UNIVERSITY OF TOLEDO

SUBJECT: NANOTECHNOLOGY SAFE WORK PRACTICES Procedure No: HM-08-038

PROCEDURE STATEMENT

The University of Toledo will establish and maintain guidelines to manage the safe handling of nanomaterials in accordance with NIOSH, DOE, and any other governing authority's guidance documents.

PURPOSE OF PROCEDURE

To ensure proper lab specific hazard controls are established for all UT staff, students and faculty that are involved in the handling, use, storage, shipment, and disposal of nanomaterials in order to protect personnel and the environment.

PROCEDURE

I. SCOPE AND APPLICABILITY

This plan describes the University of Toledo's requirements for the handling, use, storage, shipment, and disposal of engineered nanomaterials.

II. DEFINITIONS

"Engineered Nanomaterials" are intentionally created (in contrast with natural or incidentally formed) nanomaterials with dimensions <100 nanometers. This definition excludes biomolecules (proteins, nucleic acids, and carbohydrates), and materials for which the occupational exposure limit (OEL) documentation of national consensus or regulatory standards has specifically addressed nanoscale particles for that material.

"Nanoparticles" means dispersible particles having two or three dimensions greater than 0.001 micrometer (1 nanometer) and smaller than about 0.1 micrometer (100 nanometers) and which may or may not exhibit a size-related intensive property.

"Laboratory scale" describes activities involving chemical containers, reaction vessels, material transfers, and other handling of substances which are designed to be easily and safely manipulated by one person. "Laboratory scale" excludes those activities whose function is to produce commercial quantities of materials.

III. ROLES and RESPONSIBILITIES

The University of Toledo Environmental Health and Radiation Safety Department is responsible for developing and implementing university guidelines for nanotechnology. All activities involving nanotechnology fall under the provision of this plan. The Principal Investigator (PI) is responsible for ensuring compliance.

IV. PROCEDURES

A. Hazard Control Assessment

The goal of the hazard control assessment is to determine that appropriate controls are in place to contain nanomaterials, resulting in reduced exposure for users. The Environmental Health and Radiation Safety Department will conduct a lab specific hazard control assessment for all laboratory scale projects utilizing nanomaterials. All users must complete the nanotechnology safety and health survey located at **http://www.enrollmentservices.utoledo.edu/events/register.asp?event_id=1204**. The survey will provide the initial information necessary for development of a lab specific hazard control sampling strategy.

Environmental Health and Radiation Safety will contact the PI to set up an initial meeting to get a well-defined description of the work and to identify recognized and suspected hazards. Specific hazard control options will be recommended based on the results of the initial meeting. The effectiveness of the hazard controls in place may be quantitatively validated for suspect emissions using a variety of sampling techniques. Both background and source samples, during operation, will be measured during the evaluation for comparison.

B. Hazard Control Preferences

1. The hierarchy of controls (Engineering Controls, Administrative Controls, and Personal Protective Equipment) will be followed when determining control recommendations. A graded approach will also be used based on the dispersion capabilities of the nanomaterials being used. Operations involving easily dispersed dry nanoparticles deserve more attention and more stringent controls than those where the nanomaterials are imbedded in solid or suspended in liquid matrixes.

2. From the perspective of managing laboratory worker health, the order of preference (most preferred to least preferred) for handling nanomaterials is:
   a. Solid materials with imbedded nanostructures
   b. Solid nanomaterials with nanostructures fixed to the materials surface
   c. Nanoparticles suspended in liquids
   d. Dry, dispersible (engineered) nanoparticles, nanoparticle agglomerates, or nanoparticle aggregates

3. Avoid handling nanomaterials in the open air in a free particle state. Whenever possible, handle and store dispersible nanomaterials, whether suspended in liquids or in a dry particle form, in closed (tightly sealed) containers.

4. Consider the hazardous properties of the precursor materials as well as those of the resulting nanomolecular product (i.e. heavy metals). Remember, nanomaterial hazards might not be known or reliably anticipated. Environmental Health and Radiation Safety can assist with this evaluation.

5. Consider all routes of possible exposure to nanomaterials including inhalation, ingestion, injection, and dermal contact (including eye and mucus membranes).

C. Engineering Controls

1. Work Area Design
   Consider the potential need to implement additional engineered or procedural controls to ensure workers are protected in areas where engineered nanoparticles will be handled. Consider additional controls that will better ensure that engineered nanoparticles are not brought out of the work area on clothing or other surfaces, e.g., install step-off pads, create a buffer area, and ensure the availability of decontamination facilities for workers.

2. Ventilation Preferences
   a. Conduct any work that could generate engineered nanoparticles in an enclosure that operates at a negative pressure differential compared to the workers breathing zone. Examples of such enclosures include biosafety cabinets, glove boxes, glove bags, and laboratory bench-top or floor-mounted chemical hoods. In some cases, the air reactivity of precursor materials may make it unsafe to operate in a negative pressure glovebox and a positive pressure box may be used if it has passed a helium leak test. If a process (or subset of a process) cannot be enclosed, then use other engineered systems to control fugitive emissions of nanomaterials or hazardous precursors that might be released. For example, use a local exhaust system.
   b. Do not exhaust effluent (air) demonstrated or strongly suspected to contain engineered nanoparticles whose hazards are not well understood. Whenever practical, filter it or otherwise clean (scrub) it before release.
   c. HEPA filtration appears to effectively remove nanoparticles from air, at least to particles as small as 2 nanometers in diameter. Below that size, data suggests that filter performance degrades as particles experience thermal rebound and reaerosolization from the filter matrix.

d. Minimize the dispersal and environmental release of nanomaterials. Carry out all manipulations of engineered nanoparticles in a glove box, glove bag, chemical fume hood, or other airborne contaminant control system. Whenever practical, remove (scrub or capture) the contaminant from the effluent from such a control system before the effluent is released into the general environment. If it is not practicable to handle dispersible nanoparticles in such a containment system, conduct and document the results of a hazards analysis before using alternative hazard controls.
e. Exhaust the effluent from ventilated enclosures outside the building whenever feasible. Filters, scrubbers or bubblers appropriately used to treat unreacted precursors and may also be effective in reducing nanomaterial emissions. If using portable bench top HEPA-filtered units, exhaust them through ventilation systems that will carry the effluent outside the building whenever possible.
f. If it is not feasible to duct HEPA-filtered treated exhaust air outside of the building:
    (1) Follow the guidance in ANSI Z9.7, *American National Standard for Recirculation of from Industrial Process Exhaust Systems*.
    (2) Conduct a hazard assessment and implement appropriate engineering controls. (Examples of such controls include periodic air monitoring, and an accurate warning/signal capable of initiating corrective action or process shutdown before nanoparticles could be exhausted or re-entrained into the work area).
g. DO NOT use horizontal laminar-flow hoods (clean benches) that direct a flow of HEPA-filtered air into the users face for operations involving nanomaterials that might easily become entrained in the air.
h. Consider Type II biological safety cabinets, in which free nanomaterials are handled.
i. Maintain and test the effectiveness of exhaust systems and components as specified by the manufacturer.
j. Evaluate equipment previously used to synthesize, handle or capture nanoparticles for contamination and incompatibility before removing, remodeling, repairing, reusing or disposing of it. Due to the potential for residual contamination use appropriate cleaning methodologies (i.e. wet wiping).

D. Administrative Controls

1. Chemical Hygiene Plan
   As required by 29 CFR 1910.1450, the University of Toledo Chemical Hygiene Plan can be found at **http://www.utoledo.edu/depts/safety/labsafety.html**.

2. Housekeeping
   a. Practice good housekeeping in laboratories where nanomaterials are handled. Follow a graded approach paying attention where dispersible nanomaterials are handled.
   b. Insofar as practicable, maintain all working surfaces (i.e., benches, glassware, apparatus, exhaust hoods, support equipment etc.) free of engineered nanoparticle contamination and otherwise limit worker exposure engineered nanoparticles and associated hazards.
   c. In areas where engineered nanoparticles might settle, perform precautionary cleaning, for example, by wiping horizontal surfaces with a moistened disposable wipe, no less frequently than at the end of each shift.
   d. Before selecting a cleaning method, consider the potential for complications due to the physical and chemical properties of the engineered nanoparticles, particularly in the case of larger spills. Complications could include reactions with cleaning materials and other materials in the locations where the waste will be held.
   e. Clean up dry, engineered nanomaterials using:
   f. A dedicated, approved HEPA vacuum whose filtration effectiveness has been verified (Note: Consider possible pyrophoric hazards associated with vacuuming up nanoparticles)
   g. Wet wiping
   h. Other facility-approved methods that do not involve dry sweeping or the use of compressed air
   i. Dispose of used cleaning materials and wastes in accordance with the University of Toledo's hazardous-waste procedures (HM-08-001).

3. Work Practices
   a. Transfer engineered nanomaterials samples between workstations (such as exhaust hoods, glove boxes, furnaces) in closed, labeled containers, e.g., marked Zip-Lock bags.
   b. An exothermic reaction involving nanomaterials and wipes at a DOE facility reportedly resulted in discovery of an incipient fire in a domestic trash container. Take reasonable precautions to minimize the likelihood of skin contact with engineered nanoparticles or nanoparticle-containing materials likely to release nanoparticles (nanostructures).
   c. If engineered nanoparticle powders must be handled without the use of exhaust ventilation (i.e., laboratory exhaust hood, local exhaust) or enclosures (i.e., glove-box), evaluate hazards and implement alternative work practice controls to control potential contamination and exposure hazards.
   d. Handle nanomaterial-bearing waste according to the University of Toledo's hazardous chemical waste procedures (HM-08-001).
   e. Vacuum dry engineered nanoparticulates only with an approved HEPA vacuum cleaner.

4. Marking, Labeling and Signage
   a. Post signs indicating hazards, personal protective equipment requirements, and administrative control requirements at entry points into designated areas where dispersible, engineered nanoparticles are handled. A designated area may be an entire laboratory, an area of a laboratory or a containment device such as a laboratory hood or glove box.
   b. Label storage containers to plainly indicate that the contents are in engineered nanoparticulate form, e.g., nanoscale zinc oxide particles or other identifier instead of just zinc oxide.
   c. When engineered nanoparticles are being moved outside, also include label text that indicates that the particulates might be unusually reactive and vary in toxic potential, quantitatively and qualitatively, from normal size forms of the same material.

E. Personal Protective Equipment

1. Wear appropriate PPE on a precautionary basis whenever the failure of a single control, including an engineered control, could entail a significant risk of exposure to researchers or support personnel. Alternatively, ensure that engineered controls (e.g., laboratory chemical hoods) are equipped with performance monitors that will notify users if equipment malfunctions.

2. Conduct a hazard evaluation to determine the selection and use personal protective equipment (PPE) appropriate for the level of hazard as per the requirements set forth in 29 CFR 1910 Subpart I Personal Protective Equipment. Protective clothing that would typically be required for a wet-chemistry laboratory would be appropriate and could include but not limited to:
   a. Closed-toed shoes made of a low permeability material (Disposable over-the- shoe booties may be necessary to prevent tracking nanomaterials from the laboratory.) Other PPE includes long pants without cuffs, long-sleeved shirt, gauntlet-type gloves or nitrile gloves with extended sleeves, and laboratory coats.
   b. Wear polymer (e.g., nitrile rubber) gloves when handling engineered nanomaterials and particulates in liquids. Choose gloves only after considering the resistance of the glove to the chemical attack by both the nanomaterial and, if suspended in liquids, the liquid.
      (1) Recognizing that the effects of exposure to nanomaterials are not well known to have good warning properties, change gloves routinely to minimize potential exposure hazards. Alternatively, double glove.
      (2) Keep contaminated gloves in a plastic bag or other sealed container until disposed.
      (3) Wash hands and forearms after wearing gloves.
   c. Wear eye protection, e.g., chemical splash goggle, or other safety eyewear appropriate to the type and level of hazard. Do not consider face shields or safety glasses to provide sufficient protection against unbound, dry materials that could become airborne.
   d. Environmental Health and Radiation Safety will evaluate airborne exposures to engineered nanomaterials. If respirators are to be used for protection against engineered nanoparticles, the UT Respiratory Protection Program must be followed (S-08-034).

e. Remove potentially contaminated clothing and PPE in the laboratory or change-out area to prevent engineered nanoparticles from being transported into common areas.

F. Training

All personnel working with nanomaterials must complete training through Environmental Health and Radiation Safety's on-line test bank.

G. Medical Surveillance

Currently there is insufficient scientific and medical evidence to recommend the specific medical screening of workers potentially exposed to engineered nanoparticles.

Environmental Health and Radiation Safety will work with UTMC Family Medicine to define health monitoring for workers engaged in nanoscale science research and support activities if this guidance changes. If the hazard assessment indicates the potential for high occupational exposure to engineered nanomaterials, laboratory personnel **may** be offered a baseline medical evaluation and periodic medical monitoring consisting of routine non-specific medical monitoring including, for example, urinalysis, blood chemistry, and pulmonary function.

Employees involved in any incident that results in an unexpected and/or unusually high exposure to nanomaterials, through any route of entry, examined by Family Medicine for a post-incident evaluation as per OSHA 1910.1450(g)(1)(i).

H. Transportation of Nanomaterials

1. Categories of Materials

a. Recognized HazMat
Any nanomaterial that meets the definition of a hazardous material according to 49 Code of Federal Regulations (CFR) Part 171.8 and can be classified as a hazardous material in accordance with 49 CFR 173.115 through 141 and 173.403 through 173.436 must be packaged, marked, labeled, shipping papers prepared and shipped in accordance with 49 CFR 100 to 185.

Any nanomaterial being shipped by air that meets the definition of dangerous goods according to the International Civil Aviation Organization (ICAO) must be packaged, marked, labeled, and shipped, with an accompanying properly prepared dangerous goods declaration, in accordance with the ICAO technical instructions.

b. Suspected DOT HazMat
Nanomaterials that are suspected to be hazardous (e.g., toxic, reactive, flammable) should be classified, labeled, marked, and manifested as though that hazard exists in accordance with Section 5.1.1 above. These materials should be classified and shipped as samples per 49 CFR 172.101c (11) unless the material is specifically prohibited by 173.21, 173.54, 173.56(d), 173.56(e), 173.224c or 173.225(b).

c. Other Nanomaterials
Nanomaterials that do not meet the DOTs criteria listed above still may pose health and safety issues to personnel handling the material if they are released during its transport. Therefore, all shipments of nanomaterials, regardless of whether they meet the definition for hazardous materials or not, should be consistently packaged using the equivalent of a DOT-certified Packing Group I (PG I) container and labeled as described in the following section.

2. Off-site Shipments

a. Packaging
The outer and inner package should meet the definition of a Package Group I (PG I) type package. The innermost container should be tightly sealed to prevent leakage of nanomaterials. It should have a secondary seal, such as tape seal, or a wire tie to prevent a removable closure from inadvertently opening during transport.

The outer package should be filled with shock absorbing material that can:
(1) Protect the inner sample container(s) from damage.
(2) Absorb liquids that might leak from the inner container(s) during normal events in transport.

b. Labeling
The inner package should be labeled (not to be confused with DOT hazard labeling). Caution: Nanomaterials sample consisting of (technical description here). Contact (name of point of contact) at (contact number) in case of container breakage (See figure 1).

Figure 1 - Recommended Inner Packaging Label

CAUTION
Nanomaterials Sample Consisting of: [Technical Description Here] Contact: [Point of Contact] At [Contact's Phone Number] In Case of Container Breakage.

If the nanomaterial is in the form of dry dispersible particles, add the following line of text:

Nanoparticulates can exhibit unusual reactivity and toxicity. Avoid breathing dust, ingestion, and skin contact. Open only under exhaust ventilation.

Documentation and notifications for off-site transfer of nanomaterials should include the following:

- A signed and complete dangerous goods declaration or shipping papers prepared in accordance with the ICAO and DOT regulations. (Environmental Health and Radiation Safety offer training in the shipping of hazardous materials).
- Available descriptions of the material (e.g., SDSs). [With respect to samples researchers should prepare a document that describes known properties and other properties that deem reasonably likely to be exhibited by samples].
- A notification to receiving facility of the incoming shipment.

c. Modes of Transport
All materials should be transported by a qualified carrier. All transportation services must comply with the Federal Acquisition Regulations (FAR). Recommended modes for off-site shipment of nanomaterials include:
(1) FedEx or another certified hazardous-materials carrier.
(2) Roadway, UPS Ground, or another commercial LTL-certified hazardous-materials carrier.
(3) Dedicated highway hazardous-materials carriers for exclusive-use shipments.
(4) Shipments of nanomaterials classified as other materials. (neither recognized HazMat or suspected DOT HazMat) may be transported using the most expeditious method provided they are packaged as per the requirements and:
    - The driver must have a valid state driver's license appropriate for the vehicle being operated.
    - The vehicle must be in good mechanical condition and have a valid state safety inspection.
    - The vehicle must be insured with at least the required minimum liability insurance required by the state where the vehicle is registered.
    - The driver must obey all state and local traffic rules and regulations.
    - The driver must possess basic hazard information on the commodity being transported, i.e., material name, quantity, form and material safety data sheet if available.

3. On-Site Transfers of Nanomaterials
   a. Assess and record the hazards posed by the material(s) following a graded approach that takes into account the form of the material(s) (e.g., free particle vs. fixed on substrate).

b. Use packaging consistent with the recommendations for off-site shipment or packaging that affords an equivalent level of safety.
c. Mark the transfer containers in accordance with the (above) recommendations for off-site shipments.
d. Include the following documents in the package: The results of the safety assessment, and An SDS, if available, or a similar form detailing possible hazards associated with the material
e. Notify the receiving facility of the incoming arrival.

I. Destruction and Disposal

The following waste management guidance applies to nanomaterial-bearing waste streams consisting of nanomaterials (e.g., carbon nanotubes), items contaminated with nanomaterials (e.g., wipes/PPE), liquid suspensions containing nanomaterials (e.g., hydrochloric acid containing carbon nanotubes), and hazardous solids containing or coated with nanomaterials that can be released into the air or leach into liquids. This includes nanomaterials that can be dislodged via mechanical forces, such as scraping.

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.

1. Nanomaterials in Waste Streams
   a. Consider any material that has come into contact with dispersible, engineered nanoparticles (that has not been decontaminated) as belonging to a nanomaterial-bearing waste stream. This includes PPE, wipes, blotters and other disposable laboratory materials used during research activities.
   b. In order to reduce waste generated, consider reducing the risk of loss of nanomaterials into the air and surrounding environment by suspending powders in a small volume of a non-hazardous liquid. Balance the added safety, if any, against the risks and costs of the increased volume of waste.
   c. Evaluate surface contamination or decontaminate equipment used to manufacture or handle nanoparticles before disposing of or reusing it. Treat wastes (cleaning solutions, rinse waters, rags, PPE) resulting from decontamination as nanomaterial-bearing waste.

2. Classification and Disposal of Nanomaterial-bearing Waste Streams
   a. Do not put material from nanomaterial-bearing waste streams into the regular trash or down the drain. Seek evaluation and approval for disposal from Environmental Health and Radiation Safety.
   b. Do not permit nanomaterial-bearing wastes to be shipped off-site.
   c. Characterize and manage nanomaterial-bearing waste streams as either hazardous or nonhazardous waste based on the requirements in 40 CFR 261.10 to 38, or equivalent state regulations, considering their known characteristics and/or listing of the waste.
   d. Manage nanomaterial-bearing waste streams according to all applicable laboratory requirements for chemical waste. In addition:
      (1) 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 the nanomaterials.
      (2) Label the waste container with a description of the waste and the words "*contains nanomaterials.*" Include available information characterizing known and suspected properties.
      (3) Collect paper, wipes, PPE and other items with loose contamination in a plastic bag or other sealable container. When the bag/container is full, close it, take it out of the hood and place it into a second plastic bag or other sealable container.

J. Management of Nanomaterial Spill

1. Access Control
   a. Determine the extent of the area reasonably expected to have been affected and demarcate it with barricade tape or use another reliable means to restrict entry into the area.
   b. Contact Environmental Health and Radiation Safety via campus police at 419-530-2600 for cleanup of significant spills and restrict entry into the area to personnel from that organization.
   c. Allow trained personnel from the lab to clean up smaller spills.

d. Refer personnel exposed to nanomaterials as the result of a spill or in the course of a spill clean-up to Family Medicine during normal business hours and to the UTMC Emergency Department during off hours.

2. Dry Materials
   a. Position a walk-off mat (e.g., Tacki-Mat®) where clean-up personnel will exit the access controlled area to reduce the likelihood of spreading nanoparticles.
   b. Clean using wet wiping methods. Manage, collect and dispose of spill clean-up materials as nanomaterial-bearing waste.
   c. Alternatively, use a certified HEPA vacuum or other facility-approved method that doesn't involve dry sweeping or the use of compressed air.
      (1) Ensure that the effectiveness of HEPA filters is verified at a frequency consistent with manufacturer recommendations or local laboratory standards.
      (2) When feasible, use only dedicated HEPA vacuums used for nanomaterial clean up. Label the units accordingly, e.g., Use only for nanomaterial spill clean up. Use a log to record the type of material collected. Avoid mixing potentially incompatible materials in the vacuum or filters.
      (3) Characterize, collect and dispose of used HEPA filters as nanomaterial-bearing waste.
      (4) Consider the possible air reactivity of nanoparticles prior to using a vacuum cleaner. Some normally stable powders may become pyrophoric if deposited on a filter and subject to high airflow.

3. Liquids
   Employ normal response based on the spilled material's known hazards. The following are additional considerations to mitigate nanomaterials left behind once the liquids have been removed:
   a. Position an absorbent walk-off mat where the clean-up personnel will exit the access-controlled area to prevent the spread of liquids containing suspended nanoparticles.
   b. Place barriers (e.g., plastic sheeting) that will minimize air currents across the surface affected by the spill.
   c. Use a wet-wiping method to clean the spill. A HEPA-filtered vacuum dedicated to the clean up of nanomaterials may also be used to clean up residual nanomaterials left behind after the spill area has dried.
   d. Manage all materials used to clean up the spill (absorbent mats, absorbent material, wipes etc.) as hazardous or potentially hazardous waste based on the material involved.

4. Wastes
   Manage all debris resulting from the clean up of a spill as though it contains sufficient nanomaterials to be managed in accordance with the UT procedure Collection, Storage, Transport and Disposal of Hazardous Waste (HM-08-01).

V. REFERENCES

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