

Department of Energy Nanoscale Science Research Centers

Approach to Nanomaterial ES&H

Revision 2 – June 2007



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Change Log

| Revision | Date | Reason |
|-----------------|-------------|--|
| Rev 0 | 3/06 | New Document |
| Rev 1 | 4/07 | <p>Section 3.3.2 was modified to allow exhausting of HEPA filtered exhaust into a room with an engineering evaluation</p> <p>Section 3.5 was modified to include extended sleeve gloves</p> <p>Section 5.2.3 was modified to include requirements for shipping nanomaterials classified as “other”</p> <p>Attachment 1 “Sample of an IH sampling protocol” was added</p> <p>Various editorial and formatting changes</p> |
| Rev 2 | 6/07 | <p>Section 3. was modified to allow flexibility in determining exhaust ventilation engineering controls</p> <p>Section 4. “Verifying Program Effectiveness” was added to replace “Medical Surveillance</p> <p>Section 6.3 waste labeling was modified</p> <p>Various editorial and formatting changes</p> |

Nanoscale Science Research Center: Approach to Nanomaterial ES&H Rev. 2 - June 2007

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1 INTRODUCTION

1.1 Applicability and Scope

The following non-mandatory guidance is intended for the Nanoscale Science Research Centers (NSRCs)¹ funded by the Basic Energy Sciences program office under the U.S. Department of Energy’s Office of Science.

It sets forth practices for managing environmental, safety and health (ES&H) concerns associated with:

- “Engineered” nanomaterials, i.e., materials consisting of, or containing structures of between 1 and 100 nanometers (nm) that make use of properties unique to nanoscale forms of materials.
- Nanoparticles, i.e., dispersible particles having in 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.²

¹ The document necessarily deals with some issues that must be managed within individual National Laboratories at a higher level than the NSRC. The suggestions in this manual are not intended to set requirements for the National Laboratories at which the NSRCs are located, but rather to suggest a means of dealing with issues that need to be dealt with at a higher level. As specified in [DOE Policy 456.1](#), the NSRCs and their home Laboratories must resolve interface issues in a manner consistent with their respective “Integrated Safety Management Systems.”

² [ASTM E2456-06](#), “Standard Terminology Relating to Nanotechnology”

- Precursors, intermediates, and wastes used during, or resulting from synthesizing such nanomaterials.
- Laboratory scale, i.e., work with substances in which the containers used for reactions, transfers, and other handling of substances are designed to be easily and safely manipulated by one person. "Laboratory scale" excludes those workplaces whose function is to produce commercial quantities of materials.³

1.2 Purpose

This document is intended to:

- Provide guidance that will help the five NSRCs develop site-specific controls that will protect workers and the environment.
- Offer reasonable guidance for managing the uncertainty associated with nanomaterials whose hazards have not been determined and reducing to an acceptable level the risk of worker injury, worker ill-health and negative environmental impacts.
- Promote consistency in policy and procedures between the five NSRC's.

1.3 Limitations

- Information about the safety and health effects caused by nanomaterials, particle measurement, and control effectiveness is evolving. This document cannot anticipate such changes, nor can it necessarily be kept current with each new development.⁴
- The following guidelines are not intended to discourage responsible efforts to develop or refine alternative approaches to managing risks⁵.
- The guidance contained herein may conflict with regulatory requirements or the policy of the home Laboratory. The guidance contained herein is not intended to pre-empt regulations or Laboratory policy or procedures.
- This document uses imperative statements merely to concisely and clearly emphasize suggested policies and procedures.
- The NSRCs are expected to use this guidance to formulate internal documents that take account not only of the guidance in this document, but also of local requirements and other guidance. An individual NSRC's verbatim adoption of the wordage in these guidelines is not anticipated.

1.4 Background

- Nanoscale materials are of considerable scientific interest because some material properties can change at this scale.⁶ These changes challenge the researcher's,

³ 29 CFR 1910.1450(b)(2), *Occupational Exposure to Hazardous Chemicals in Laboratories, Definitions*

⁴ Please communicate concerns about the accuracy or validity or effectiveness of information in this document to the Environment, Health and Safety Working Group of the DOE's Nanoscale Science Research Centers to help improve the document when it is updated. Send comments to Ken Rivera at: kensley.rivera@science.doe.gov

⁵ In this document, "managing" risks means evaluating hazards, controlling hazards, and verifying the sufficiency of hazard controls whose purpose is the protection of the environment and human health.

manager's, and safety professional's understanding of hazards, and their ability to anticipate, recognize, evaluate, and control potential health, safety, and environmental risks.

- Exposures to these materials may occur through inhalation⁷, dermal contact, and ingestion. Animal studies indicate that low-solubility ultra fine particles might be more toxic than larger ones on a mass-for-mass basis. Because of their tiny size, they can penetrate deep into the lungs and may translocate to other organs following pathways not demonstrated in studies with larger particles.
- The nanoparticulate forms of some materials show unusually high reactivity, especially for fire, explosion, and in catalytic reactions. Engineered nanoparticles and nanostructured porous materials have been used effectively for many years as catalysts for increasing the rate of reactions, or decreasing the temperature needed for reactions in liquids and gases. Depending on their composition and structure, some nanomaterials may initiate catalytic reactions that would not otherwise be anticipated from their chemical composition.
- The Department of Energy has made clear that it expects those engaged in the emerging field of nanotechnology to act responsibly in evaluating and controlling the associated environmental, health and safety risks.
- Although there is no specific guidance on evaluating and controlling the risks posed by nanomaterials, preliminary research suggests that some controls used in conventional laboratory settings will work effectively for them.
- Lacking other guidance and recognizing the benefits to themselves, their sponsors, and their shared user-community, the five Centers have agreed to work in conformance with the following relatively conservative policies and risk-control strategies until more authoritative guidance is available.

2 CONCEPTUAL FOUNDATIONS

- The DOE's NSRCs, in developing state-of-the-art capabilities for fabricating and studying nanoscale materials, will endeavor to ensure that adequate ES&H controls are applied at the Centers. "Adequate" means sufficient to reduce to an acceptable level:
 - The risk of worker injury or ill-health
 - The risk of negative environmental impacts
- The NSRCs will comply with the [DOE Policy 456.1, Secretarial Policy Statement on Nanoscale Safety](#) by carrying out their site-specific implementation plans for P 456.1, and by applying the guidance contained herein.

⁶ ASTM's Terminology for Nanotechnology (ASTM E 2456-06) use the term "transitive nanoparticles" to refer to nanoparticles that exhibit a size-related intensive property that differs significantly from that seen in fine particles or bulk materials.

⁷ [Approaches to Safe Nanotechnology](#), National Institute for Occupational Safety and Health, Version 1.1 (July 2006), p. vi

- In conformance with the general principle in the National Research Council's *Prudent Practices for Handling Hazardous Chemicals in Laboratories*, Laboratory personnel should treat "all new compounds, or those of unknown toxicity, as though they could be acutely toxic in the short run and chronically toxic in the long run."⁸ Moreover, although exposures are believed likely to be extremely low in comparison to those that might be seen in other workplaces, the NIOSH observation⁹ that all poorly soluble, low toxicity ultra fine particulates might be carcinogenic, even those normally considered to be nuisance particulates, makes it important to carefully manage worker exposure and avoid environmental releases.
- Nanomaterials whose hazards have been studied will be managed in a manner consistent with the disclosed risks.

3 CONTROLS FOR R&D LABORATORY OPERATIONS

3.1 Work Planning

Review all work with nanomaterials for ES&H concerns following an established safety-assessment process. Before starting work, the Center should carry out a safety assessment consistent with the home Laboratory's process. The assessment should, as needed,

- Begin with a well-defined description of the work
- Involve subject matter experts (SMEs)
- Specify hazard controls, including
 - Engineered controls
 - Design reviews
 - Formal procedures
 - Use of personal protective equipment (PPE)
 - Training
 - Other administrative controls
 - Defined criteria for work-change control
- Consider chemical hazard information for bulk/raw materials when developing controls for nanomaterials, and any new information specific to the material at the scale being used.

⁸ *Prudent Practices in the Laboratory: Handling and Disposal of Chemicals*, National Research Council, National Academy Press, Washington, D.C. 1995 – [page 3](#)

⁹ NIOSH draft [CURRENT INTELLIGENCE BULLETIN: Evaluation of Health Hazard and Recommendations for Occupational Exposure to Titanium Dioxide](#), lines 86 through 89: "While the potential cancer potency of fine TiO₂ appears to be relatively low at current occupational exposures, NIOSH is concerned about the potential carcinogenicity of ultrafine TiO₂ if workers are exposed at the current mass-based exposure limits for respirable or total mass fractions of TiO₂."

- Before starting any new work, ensure that the Center’s ES&H subject matter expert (SME) or the home Laboratory’s authority over waste management
 - Evaluates the potential for generating new nanomaterial-bearing waste streams and
 - Defines waste management procedures for wastes that contain nanomaterials
- Evaluate the potential for worker exposure to nanomaterials and their escape into the environment before removing, remodeling, servicing, maintaining, or repairing laboratory equipment and exhaust systems.
- Consider the recognized and foreseeable hazards of the precursor materials and intermediates as well as those of the resulting nanomaterials.
- Consider the higher reactivity of some nanoscale materials as requiring that they be treated as potential sources of ignition, accelerants, and fuel that could result in fire or explosion.
- Consider the potential for reactions involving nanomaterials already “captured” in exhaust air filters.

3.2 Control Preferences

1. Follow a graded approach in specifying controls. Operations involving easily dispersed dry nanomaterials deserve more attention and more stringent controls than those where the nanomaterials are imbedded in solid or liquid matrixes.
2. From a laboratory worker health management perspective, the following represents the order of preference (most preferred to least preferred) for handling nanomaterials:
 - a. Solid materials with imbedded nanostructures
 - b. Solid nanomaterials with nanostructures fixed to the material’s surface
 - c. Nanoparticles suspended in liquids
 - d. Dry, dispersible (engineered) nanoparticles, nanoparticle agglomerates, or nanoparticle aggregates

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.

3. Consider the hazardous properties of the precursor materials as well as those of the resulting nanomolecular product. Remember, nanomaterial hazards might not be known or reliably anticipated. An environment, health and safety professional can assist with this evaluation.

3.3 Engineered Controls

3.3.1 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.

3.3.2 Ventilation Preferences

- Conduct any work that could generate engineered nanoparticles in an enclosure that operates at a negative pressure differential compared to the worker's breathing zone. Examples of such enclosures include gloveboxes, glove bags, and laboratory bench-top or floor-mounted chemical hoods. 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 like a "snorkel hood."
- Do not exhaust effluent (air) reasonably suspected to contain engineered nanoparticles whose hazards are not well understood. Whenever practical, filter it or otherwise clean (scrub) it before release.
- HEPA filtration appears to effectively remove nanoparticles from air.¹⁰
- 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.
- Duct the exhaust stream outside the building whenever feasible. Filters, scrubbers or bubblers may be appropriate 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.
- If it is not feasible to duct HEPA-filtered treated exhaust air outside of the building:
 - Follow the guidance in ANSI Z9.7, *American National Standard for Recirculation of from Industrial Process Exhaust Systems*.

¹⁰ Current knowledge indicates that a well-designed exhaust ventilation system with a high-efficiency particulate air (HEPA) filter should effectively remove nanoparticles [Hinds 1999]. Filters are tested using particles that have the lowest probability of being captured (typically around 300 nm in diameter). It is expected that the collection efficiencies for smaller particles should exceed the measured collection efficiency at this particle diameter [Lee and Liu 1982]. NIOSH is conducting research to validate the efficiency of HEPA filter media used in environmental control systems and in respirators in removing nanoparticles. As results of this research become available, they will be posted on the NIOSH Web site.

If HEPA filters are used in the dust collection system, they should be coupled to a well- designed filter housing. If the filter is improperly seated, nanoparticles have the potential to bypass the filter, leading to filter efficiencies much less than predicted [NIOSH 2003].

[This text appears on page 22 of Version 1.1 of NIOSH's [Approaches to Safe Nanotechnology](#). Please consult the original document for more information on cited source material. The document can be found at: <http://www.cdc.gov/niosh/topics/nanotech/safenano/>]

- Conduct a hazards 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).
- Do not use horizontal laminar-flow hoods (“clean benches”) that direct a flow of HEPA-filtered air into the user’s face to control exposure to nanomaterials.
- Consider exhausting Type II biological safety cabinets, in which free nanomaterials are handled, directly to the exterior (hard ducted) or through a thimble connection over the cabinet’s exhaust. Air from inside the cabinet, even if HEPA-filtered, should not be recirculated within the laboratory except as provide for in ANSI Z9.7, *American National Standard for Recirculation of Air from Industrial Process Exhaust Systems*.
- Maintain and test the effectiveness of exhaust systems and components as specified by the manufacturer. Evaluate equipment previously used to synthesize, handle or capture nanoparticles for contamination and incompatibility before reusing or disposing of it.
- Evaluate laboratory equipment and exhaust systems for contamination before removing, remodeling, or repairing them.

3.4 Administrative Controls

3.4.1 Chemical Hygiene Plan

As required in 10 CFR 851.23, develop and implement a chemical hygiene plan satisfying the criteria in 29 CFR 1910.1450. The plan should be specific to the Center’s scope of activities.

3.4.2 Housekeeping

Practice good housekeeping in laboratories where nanomaterials are handled. Follow a graded approach paying attention where dispersible nanomaterials are handled.

- 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.
- 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.
- 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. Such locations include vacuum cleaner filters and canisters.
- Clean up dry, engineered nanomaterials using:
 - A dedicated, approved HEPA vacuum whose filtration effectiveness has been verified
 - Wet wiping

- Other facility-approved methods that do not involve dry sweeping or the use of compressed air
- Dispose of used cleaning materials and wastes in accordance with the home Laboratory's hazardous-waste procedures. (See Section 6, "Management of Nanomaterial-Bearing Waste Streams").

3.4.3 Work Practices

- Transfer engineered nanomaterials samples between workstations (such as exhaust hoods, glove boxes, furnaces) in closed, labeled containers.
- Take reasonable precautions to minimize the likelihood of skin contact with engineered nanoparticles or nanoparticle-containing materials likely to release nanoparticles (nanostructures).
- 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.
- Handle nanomaterial-bearing waste (see definition above) according to the home Laboratory's hazardous chemical waste guidelines and Section 6 "Management of Nanomaterial-Bearing Waste Streams."
- Vacuum dry engineered nanoparticulates only with an approved HEPA vacuum cleaner that has been performance tested and certified according to the Centers policies and procedures.

3.4.4 Inventory Requirements

[Reserved.]

3.4.5 Marking, Labeling and Signage

- 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.
- Where appropriate, 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."
- When engineered nanoparticles are being moved outside a Center, also include label text that indicates that the particulates might be unusually reactive and vary in toxic potential, quantitatively and qualitatively, from normal scale forms of the same material.

3.5 Clothing & Personal Protective Equipment

- 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 such as, e.g.,

laboratory chemical hoods are equipped with performance monitors that will notify users of equipment malfunction.¹¹

- 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. Protective clothing that would typically be required for a wet-chemistry laboratory would be appropriate and could include but not limited to:
 - Closed-toed shoes made of a low permeability material. (Disposable over-the-shoe booties may be necessary to prevent tracking nanomaterials from the laboratory)
 - Long pants without cuffs
 - A long-sleeved shirt
 - Gauntlet-type gloves or nitrile gloves with extended sleeves
 - Laboratory coats
- Wear polymer (e.g., nitrile rubber) gloves when handling engineered nanomaterials and particulates in liquids.¹² 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.
 - Recognizing that exposure to nanomaterials is not known to have “good warning properties,” change gloves routinely to minimize potential exposure hazards. Alternatively, double glove.¹³
 - Keep contaminated gloves in a plastic bag or other sealed container in a hood until disposed.
 - Dispose of contaminated gloves in accordance with Section 6 of this document.
 - Wash hands and forearms after wearing gloves.
- Wear eye protection, e.g., (spectacle type) safety glasses, face shields, 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.
- Use industrial hygiene professionals or paraprofessionals working under the direction of an industrial hygiene professional to evaluate airborne exposures to engineered nanomaterials. If respirators are to be used for protections against engineered nanoparticles, select and use half-mask, P-100 cartridge-type respirators or respirators that provide a higher level of protection.

¹¹ This is not meant, in any sense, to suggest that if such a monitoring system is in place, that PPE is not required.

¹² When handling articles having nanomaterials in a securely bound form, i.e., when protection from nanoparticles and other hazards is not needed, cotton gloves and other gloves not typically appropriate in chemical laboratories can be considered. However, steps must be taken to avoid their misuse as protective equipment.

¹³ Wearing an inner glove can lessen the likelihood of contaminating hands while removing a contaminated outer glove.

- Keep potentially contaminated clothing and PPE in the laboratory or change out area to prevent engineered nanoparticles from being transported into common areas.
- Clean and dispose of all potentially contaminated clothing and PPE in accordance with the Center's home Laboratory procedures.

3.6 Monitoring and Characterization

- In consultation with Laboratory's SMEs, use a direct-reading particle-measuring device to screen for suspect emissions.
- Use more sophisticated techniques, to collect samples to characterize emissions and determine if a control is needed or must be upgraded or serviced. Attachment 1 contains an example of a sampling protocol.
- Use the home Laboratory's data management system to link environmental data indicative of exposure to nanoparticulate workers working for the Center.

3.7 Worker Competency

- Use a worker identification tool to ensure that staff members and support personnel with potential exposure to engineered nanoparticles are given appropriate training. The tool could use the same criteria set forth in section 4.1, *Nanoparticle Worker Identification*, (below).
- Do not assume that staff members and visiting researchers are aware of the health and safety concerns posed by nanomaterials. At a minimum, provide such personnel conducting hands-on work with an awareness-level orientation that will alert them to concerns (potential hazards) and to the Laboratory's and the NSRC's policies.
- To better ensure understanding and competence, incorporate specific procedural requirements into written procedures or instructions provided to facility users by the host NSRC's personnel.

4 VERIFYING PROGRAM EFFECTIVENESS

Section 3 of this document defines policies and procedures intended to ensure that worker exposure to all chemicals, including engineered nanoparticles whose hazards are not well understood, is kept as low as practicable in the research environment.¹⁴ While effective management of engineered nanoparticulates should ensure that ill-health effects and adverse environmental consequences will not result, the general uncertainty associated with engineered nanoparticle toxicology and environmental fate and reports of ill-health effects in test animals make it appropriate to attempt to verify the absence of unusual health effects in exposed workers. Respecting the limits imposed by current knowledge and the absence of consensus standards, this document recommends basic worker health and environmental monitoring consisting of:

¹⁴ *Prudent Practices in the Laboratory: Handling and Disposal of Chemicals*, National Research Council, National Academy Press, Washington, D.C. 1995 – [page 3](#)

1. Identifying staff¹⁵ (hereafter “nanoparticle workers”) exposed to engineered nanoparticles of unknown health effects.
2. Conducting workplace characterization and worker exposure assessments
3. Providing nanoparticle workers with “baseline” medical evaluations and including them in a nonspecific routine health monitoring program
4. Checking wastes for evidence of uncontrolled release of engineered nanomaterials
5. Effluent monitoring

Each of these program elements should be periodically reviewed by the NSRC ES&H Working Group and the approaches refined in a manner reflective of newly available knowledge about human and environmental health effects. They should also be kept as rigorous as current recommendations in professionally-recognized national and international consensus standards.

4.1 Nanoparticle Worker Identification

Unlike substances whose effects have been more thoroughly studied, there are no definitions of an action (exposure) level for nanoparticles that should trigger worker inclusion in a more formal medical surveillance program. Consequently, this document recommends that facilities adopt a broad definition of nanoparticle-exposed workers that can (and should) be refined as more reliable information on human health effects becomes available. This definition should be understood as initially causing identification of a larger, group than is at significant risk.

Any staff member meeting one or more of the following criteria be considered an “engineered nanoparticle worker”:

- Handles engineered nanoscale particulates that have the potential to become dispersed in the air
- Routinely spends (significant amounts of) time in an area in which engineered nanoparticles have the potential to become dispersed in the air
- Works on equipment that might be contaminated with materials that could foreseeably release engineered nanoparticles during servicing or maintenance

Note: Given the lack of current understanding about dose-response, this document suggests inclusion of workers whose exposures might be relatively high and those whose exposures might be relatively low. This suggestion also reflects the lack of consensus on how to measure worker exposure.

Each Center should:

- Record the identity of personnel who satisfy the preceding definition of *engineered nanoparticle workers*

¹⁵ Attempting to include “non resident users” presents problems that make it appropriate to limit this recommendation to personnel employed at the NSRCs and elsewhere in the National Laboratories at which the Centers are located.

- Consistent with the recommendation in section 3.7, *Worker Competency*, ensure that personnel who satisfy the preceding definition of *engineered nanoparticle workers* take the Laboratory's or Center's nanomaterial hazards awareness training
- Use available methods to characterize workplace conditions and exposures of *engineered nanoparticle workers* (as described elsewhere in this document)
- Ensure that engineered nanoparticle workers are offered periodic medical evaluations that may include routine tests such as pulmonary, renal, liver, and hematopoietic function and pulmonary function testing.
- Revisit and refine the definition of *engineered nanoparticle workers* and make recommendations to the Site Occupational Medical Director for changes to any applicable medical examination program.

4.2 Workplace Characterization and Exposure Assessments

Workplace characterization and nanomaterial exposure assessment challenges include:

- Substantially different "parameters" may prove hygienically significant for different nanomaterials
- Materials of the same chemical composition can have markedly different forms at the nanoscale and the different forms can have markedly different properties.
- No professional consensus on monitoring instrumentation and protocols exists and it may be a decade (or more) before one emerges.

Note: This document suggests that there is value in attempting to measure workplace conditions and characterize worker exposures to nanoparticles in the interim.¹⁶ [There may also be value in characterizing airborne and waterborne emissions.]

Although there is no validated or consensus approach for characterizing worker exposure, this document recommends a good faith effort to characterize the exposures of personnel exposed to engineered nanoparticles and to link the resulting data to those nanoparticle-exposed personnel.

Use available instruments and methods to characterize workplace conditions and estimate exposures of engineered nanoparticle workers.

- Conduct "baseline" monitoring by measuring conditions prior to start up. Measure again at the conclusion of system commissioning and periodically thereafter. These efforts should be considered a vital part of an overall strategy of ensuring that controls are well conceived, well constructed, and remain effective. Investigate significantly atypical and unexpected measurements.
- In consultation with Laboratory's SMEs, use direct-reading particle-measuring devices to screen for suspect emissions and atypical conditions that deserve further investigation.
- Use more sophisticated techniques, to collect and analyze samples that will be used to characterize emissions and potential exposures.
- Attachment 1 contains an example of a sampling protocol.

¹⁶ [Commentary: Safe Handling of Nanotechnology, Maynard, A. et al., Nature, Vol. 444, 16 November 2006, p. 268](#)

4.3 Worker Health Surveillance

Consistent with 10 CFR 851.24, this document suggests that the medical directors responsible for each Center define health monitoring for workers engaged in nanoscale science research and support activities. Ideally, discussions between NSRC Site Occupational Medical Directors will lead to development and implementation of policies and procedures that are relatively consistent at the Laboratories that house NSRCs.¹⁷ This section then should be revised to reflect their consensus recommendations.

Until a consensus emerges, this guidance suggests that each Center's ES&H manager contact the Site Occupational Medical Director to determine the advisability of having:

- Center staff and other Laboratory employees with jobs involving the potential for respiratory or skin exposure to engineered nanomaterials 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.
- Having Center employees involved in any incident that results in an unexpected and/or unusually high exposure to nanomaterials, through any route of entry, examined by the home Laboratory's occupational medical clinic for a post-incident evaluation as per OSHA 1910.1450(g)(1)(i).
- Exempting non-resident (e.g., user facility) personnel from medical surveillance.

4.4 Domestic Waste Surveys

Currently, methods for surveying wastes for nanoparticles have not yet been established. However, rather than reserving this section, this document suggests that each Center's staff members be instructed to visually inspect domestic wastes periodically and instructed to report to the Center's ES&H officer instances involving the appearance of suspect nanomaterial, including contaminated wipes, in domestic trash containers.

4.5 Effluent Monitoring

[Reserved – Techniques for monitoring have not yet been established. However, this should not be interpreted as discouraging interested Centers from collaborating on the development of methods.]

5 TRANSPORTATION OF NANOMATERIALS

The guidance under this heading applies to the movement of material from the NSRCs to and from off-site locations. It assumes that NSRC personnel who package and prepare nanomaterials for shipment off-site have and are current on HazMat Employee training required by 49 CFR Subpart H. Consult your institution's shipping department for assistance and routing of your materials.

¹⁷ This recommendation is not meant to exclude site industrial hygiene program managers (or NSRC ES&H personnel) from deliberations. Indeed, the NSRCs recommend the inclusion industrial hygiene program managers.

5.1 Categories of Materials

5.1.1 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 and applicable DOE Orders.

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.

5.1.2 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). These suspect materials should be packaged in accordance with section 5.2.1 below.

5.1.3 Other Nanomaterials

Nanomaterials that do not meet the DOT's 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 below.

5.2 Off-site Shipments

The information under this heading applies to materials sent to NSRCs, and materials sent from NSRCs to off-site locations, that do not otherwise meet DOT's definition of "hazardous material".

5.2.1 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.

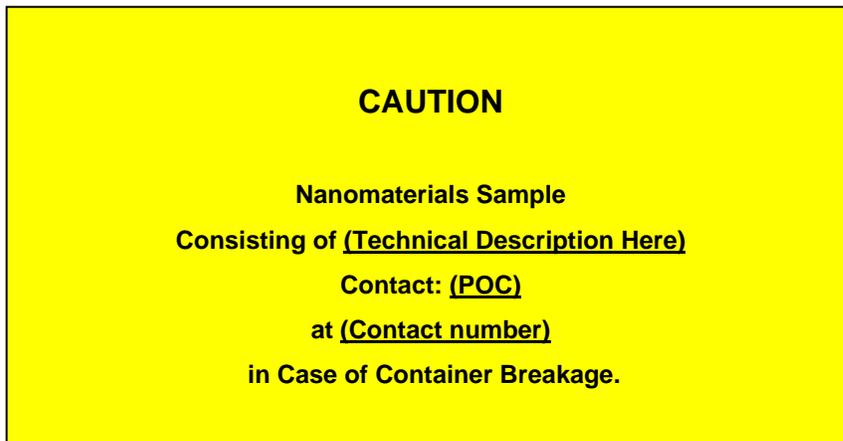
The outer package should be filled with shock absorbing material that can:

- Protect the inner sample container(s) from damage
- Absorb liquids that might leak from the inner container(s) during normal events in transport.

5.2.2 **Labeling**

As depicted in Figure 1, 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



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.

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 by certified/qualified HazMat employees who are authorized to release materials from the site.
- Available descriptions of the material (e.g., MSDSs). [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.

5.2.3 **Modes of Transport**

All materials should be transported by a qualified carrier, for which the DOE or the GSA has a tender on file. All transportation services must comply with the Federal Acquisition Regulations (FAR). Recommended modes for off-site shipment of nanomaterials include

- FedEx, or other certified hazardous-materials carrier
- Roadway, UPS Ground, or other commercial LTL-certified hazardous-materials carrier

- Dedicated highway hazardous-materials carriers for exclusive-use shipments using a carrier approved by the DOE's Motor Carrier Safety Program (MCEP).
- 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 in section 5.2.1 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

5.3 On-Site Transfers of Nanomaterials

The on-site transfer of nanomaterials should follow the DOE-approved, site-specific, transportation safety document or other institutional document (i.e., chemical hygiene plan); in lieu of such a document, the transfer should fully comply with the DOTs' requirements. The site's transportation authority (e.g., Transportation Safety Officer or equivalent) should be the authority having jurisdiction on the requirements for packaging, marking, and documentation necessary for on-site transfers. For nanomaterials, the following is suggested:

- 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).
- Use packaging consistent with the recommendations for off-site shipment or packaging that affords an equivalent level of safety.
- Mark the transfer containers in accordance with the (above) recommendations for off-site shipments.
- Include the following documents in the package:
 - The results of the safety assessment, and
 - An MSDS, if available, or a similar form detailing possible hazards associated with the material; otherwise, if an MSDS is unavailable, the principal investigator should supply material-specific knowledge.
- Notify the receiving facility of the incoming shipment.

6 MANAGEMENT OF NANOMATERIAL-BEARING WASTE STREAMS

6.1 Applicability

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 (e.g., hydrochloric acid containing carbon nanotubes)
- Solid matrixes 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.

6.2 Nanomaterials in Waste Streams

- 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.
- 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.
- 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.

6.3 Classification and Disposal of Nanomaterial-bearing Waste Streams

- Do not put material from nanomaterial-bearing waste streams into to the regular trash or down the drain. Seek evaluation and approval for sink discharge from your home institution's environmental subject matter expert.
- Do not permit nanomaterial-bearing wastes to be shipped to off-site researchers' home institutions for disposal.
- Characterize and manage nonmaterial-bearing waste streams as either hazardous or non-hazardous 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.
- 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.
- Label the waste container with a description of the waste and the words "contains nanomaterials". Include available information characterizing known and suspected properties.
- Collect paper, wipes, PPE and other items with loose contamination in a plastic bag or other sealing container stored in the laboratory hood. When the bag is full, close it, take

it out of the hood and place it into a second plastic bag or other sealing container. Label the outer bag with the laboratory's proper waste label.

- Send otherwise non-hazardous nanomaterial-bearing waste to a RCRA-permitted treatment, storage and disposal facility (TSD). Direct the TSD as to the selected treatment method best suited to controlling hazards associated with the waste.

7 MANAGEMENT OF NANOMATERIAL SPILLS

7.1 Access Control

- 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.
- Consider using a HazMat crew from the home Laboratory's waste management organization for clean up of significant spills and restrict entry into the area to personnel from that organization.
- Allow trained personnel from the Center to clean up smaller spills, following the home institution's cleanup procedures.
- Refer personnel exposed to nanomaterials in the course of a spill to the Center's medical dept.

7.2 Dry Materials

- 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.
- Clean using wet wiping methods. Characterize, collect and dispose of spill clean-up materials as nanomaterial-bearing waste.
- A tested and certified HEPA vacuum or other facility-approved methods that don't involve dry sweeping or the use of compressed air can also be used.
 - Ensure that the effectiveness of HEPA filters is verified at a frequency consistent with manufacturer recommendations.
 - 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 and avoid mixing potentially incompatible materials in the vacuum or filters.
 - Characterize, collect and dispose of used HEPA filters as nanomaterial-bearing waste.

7.3 Liquids

Employ normal HazMat 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:

- 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.

- Place barriers (e.g., plastic sheeting) that will minimize air currents across the surface affected by the spill.
- 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.
- Treat 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.

7.4 Wastes

- Manage all debris resulting from the clean up of a spill as though it contains sufficient nanomaterials to be managed in accordance with Section 6 of this procedure.

Attachment 1: Example Industrial Hygiene Sampling Protocol

Nanoscale Science Research Center Industrial Hygiene Sampling for Nanomaterials

Purpose

The purpose of this protocol is to characterize the nanomaterials being generated as a result of research at Department of Energy Nanoscale Science Research Centers (NSRC). The characterization will be used to identify sources, enumerate nanomaterial concentrations, implement controls where necessary, and document parameters and key attributes of nanomaterial generation and potential health effects.

For the purpose of this protocol, nanomaterials are defined as engineered materials with an aerodynamic diameter between 1 – 100 nanometers, manipulated in a laboratory-scale operation.

Background

As an emerging technology, the human health implications of nanomaterials are not clearly defined. Based on this, all work with nanomaterials should be handled as if they could be “acutely toxic in the short run and chronically toxic in the long run” (National Research Council, 1995, p. 3).

Traditionally, industrial hygienists have evaluated respiratory hazards in terms of total mass or respirable mass. The characteristics of nanomaterials have unique properties that may not predict health hazard as well as traditional mass measurements. Hazard potential may relate more profoundly to surface area, particle number, and/or solubility than mass (NIOSH, 2005). Further, the scale and properties of nanoparticles may permit them to pass through intact skin or gastrointestinal system and travel throughout the body, initiating systemic effects.

Sampling Protocol

Based on the unique properties of nanomaterials, total and respirable mass sampling is not adequate to characterize nanomaterial and assess exposure. Further, the experimental nature of research involves changing nanomaterial composition and structure (often with metals with inherent health hazards) and requires a more thorough analysis.

The first step of the sampling protocol requires a background sample of the room to be measured with the TSI Model 3007 Condensation Particle Counter (CPC). This sampling protocol is a four-pronged approach based on available equipment and technology: total particulate concentration (particle / cubic centimeter) using the TSI Model 3007 Condensation Particle Counter; particle concentration based on size distribution (particles / liter) using GRIMM Model 1.108 SubMicron Aerosol Spectrometer (particles / liter); and particulate characterization with active and passive sampling (elemental analysis and morphology) using SEM and TEM. From this sampling protocol, the total mass, particle size distribution, morphology, and composition will be determined. This information, along with detailed field notes and electronic images

(video/photo) will provide a record of nanomaterials in the laboratory, providing a basis for controls and documentation for the future.

There are currently no occupational exposure limits for nanomaterials; therefore there is no documented level that workers can be exposed to “safely.” Nanomaterials are present in the atmosphere due to car exhaust, smoke, and other phenomenon. The purpose of this protocol is to characterize background exposure to nanomaterials (outside, office areas, laboratories) and then identify if a significant amount is being released during research operations. This protocol will serve to identify sources of nanomaterials, and ensure that they are controlled through prudent research and safety practices.

Preparation

Preparation for sampling protocol must be coordinated with the NSRC organization/group (i.e., Industrial Hygiene Department) responsible for preparing, calibrating, and running the GRIMM portable dust monitor and the active air sampling train. In addition, the IAQ monitor may be used to record temperature, relative humidity, and carbon dioxide. The carbon dioxide decay curve can be used to estimate room air changes per hour. A competent individual at each NSRC shall be responsible for preparing and running the TSI Condensation Particle Counter.

Documentation

For each air sampling campaign, the research process, materials, ambient environmental conditions, and other relevant factors must be carefully documented. If possible, the air sampling should be videotaped and digital pictures taken to record events and locations.

The following items should be specifically and carefully documented:

- Date and sampling start and stop times
- Ambient outside weather conditions
- Indoor temperature and relative humidity
- Status of the building HVAC system
- Air changes in the room being monitored
- Is the room under positive or negative pressure
- How many people and processes are active during air monitoring
- Type of process generating nanomaterials (laser ablation, CVD)
- Description of nanomaterial processing (harvesting, weighing, transferring)
- Controls used with nanomaterials (isolation, ventilation)
- Personal protective equipment used by researcher during work with nanomaterials
- Anticipated chemical composition of nanomaterials (presence of catalyst, metals, other chemicals)
- Anticipated frequency of this operation in the future and any potential changes which may affect the hazard analysis of the process

- Exact location of air sampling equipment with respect to research process while monitoring takes place

Sampling Procedures

The air sampling equipment (Condensation Particle Counter, Aerosol Spectrometer; and sampling pump and filter) will be placed on a small cart side by side and as close to the operation as feasible without interfering with research process. The purpose of the cart is to provide a stable surface for equipment, ensure standard height for equipment during each nanomaterial process that is monitored and to keep equipment close together so that exposure to potential nanomaterials is as homogeneous as possible for each monitoring device.

The TSI Condensation Particle Counter (CPC) can be run using batteries or the AC adapter if power is readily available. The CPC must warm up for ten minutes, then the daily zero check should be successfully performed. Log mode 1 should be used to collect data. Sample flow rate is regulated by instrument at approximately 0.1 Lpm.

The GRIMM Aerosol Spectrometer can be run in one of three modes:

1. Occupational (inhalable, thoracic and respirable);
2. Mass ($\mu\text{g}/\text{m}^3$ in 15 size channels); and
3. Particle count (particles/liter in 15 sizes).

The particle count mode should be used for this protocol. Ensure that the box for “Mean Surface Area” is NOT checked. If this box is checked, the instrument will not download particle counts, only mean surface area. Sample flow rate is regulated by instrument at approximately 1.2 Lpm.

The CPC and GRIMM instrument times, as well as industrial hygienist’s watch should be synchronized to compare results and field notes of activities.

The air sampling train will be run in accordance with ASTM D 6095, “Standard Test Method for Determining Airborne Single-Crystal Ceramic Whiskers in the Workplace Environment by Scanning Electron Microscopy” (ASTM, 2001). The method specifies a 25 mm electrically conductive cassette assembly with an extension cowl or retainer ring containing a 0.45 μm MCE filter and support pad. RJ Lee Group has provided 0.1 μm neopore filters for the active sampling protocol. Filter assembly will be suspended on an extension rod open-face and upside down at a 45° angle (area sample), as described in ASTM D 6059 and NIOSH Method 7402, “Asbestos by TEM” (Schlecht & O’Connor, 1994).

NIOSH Method 7402 suggests a minimum sampling volume of 400 liters; both methods suggest a sampling pump flow rate from 0.5 to 16 Lpm, which can be adjusted to obtain 100 to 1300 fibers/ mm^2 . A high volume air sampling pump with rotometer should be used in order to potentially adjust flow while sampling takes place. A calibration curve should be developed prior to sampling with the rotometer and a primary standard (DryCal).

The airflow rate can be adjusted while sampling by using the CPC to establish an expected concentration (C) for filter sampling flow rate (Q),

$$Q = \frac{d * A}{C * T} \text{ and } Q * T \geq 400$$

Such that:

d = filter loading or particle density (100 to 1300 particles / mm²)

T = job duration or sampling time

A = effective filter area = 385 mm²

For example, if the concentration (C) measured with the CPC is 1 particle / mL (1000 particles / liter), and the sampling time (T) is 60 minutes:

$$Q_{\min} = \frac{100 * 385}{1000 * 60} = 0.64 \text{ Lpm} \quad Q * T = 0.64 * 60 = 38.4 \leq 400; \text{ therefore } Q \text{ is too low}$$

$$Q_{\max} = \frac{1300 * 385}{1000 * 60} = 8.34 \text{ Lpm} \quad Q * T = 8.34 * 60 = 500.4 > 400; \text{ therefore } Q \text{ is adequate}$$

Analysis

The analysis of the CPC and GRIMM is completed by downloading data and review of particle counts at various times and sizes. The air sampling cassettes and passive monitors shall be sent to Gary Casuccio with *RJ Lee Group* for SEM and TEM analysis in accordance with ASTM D 6058 and 6059. Analysis of active air sampling cassette will yield count, filter loading, and airborne concentration, as well as morphology and chemical composition. Analysis of passive monitor will also provide information on morphology and chemical composition. The passive sampler can yield particle concentration and size distribution (Wagner & Macher, 2003; Wagner & Leith, 2001).

References for Attachment 1

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