# Local Rule:
# Safe Use of Nanomaterials

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## 1. Occupational Health and Safety Concerns

It is widely accepted that there is at present a lack of information and **knowledge** concerning the implications of manufactured nanomaterials on human health and the environment. Concerns have been voiced in several academic papers regarding potential risks to health that may arise during the manufacture, manipulation, use and disposal of these materials. There are emerging concerns regarding the potential risks to health from the inhalation of nanomaterials and, following evidence published in 2008 in Nature Nanotechnology particular concern regarding carbon nanotubes (CNTs). Recent concerns in 2010 have also been voiced about the potential risks to health from dermal exposure or ingestion and the possible risk of fire and explosion. The increasing volumes of nanomaterials that are being produced and introduced into commerce have resulted in an urgent need to address exposure and risk assessment data gaps. A growing body of literature indicates a potential hazard from exposure to various types of carbon nanotubes and nanofibers. A number of studies in rodents have shown adverse lung effects at relatively low mass doses of CNT including pulmonary inflammation and rapidly developing, persistent fibrosis. Similar effects have been recently observed with exposure to Carbon Nano Fibers (CNF) It is not known how universal these adverse effects are, i.e., whether they occur in animals exposed to all types of CNT and CNF, and whether they occur in additional animal models. Most importantly, it is not yet known whether similar adverse health effects occur in humans following exposure to CNT or CNF.

### 1.1. Occupational Health Effects

Inhalation studies have shown that nanomaterials have the ability to transverse even when thought to be in a safe physical state. Estimates are somewhat crude, and do not take into account what happens when there is a range of particle sizes in the aerosol - a factor which can significantly increase the rate of agglomeration(formation of a rounded mass). But these estimates are good enough to give a rough idea of how rapidly or slowly nanomaterials will agglomerate. They eloquently demonstrate that, in some cases, people are likely to encounter and inhale airborne nanomaterials, while in other cases they will be exposed to particles that have grown through a process of agglomeration. If inhaled, these larger agglomerates are able to penetrate to, and deposit in, the deepest part of the lungs, at the fragile interface between the air and the blood.

### 1.2. Principal Legislation - The Control of Substances Hazardous to Health 2002 Regulations (COSHH)

These are the regulations that relate to the use of chemicals and other hazardous substances in the UK. The Regulations require that, in order to prevent ill health, employers control the exposure of their employees and others to hazardous substances, to a level that is as low as is reasonably practicable.

## 2. Key Definitions

### 2.1. Nanomaterial[1]

**2.1.1** Nanomaterial means a natural, incidental or manufactured material containing particles, 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.

**2.1.2** 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 %.

**2.1.3** By derogation, fullerenes, graphene flakes and single wall carbon nanotubes with one or more external dimensions below 1 nm should be considered as nanomaterials.

"Particle", "agglomerate" and "aggregate" are defined as follows:

(a) "Particle" means a minute piece of matter with defined physical boundaries;
(b) "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;
(c) "Aggregate" means a particle comprising of strongly bound or fused particles.

**2.1.4** Where technically feasible and requested in specific legislation, compliance with the definition in point (2.11) may be determined on the basis of the specific surface area by volume. A material should be considered as falling under the definition in point (2.11) where the specific surface area by volume of the material is greater than 60 $m^2$ / $cm^3$. However, a material which, based on its number size distribution, is a nanomaterial should be considered as complying with the definition in point (2.12) even if the material has a specific surface area lower than 60 $m^2/cm^3$.

[1] EC Commission 2011

### 2.2. Nanotechnology

This involves the creation and/or manipulation of materials at the nanometre (nm) scale (1-100nm) either by scaling up from single groups of atoms or by refining or reducing bulk materials. A nanometre is 1 x $10^{9}$m or one millionth of a millimetre. To give a sense of this scale, a human hair is of the order of 10,000 to 50,000 nm, a single red blood cell has a diameter of around 5000 nm, viruses typically have a maximum dimension of 10 to 100nm and a DNA molecule has a diameter of 2 - 12 nm. (www.nano.gov/)

## 3. Identifying the hazards

### 3.1. COSHH

These regulations are risk assessment based and require that risk assessment is undertaken to arrive at conclusions as to which methods of exposure controls are appropriate and sufficient to ensure prevention or adequate control of exposure. COSHH relies on having good information about the hazardous nature of materials, the effectiveness of control approaches and convenient and accessible ways to monitor exposure. One of the difficulties in applying a COSHH approach to nanoparticles is that the information available might be incomplete or, worse, incorrect.

The knowledge gaps concerning the health hazards of new nanomaterials introduce significant uncertainty into any risk assessment.

### 3.2. Assessing the risk

Assessing the potential health risks of nanomaterials will involve adequately characterizing the toxicity potential of nanomaterials and the exposures that the user may experience. In order to undertake a suitable and sufficient assessment of risk one has to have good information regarding the hazardous properties of the substances, their health effects and the effectiveness of preventive and control measures which have been or will be taken.

The first step of the risk assessment approach is to gather all the available written information allowing identification of the health and safety risk factors in the workplace.

It is inappropriate **in the absence of knowledge** to assume that a nanoparticle form of a material has the same hazard potential as it has in a larger particulate form. Of concern is the uncertainty that is introduced into any risk assessment involving exposure to nanomaterials because of the knowledge gaps concerning their health hazards.

**Where there are gaps in knowledge the more cautious and robust the risk assessment should be**.

When introducing control measures, related to exposure to nano range sized materials, one should always err on the side of caution and aim to control for the most serious risk scenario. Another area of concern is the amount of measurable exposure form nanomaterials which involves the discipline of Nanometrology (the science of measuring things on a scale of a nanometre) from a Health and Safety point of view, this is difficult to put into context however researchers at Strathclyde University are currently involved in this discipline and in-house expertise is available.

## 3.3. Understanding the Risk

The term “engineered nanomaterials” covers a wide variety of different materials/substances which may present a range of different hazards. The hazardous properties of nanomaterials are determined by their physical properties e.g. size, shape, crystal structure, surface coating, surface reactivity, etc, and their chemical composition. The scientific community still does not have a good understanding of all of the health effects likely to arise from exposure to different types of engineered nanomaterials, and while there are many peer-reviewed papers discussing health effects for engineered nanomaterials, a lack of information on the physical and chemical characteristics of the materials studied has meant that the results of some studies cannot be effectively used for risk assessment purposes. HSE therefore advises that nanomaterials should be characterised before they are used.

### 3.3.1 What does characterisation mean?

It is important to understand as much as possible about the physical characteristics **and the chemical composition of a** nanomaterial before work commences since this information is a key element of the COSHH risk assessment. In the absence of adequate information about the physical characteristics (size, shape, crystal structure, surface coating, surface reactivity, etc), of the particular nanomaterial to be worked with, it is unwise to make general conclusions about its potential hazards based on ‘other’ nanoparticles which may have a similar chemical composition, unless good data is available to confirm that this approach is appropriate. Characterisation information for engineered nanomaterials should be available from manufacturers or suppliers along with a safety data sheet.

If this information is not available contact should be made with the manufacturers or suppliers and ask them to provide this information.

### 3.3.2 High Aspect Ratio Nanomaterials (HARN)

Emerging scientific evidence suggests that high aspect ratio nanomaterials that have the following characteristics:

- are thinner than 3 µm;
- are longer than 10-20 µm;
- are biopersistent; and
- do not dissolve/break into shorter fibres

may be retained within the narrow space surrounding the lungs - the ‘pleural cavity’ - for long periods of time.

In light of this emerging information, together with existing knowledge that long fibres retained in the pleural cavity can cause persistent inflammation, which may lead to diseases such as lung cancer, HSE advice is to take a precautionary risk management approach when there is the potential for workers to inhale nanomaterials with these characteristics.

## 3.4. Hazard Control Banding

Control banding can only be used to determine the risks to health. The approach does not address safety risks (fire-explosion risk) or risks to the environment. Nevertheless, just as with conventional dust clouds, it is reasonable to assume that clouds of nanomaterials may be explosive if their particles are capable of burning in air (aluminium, magnesium, lithium, etc.*).* The control banding approach should therefore be integrated into a wider process of chemical risk assessment, mainly to avoid disregarding fire-explosion risks and risks to the environment, or it should evolve to also include the determination of these risks, whose consequences may be severe for employees, the environment and the general population.

The control banding tool is required to be reasonable or even conservative. This is because while it is intended to manage an element of uncertainty, its use is currently restricted by two major limitations: the lack of toxicological data and the metrological limits for measuring exposure. In addition, the user should always be able to assess the limitations of the method, which was developed for use in a laboratory or industrial production environment, and may be poorly suited to certain applications. Thus the method is not adapted to extreme situations, for example:

- if the nanomaterials are an extremely diluted component of the product used; or
- when handling large volumes, which requires special expertise.

Similarly, the method does not dispense the user from the usual/common sense individual protective measures. For example, applying the method to a nanomaterial that is toxic/hazardous but confined in a highly stable solid matrix (solid or viscous liquid, low volatility) will result in a recommendation for general or local ventilation, which should not prevent common sense measures being taken such as the wearing of personal protective equipment.

## 3.5. Competence of person undertaking the risk assessment

The current state of knowledge and in particular the large knowledge gaps, concerning the creation and manipulation of NPs and CNTs suggests that it would be difficult and inappropriate for a person with no prior background knowledge of nanomaterials risk issues to make effective judgements as to appropriate steps that may need to be taken and implemented in order to ensure that risk is reduced to the lowest level practicable. It is strongly recommended that those involved in undertaking and developing risk assessments for work processes involving nanomaterials seek information from as wide a combination of sources and in particular consult with those already working in the ever-growing nanotechnology world. In an effort to aid this some sources of information are in Section 10.

# 4. Control Measures

HSE Report 274 advises that 'For air velocities prevailing in workplaces, airborne nanomaterials can be considered as having no inertia. They will therefore behave in a similar way to gas and if not fully enclosed will diffuse rapidly and will remain airborne for a long time. Because of their high diffusion velocity, these particles will readily find leakage paths in systems in which the containment is not complete.

**Engineering control systems designed for use to control nanomaterials such as enclosures, local exhaust ventilation (LEV), fume cupboards and general ventilation therefore need to be of similar quality and specification to that which is normally used for gases rather than particulate challenges'**.

## 4.1. Inhalation Exposure Control Methods

Because of the unknown toxicity exposure of most nanomaterials, it is now best practice to conduct all possible exposure to nanomaterials, especially CNT's and substances in powdered or dust form, within a HEPA filtered local exhaust ventilation cabinet. Nanomaterials will follow airstreams so they can be easily collected and retained in standard ventilated enclosures such as chemical weighing cupboards, fume hoods and biosafety cabinets all fitted with HEPA filters.

### 4.1.1 Ducted microbiological safety cabinets can be used*

The Class II and III microbiological safety cabinets, unlike the Class I type, provide protection for both the user and the material in the cabinet's working environment. All these cabinets exhaust air through a HEPA filter*

***It should be noted that a Class II cabinet is not suitable for handling large quantities of CNTs (>1g) because it re-circulates up to 70% of its air**.

### 4.1.2 Ductless recirculating HEPA filtered safety cabinets and recirculating microbiological safety cabinets

Safety cabinets and microbiological safety cabinets which recirculate air from the cabinets interior, thorough a HEPA filter, back into the laboratory can be used for small quantities of CNTs (<1gram) in the absence of hazardous vapours or gases. **HEPA filtered recirculating cabinets do NOT absorb or capture fumes, gases or vapours, for which external venting to a safe place would be required in addition to the HEPA filter.**
Further information can be found in the Local Rule for Safe Use of MSC's on Safety Services website.

## 4.2. Respiratory Protective Equipment (RPE)

**HSE advises that RPE should only be used for emergencies and then in addition to other control measures.**

If the nanomaterial is a dry powder it may be necessary to provide respiratory protective equipment (RPE). HSE recommends RPE with an assigned protection factor (APF) of 40 or higher. In the UK information on the selection and use of respirators is given in HSE guidance document HSG53.Depending on the outcome of the risk assessment process, appropriate types of respiratory protective equipment (RPE) include disposable filtering face-pieces, half and full facemasks and a range of powered (air supplied) hoods, helmets, blouses and suits. High efficiency filters (P3 and FFP3 type) should always be used. All wearers of RPE should undergo face-piece fit testing to ensure correct fitting and proper wearing. Incorrect selection or fitting or insufficient use can render it ineffective.

## 4.3. Dermal Exposure Control Measures

Since the ability of nanomaterials to penetrate skin is unknown at this time, gloves should be worn when handling particulates or particles in solution. The following points must be borne in mind:

- for liquids, the glove should have good chemical resistance to the solute;
- for dry particulate, a sturdy glove, such as nitrile lab gloves with good integrity, should be used; for all types of Carbon Nano tubes, double gloving is recommended;
- disposable nitrile lab gloves should provide good protection for most lab procedures that don't involve extensive skin contact;
- if contact is extensive, then double-gloving should be performed;
- there should be no exposed skin around the hands and wrists;
- check gloves regularly for holes, cracks etc; and
- wash hands immediately after removing gloves.

## 4.4. Ingestion Control Measures

The following points must be adhered to:

- follow normal hygienic principles:
- scrupulously avoid hand-to-mouth contact;

- wear gloves at all times where there is potential for exposure to nanomaterials;
- wash hands immediately after removing gloves; and
- no eating, drinking, smoking, applying cosmetics, etc. in the lab or before hands are washed.

## 5. Health Surveillance and Record Keeping

Ongoing research on the hazards of engineered nanomaterials is needed along with the continual reassessment of available data to determine whether specific medical screening is warranted for workers who are producing or using nanomaterials.

**It is now considered best practice to keep a record of all those working with nanomaterials.**

**The University's Form (S29) must be used to record personal work activity involving the use of nanomaterials with unknown toxicity.**

## 6. Health and Safety Executive (HSE) Guidance

There is now a dedicated Nanotechnology website, which will be regularly reviewed and updated with new and emerging data, however the main points below should be considered.

**At the time of writing the HSE are in the process of updating the guidance for nanomaterials**.

## 7. Risk of Explosion or Fire

In the UK issues relating to fire and explosion are covered by the **Dangerous Substances and Explosive Atmospheres Regulations 2002.**

If it is thought that risk of explosion and fire, due to the manipulation of nanomaterials, is an issue then a risk assessment must be undertaken in order to comply with these Regulations and suitable control measures implemented to control such risk to a suitably acceptable level. Ease of ignition and violence of a dust explosion tend to increase as the particle size decreases.

Whilst this tendency levels out for many dusts at particle sizes in the tens of micrometres, a particle size limit below which dust explosions cannot occur has not been established, and so it is therefore prudent to assume that many nanomaterial types will have the potential to cause an explosion. Unfortunately, at present there is almost no data available on the fire and explosion hazards of nanomaterials. Current advice is to take risk reducing precautions and explosion protection measures in line with those commonly implemented for dust control and dispersion of hazardous quantities of dust particles of a larger size.

## 8. Waste

When thinking about how to manage nanomaterial waste, it is important to examine the entire life cycle of nanomaterials, from synthesis to disposal. Little is known about the ignitability, corrosivity, reactivity, and toxicity of nanomaterials. Those four characteristics must be assessed to determine whether solid waste must be handled as hazardous waste or whether it can go to a regular landfill.

### 8.1. Waste Disposal

Key points to remember are:

- never dispose of nanomaterial waste in regular waste streams e.g. discharge to drain through the public sewerage system or normal household solid waste systems;
- when disposing of dry nanomaterial waste, use a sealable container that remains closed. Dispose of all nanomaterial waste, including contaminated debris, as you would the base material (i.e., carbon nanotubes should be disposed of as carbon, metallic particles consistent with the base metal);
- if the nanomaterials are in solution, they should be managed as a solution of the solvent and the parent nanomaterial (e.g., flammable solvents are handled as flammable waste materials); and
- all nanomaterial waste must be labelled with the base metal or solute and identified as containing nanomaterial.

Proper disposal of nanomaterial waste will be based on the type of material and will be coordinated through our hazardous waste disposal contractor. The waste management guidance given in is based on guidance developed and used by the UK Environment Agency (EA). Guidance for the disposal of hazardous materials can be found in the
Enivronment Agency: HWRO1 document
and applies to nanomaterial-bearing waste streams (solid and liquid waste), including:

- pure nanomaterials;
- items contaminated with nanomaterials, such as containers, wipes and disposable PPE;
- liquid suspensions containing nanomaterials; and
- 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 force.

## 8.2. Storage of Nanomaterial Waste prior to Disposal

The following are appropriate approaches for collection and storage of nanomaterial waste prior to disposal:

- **Storage in waste containers**. Package nanomaterial-bearing wastes in compatible containers that are in good condition and afford adequate containment to prevent the escape of the nanomaterials. Label the waste container with a description of the waste and include available information characterizing known and suspected properties; and
- **Storage in plastic bags**.
  Collect paper, wipes, PPE and other items with loose contamination in a plastic bag or other sealable container stored in the laboratory fume cabinet.

  When the bag is full, close it and carefully place it into a second plastic bag or other sealing container, avoiding outside contamination. Take it out of the fume cabinet and label the outer bag with an appropriate waste label.

**All waste deemed hazardous must be processed through the Universities hazardous waste stream.**

## 9. Further Information, Guidance and References

University's Occupational Health & Safety Policy

Local Rules on the Control of Substances Hazardous to Health

The Health and Safety Executive dedicated website for Nanotechnology (www.hse.gov.uk)

The Health and Safety Executive 'Risk Management of Carbon Nanotubes'

Nanotechnology: Hazard and Risk, SAFENANO at: http://www.safenano.org/

British Standards (BSI) has produced a published document (PD) Nanotechnologies Part 2: Guide to safe handling and disposal of manufactured nanomaterials.
Free download at http://www.bsigroup.com/en/Standards-and-Publications/Industry-Sectors/Nanotechnologies/PD-6699-2/Download-PD6699-2-2007/

British Standards (BSI) has published a further eight other guidance documents for nanotechnologies, addressing nanotechnology terminology, and product labelling. These are free to download at:
http://www.bsigroup.com/en/Standards-and-Publications/Industry-Sectors/Nanotechnologies/Nano-Downloads/

HSE Research Report 274, Nanomaterials: An occupational hygiene review (www.hse.gov.uk)

Environment Agency http://www.environment-agency.gov.uk/netregs/businesses/chemicals/112767.aspx

The Dangerous Substances and Explosive Atmospheres Regulations, SI 2002, No. 2776, London: HMSO
(www.hse.gov.uk)

### References


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The following summarises how departments can effectively implement this Local Rule and integrate it into its management systems. These processes will be monitored as part of Safety Services' Audit Programme, and where departments are able to demonstrate fulfilment of key actions, this is likely to provide strong evidence of good practice**.**

| | | Key Management Actions |
|---|---|---|
| **1.** | **Departmental Roles** | • ensure that appropriate health and safety management arrangements are put in place relating to the control of use of nanomaterials;<br>• ensure that Departmental Occupational Health and Safety Arrangements are updated;<br>• ensure that through management arrangements nanomaterials are supplied by a reputable supplier; and<br>• ensure that all COSHH risk assessments involving work with nanomaterials are registered with the University Nanosafety Committee. |
| **2.** | **Identifying Hazards** | • ensure that work activities and equipment which utilise nanomaterials are identified by completing COSHH risk assessments; and<br>• ensure that the level of current knowledge of the assessor is adequate. |
| **3.** | **Evaluating Risks** | • ensure that all appropriate controls have been assessed and are suitable for purpose in line with the risks identified. |
| **4.** | **Implementing Risk Control Measures** | • ensure that once in receipt of the COSHH risk assessments, implement any recommendations made regarding controlling exposure;<br>• consider the range of risk control measures available and implement those measures that will reduce exposure to nanomaterial. |
| **5.** | **Recording Risk Assessments** | • ensure records of COSHH risk assessments for use of nanomaterials are maintained;<br>• ensure assessment(s) are reviewed annually or sooner if significant changes have been made or exposure data is updated; and<br>• ensure recommendations and action points are implemented and monitored. |
| **6.** | **Occupational Health Effects** | • ensure that where the risk assessment identifies potential health effects, a confidential list of all workers exposed to nanomaterials is held within the department. |
| **7.** | **Waste** | • ensure that adequate packaging and storage is available; and<br>• ensure that all nanomaterial waste is disposed of appropriately through the nominated hazardous waste co-ordinator. |
| **8.** | **Information, Instruction, Supervision and Training** | • ensure staff and students exposed to nanomaterials are provided with relevant information, instruction, supervision and training about the risks and retain a record of the training provided, staff attending and any information issued. |