of nanomaterials handled, the frequency and duration of use and the number of people potentially exposed.
- Employ handling methods that reduce the chance of the material becoming airborne- keep the material wet or damp.

Control Measures for inhalation risk

Where there is a risk of particulate nanomaterials becoming airborne, the following measures should be used to control and prevent exposure:

Where possible:

- Use engineering controls such as Local Exhaust Ventilation (LEV) to control airborne exposure.
- Minimise the quantity of particulate nanomaterials in use at any one time.
- Minimise the number of people potentially exposed.
- Minimise the potential exposure time.
- Ensure that all those potentially exposed to particulate nanomaterials have had suitable and sufficient information, instruction and training.

Avoid contact with the skin. Always wear suitable disposable, single-use gloves.

Where dust exposure from contamination of work clothing could be significant, use clothing made from a low dust-retention and low dust-release fabric.

Keep all bottles/vessels containing particulate nanomaterials sealed when not in immediate use since it has been shown that the action of opening vessels containing free particulate nanomaterials can cause them to be drawn from the vessel so that they become airborne.

- Where possible, keep the particulate nanomaterial wet or damp, or use slurries, and avoid energetic processes that might generate airborne dusts or aerosols to reduce the risk of particulate nanomaterials becoming airborne.
- Use a damp sheet of paper towel or tissue on the bench when weighing out particulate nanomaterials and dispose of it in a sealed plastic bag whilst it is still damp.
- Use a damp paper towel or tissue to wipe up spilt particulate nanomaterials and dispose of it in a sealed plastic bag whilst it is still damp.

Control Measures for Dermal and ingestion risk

Where there is a risk of particulate nanomaterials contacting the skin, the following measures should be used to control and prevent exposure:

Where possible:

- Minimise the quantity of particulate nanomaterial in use at any one time.
- Minimise the number of people potentially exposed.
- Minimise the potential exposure time.
- Ensure that all those potentially exposed to particulate nanomaterials have had suitable and sufficient information, instruction and training.
- Use engineering controls such as LEV to control airborne exposure.
- Avoid contact with the skin. Always wear suitable disposable, single-use gloves.
- Change the disposable gloves after every task.
- Ensure gloves are removed in a safe manner and disposed of safely.
- If possible, use instruments/tools to prevent contact with the skin.
- Good housekeeping is important with easy to clean surfaces, containment of spills and keeping the workplace surface clean using wet wipes.

- Good personal hygiene/skin care is also important; suitable welfare facilities should be provided.
- Use a damp sheet of paper towel or tissue on the bench when weighing out particulate nanomaterials and dispose of it in a sealed plastic bag whilst it is still damp.

Use a damp paper towel or tissue to wipe up spilt particulate nanomaterials and dispose of in a sealed plastic bag whilst it is still damp

Always wash hands before leaving the laboratory/work area.

7. Engineering Control Measures

Engineering control measures will vary depending on the requirements of each project. It may be necessary for those working with particulate nanomaterials to use a combination of methods to control exposure.

These methods range from total enclosure of the process and automatic handling techniques, to partial containment by LEV, such as extracted enclosures and fume cupboards. Total enclosure or partial enclosures such as fume cupboards will be reasonably practicable for many operations with particulate nanomaterials, including manufacture/synthesis and weighing.

For cutting, sawing or polishing, simpler extracted enclosures and other LEV devices such as capturing/receiving hoods or down-draught benches may be appropriate. However, certain work activities may lead to higher potential exposure and therefore additional control measures may be necessary.

All LEV equipment should be designed and installed to **HSG 258** standards.

The exhaust air from an LEV system should be filtered through a **High Efficiency Particulate Air (HEPA) filter**, **HP14**, to remove the airborne particulate nanomaterials before venting to a safe place outside the building. This is particularly important when handling HARNs such as carbon nanotubes or other fibrous/rod like nanomaterials.

If it is not reasonably practicable to vent the exhaust air to a safe place outside, it must never be re-circulated directly back into the workplace unless it has been effectively filtered to remove airborne particulate nanomaterials by at least one HEPA HP14 filter

Local Exhaust Ventilation (LEV)
The most effective class of LEV are enclosures. In the laboratory setting there are generally two types: full or partial.

Full enclosures (e.g. glove box/Isolators are the most effective as they provide physical separation between the worker and the material. However, their inherent features can make them impractical as a control option and therefore **partial enclosures** are frequently used. These may be designed specifically for the process or be commercially available units. Examples of partial enclosures suitable for handling particulate nanomaterials include: HEPA-filtered fume cupboards, HEPA-filtered containment cabinets or a HEPA-filtered microbiological safety cabinets (MSCs). The small size and ”low inertia” of particulate nanomaterials means they move with the air generated by the process in a manner more akin to gases than conventional particles. Therefore correctly designed LEV systems should be an effective control measure.

It is important to make sure that the LEV achieves and maintains adequate control of exposure at all times. The system requires regular maintenance/periodic monitoring to ensure controls are working and thorough examination and testing annually (COSHH allows a maximum of 14 months between tests).

In most circumstances, face velocity measurements will suffice, but a smoke test will show whether the LEV is truly effective. Furthermore, if a smoke test is performed with the process/operation running, it will show:

- The size, velocity and behaviour of airborne contaminants.
- The capture zones and boundaries.
- Whether containment is maintained within the hood.
- Draughts, their direction and size.
- The general movement of air around the hood.
- Eddying and encroachment into the operator’s breathing zone.

If there is any doubt about the capability of a fume cupboard, then it may be necessary to carry out a full containment test, as detailed in **BS EN 14175-4:2004**.

All users should be trained in how to check and use the LEV and records should be kept of all the daily, weekly, monthly and annual LEV checks.

Ducted/Ductless Microbiological Safety Cabinets (MSCs)
MSCs can be used to handle particulate nanomaterials in a similar way to other HEPA-filtered containment cabinets. A Class I MSC operates in a similar way to a fume cupboard and protects the worker by drawing air through the front opening. Class II and III MSCs provide protection for both the user and the material in the cabinet. All these cabinets exhaust air through a HP14 filter.

8. Labelling, cleaning up, waste disposal, transport, emergencies

Containers which are known to contain engineered nanomaterials must be clearly labelled to show that contents contain particles of nanoscale size.

Use wet wiping techniques for cleaning work areas and avoid use of vacuum cleaners unless they are HEPA filtered and are designed to minimise the risk of ignition of an combustible nanomaterials. Do not brush or use a standard vacuum cleaner.

Waste nanomaterials, contaminated wet wipes, HEPA filters and protective clothing/gloves should be double bagged and incinerated as hazardous waste. No free nanomaterials should enter any non-hazardous waste stream or be disposed of via the drains.

Risk assessment must define suitable procedures for dealing with process equipment that needs to be cleaned for re-use to ensure that other workers involved in this are aware of the procedure and not put at risk.

Nanomaterials being transported between labs and buildings must be appropriately enclosed, double contained and labelled.

Nanomaterials being transported to other facilities outside the university must be transported using a licensed transport company and must not be transported in private vehicles or on public transport.

Emergency procedures and equipment must be in place to deal with spills, accidents and emergencies.

9. Health surveillance and recording exposure

Health surveillance is only appropriate in circumstances where:

- There is a disease associated with the substance in use (e.g. asthma, dermatitis, cancers)
- It is possible to detect the disease or adverse change [i.e. a biological effect] and reduce the risk of further harm
- The conditions in the workplace make it likely that the disease will appear

There is currently no research data to suggest any *specific* biological effect from nanomaterials that could be monitored and, providing the control measures detailed above are adopted and adhered to, individuals' exposure will be adequately controlled.

Therefore health surveillance is not considered appropriate or necessary specifically for work with nanomaterials. However, other hazards relating to the work should still be considered as part of the usual COSHH risk assessment and if necessary the appropriate health surveillance should be undertaken.

Additionally, as there is no known safe level of exposure, Faculties must ensure that there is a recording system in place that enables individuals who have been involved in such work to be identified. This can best be achieved by ensuring that a list of authorised users is appended to the risk assessment for the procedure in which the nanomaterial is used. **These records must be kept for 40 years.**

10. Accident/Incident recording

Where an incident occurs, that results in the potential or actual exposure of any individual to nanomaterial, even if there is no apparent health effect, it must be recorded on the University Accident/Incident reporting system. The Central Health & Safety Section must be immediately informed as such an occurrence may be reportable to the HSE.

A copy of the incident report will be forwarded to Occupational Health who will review the circumstances of the exposure and ensure an appropriate entry is made on the individual's health record, and if deemed necessary invite the individual to attend for an appointment.
The above records must be kept for **40 years** and be available for inspection.

11. Maintenance and monitoring of control measures

Fume cupboards/LEV
It is critical that LEV achieves and maintains adequate control of exposure at all times. The system requires regular maintenance, periodic monitoring to ensure controls are working and thorough examination and testing by a competent person at periods not greater than 14 months and more frequently if the assessment indicates a higher risk.

In addition you should establish a suitable frequency of regular in-house testing, training local users in how to undertake these checks. Records must be kept of daily, weekly and monthly checks, in addition to the checks undertaken by the competent person.

12. Procurement

All nanoparticles are to be supplied by reputable suppliers in agreement with the Faculty Technical Manager. Any new sample brought into the University must be included in a risk assessment and its details must be passed on to Technical Manager prior to use.

13. Storage of Nanomaterials

Details on the storage requirements of chemicals/nanomaterials are given in Section 7 of the MSDS. Any special measures (desiccation, storage under N_2, etc.) should be discussed with the Technical Manager prior to being brought into the University.

UNDER NO CIRCUMSTANCES should a chemical/substance be left unidentified or undisposed of in the laboratory.

14. Disposal

All waste **must** be disposed of appropriately. A summary of the waste disposal routes is as follows:

- Solid nanoparticle waste and contaminated glassware must be contained in a sealable container (zip-lock bag, screw-top plastic bottle etc.) and sent for high-temperature incineration.
- Nanoparticles embedded in composites or epoxy resins should also be disposed of by this route.
- Nanoparticles in solution/suspension with water/detergent/solvent must be collected separately in a designated **Winchester**.
- All CNT and other bio persistent HARNs should be classified and coded as 'hazardous waste'
- All waste must be labelled with details of substance/ concentration; they must be stored as appropriate until collection.

15. Training

To enable safe working with nanoparticle materials it is expected that the person would have completed the following training:-

- Laboratory induction and safe working practices in laboratories
- COSHH
- Read and understood this guidance note
- The use of any LEV and PPE.

This must be recorded.