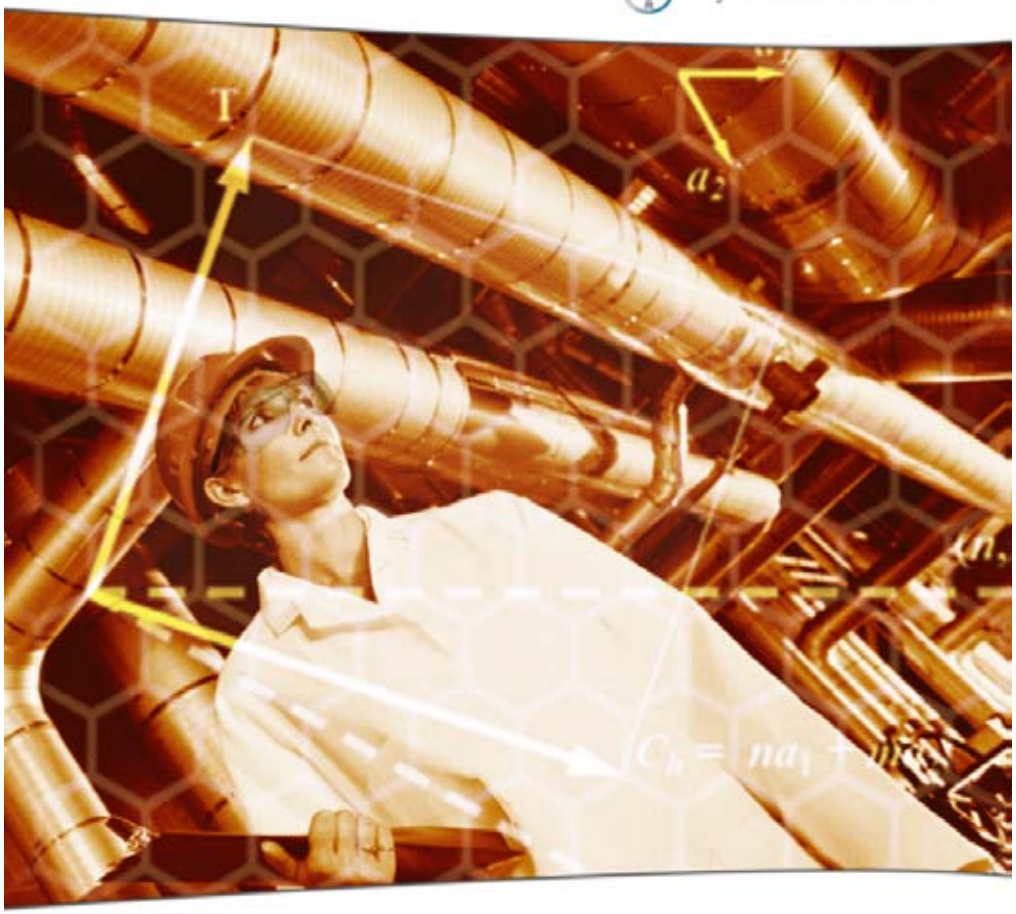
Recognize, Evaluate, Control



Lots of Questions for Occupational Health!

- What is a safe exposure limit?
- How to I measure employee exposure?
- Should I treat nanowaste as hazardous waste?
- Should I offer medical exams for my employees?
- Should I filter my exhaust stack effluent?
- Do respirators and other filters work for nanoparticles?
- What should I tell people who handle nanoparticles?

Exposure Limits

Proposed OELs for Nanoparticles

Table 2 Proposed OELs for engineered nanoparticles

Nanomaterial	Parameter	OEL	References
General	0.004% risk level	Mass-based OEL: 15	OECD (2008)
Titanium dioxide	0.1 risk level particles < 100 nm	0.1 mg/m^3	NIOSH (2005)
General dust		3 mg/m^3	BAuA (2009)
Photocopier Toner	Tolerable risk	0.6 mg/m^3	BAuA (2008b)
	2009 acceptable risk	0.06 mg/m^3	
	2018 acceptable risk	0.006 mg/m^3	
Biopersistent granular materials (metal oxides, others)	Density $> 6{,}000$ kg/m^3	20,000 particles/cm^3	IFA (2009)
Biopersistent granular materials	Density $< 6{,}000$ kg/m^3	40,000 particles/cm^3	IFA 2009
CNTs	Exposure risk ratio for asbestos	0.01 f/cm^3	IFA (2009)
Nanoscale liquid		Mass-based OEL	IFA (2009)
Fibrous	3:1; length 75,000 nm	0.01 f/cm^3	BSI (2007)
CMAR[a]		Mass-based OEL: 10	BSI (2007)
Insoluble	Not fibrous	Mass-based OEL: 15	BSI (2007)
Soluble	Not fibrous	Mass-based OEL: 10	BSI (2007)
	Not CMAR		
MWCNT	Bayer product only	0.05 mg/m^3	Bayer (2010)
MWCNT	Nanocyl product only	0.0025 mg/m^3	Nanocyl (2009)

[a] Carcinogenic, mutagenic, asthmagenic, and reproductive toxicants

Carbon Nanotubes?

- Graphite standard (OSHA): 5000/15000 µg/m^3 averaged over an 8 hour day– clearly not appropriate
- Graphite Standard (ACGIH) : 2000µg/m^3 averaged over an 8 hour day– clearly not appropriate
- Carbon Black (ACGIH): 3500 µg/m^3– clearly not appropriate
- Bayer (Baytube: MWCNT) Corporate Standard: 0.05 mg/m^3*
- Nanoctyl MWCNT Corporate Standard: Standard: 0.0025 mg/m^3
- Pending NIOSH MWCNT proposal: 0.007 mg/m^3 (based on limit of ability to measure)
- Asbestos Standard (OSHA-Optical): 0.1 fiber/cc
- Asbestos Standard (EPA-PCM): 0.01 fibers /cc
- Asbestos Standard (EPA-TEM): 0.02 structures/cc
- Molecular Foundry: Background--No exposure permitted

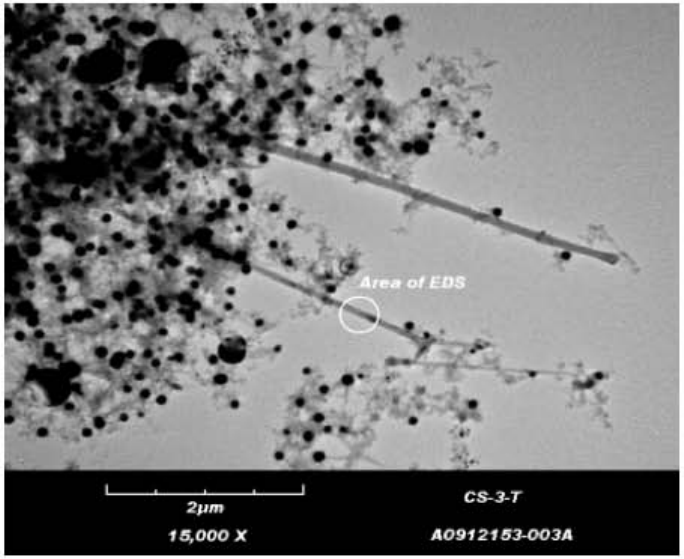
* For Bayers "short-tangled" and thus "low toxicity" MWCNTs. Implication is that this standard may be inadequate for longer/thicker/less tangled and thus potentially more toxic MWCNTs

Where do Exposures Occur?

Industrial Exposures (NIOSH)

Harvesting SWCNT's from a Carbon Arc Reactor

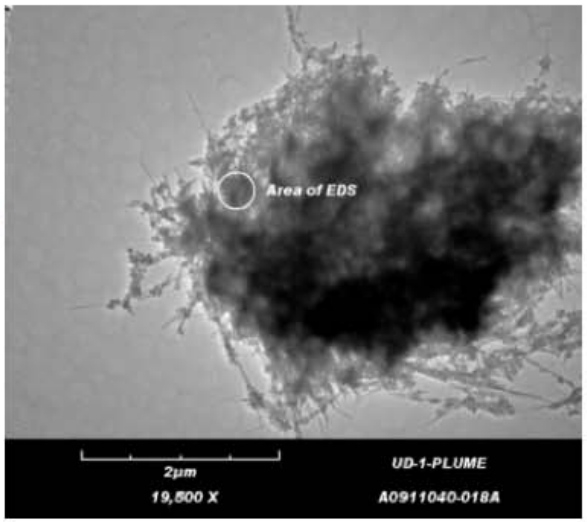
Task-based PBZ air sample analyzed via TEM w/ EDS



Limitation of Wet Methods

Droplet plume deposition onto unprotected skin during wet saw cutting of CNF composite

TEM of droplet plume emitted from diamond saw blade during wet saw cutting of CNF



Do Exposures Occur in Labs?

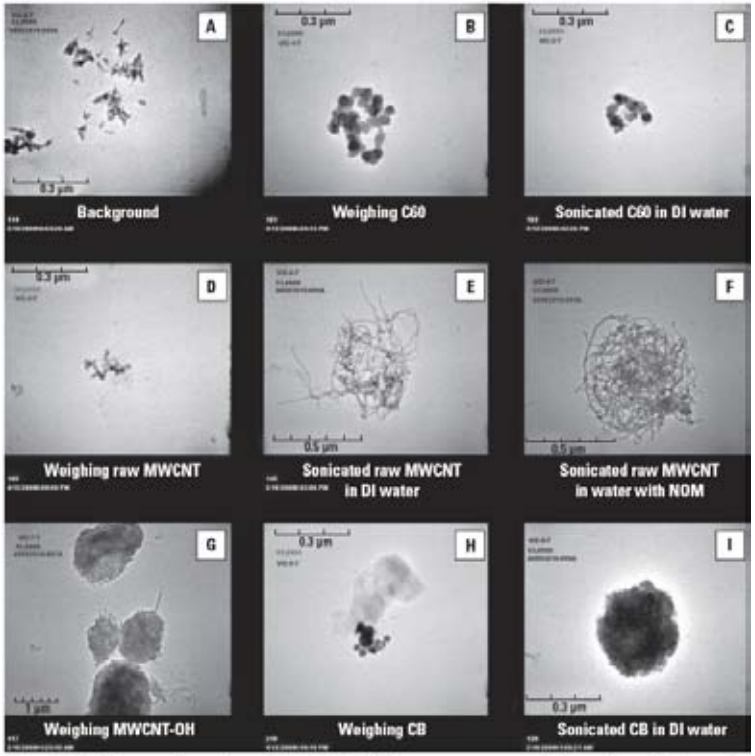
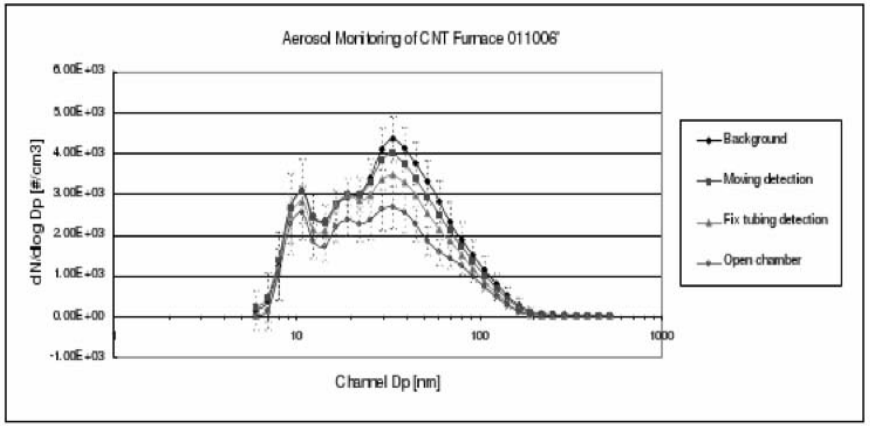


Figure 3. TEM images of engineered CNMs during laboratory processes. (*A*) Background air sample; bar = 0.3 μm. (*B*) Weighing/transferring C60 inside hood with no ventilation; bar = 0.3 μm. (*C*) Sonicating C60 in DI water inside unventilated enclosure; bar = 0.3 μm. (*D*) Weighing/transferring raw MWCNT inside hood with no ventilation; bar = 0.3 μm. Note that no tubular structures are present. (*E*) Sonicating raw MWCNT in DI water inside unventilated enclosure; bar = 0.5 μm. (*F*) Sonicating raw MWCNT in reconstituted water containing 100 mg/L (parts per million) NOM inside unventilated enclosure; bar = 0.5 μm. (*G*) Weighing/transferring MWCNT-OH inside hood with no ventilation; bar = 1 μm. (*H*) Weighing/transferring CB inside hood with no ventilation; bar = 0.3 μm. (*I*) Sonicating CB in DI water inside unventilated enclosure; bar = 0.3 μm.

✓**Several reports in the literature of researchers being exposed during manufactureing, harvesting and handling of CNTs**

Air Monitoring for Carbon Nanotubes Around Furnace During Growth and Purge Cycles (at MIT Lab)



From Marylin Hallock, MIT

From A. Maynard, NIOSH

NIOSH Findings

Examples of NIOSH field investigations: basic metrics			
Type of Facility	**Type of Particle, Morphology**	**Size of Particle**	**Range of "Potential" Exposure Concentrations**
University Research lab	Carbon Nanofibers	Approx. 100 nm diameter, 1–10 microns long	60-90 µg/m^3 Total Carbon
Metal Oxide Manufacturer	TiO_2, Lithium Titanate, powder	100–200 nm	<100 nm: 1.4 µg/m^3 (TiO_2) Total dust: 4-149 µg/m^3 (TiO_2) <100 nm: ND (Li) Total dust: ND -3 µg/m^3 (Li)
Manufacturer	Carbon Nanofibers	Approx. 100 nm diameter, 1–10 microns long	15 - 1800 µg/m^3 Total carbon
Research and Development lab	Quantum Dots, spheres	2–8 nm	ND
Metal Oxide Manufacturer	Manganese, Silver, Nickel, Cobalt, Iron oxides, spheres	8–50 nm	67 - 3619 µg/m^3 Mg, Ag, Ni, Co, Fe
Research and Development lab (Pilot-Scale)	Aluminum, spheres	50–100 nm	40 - 276 µg/m^3 Al
Research and Development lab	Elemental metals: Silver, copper, TiO_2	15–40 nm	ND
Filter Media Manufacturer	Nylon 6 Nanofiber	70–300 nm diameter, continuous length	ND

Measuring Exposures

How to I measure employee exposure?

- Minimally, use a direct reading instrument to measure airborne nanoparticle level--
  - — IPA CNC laser scattering photometer
  - — not chemistry or size specific, measures particles from 10-3000 nm
  - — Reads in units of particles/cc
  - — High background limits sensitivity

TSI 3007

TSI surface area meter

- Use “surface” area meter, nothing to compare results to, better suited for things like metal oxides, where catalysis of ROS is the main tox driver
  - — reads in units of $\mu m^2/cc$

- Very expensive particle size selective direct reading instruments, e.g. SMPS ($60K+) p/cc
  - — Research tools only

Metals and Metal Oxides

- Use traditional filter collection and elemental analysis
- Use size selective sampler
  - —Cyclone
  - —Cascade impactor
- Not very useful for short duration operations of the type found in labs, maybe better in a factory setting
- Sensitivity varies and may not be adequate

CNTs: Use Residual Metal Catalyst as a Surrogate

- Characterize residual metal concentration in bulk
- Measure worker airborne exposure to that metal via filter sampling and ICP or AA analysis
- Back-calculate CNT exposure

- Example
  - —Measure 1.0 mg/m^3 of iron catalyst in air sample
  - —Catalyst is present at 10% in the CNT
  - —CNT exposure = 1.0 mg/m^3 x 100%/10% = 10 mg/m^3

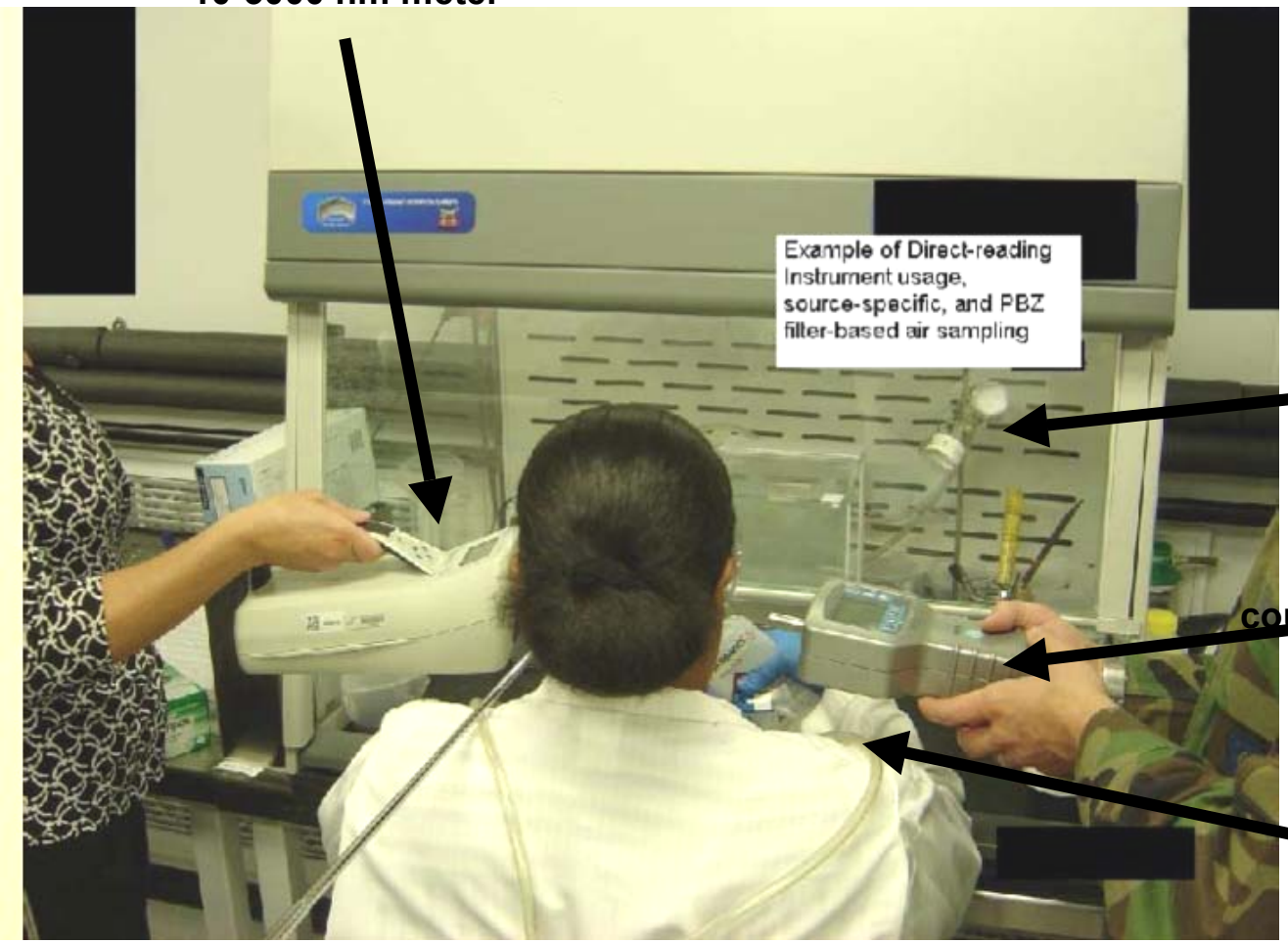
NIOSH's Approach

Some degree of size specificity can be had by using a micro particle meter and a nano particle meter in parallel (NIOSH)

Filter collection for metal analysis or TEM analysis

Looking for levels 25% above background with the direct reading instruments

NIOSH's Approach



10-3000 nm meter

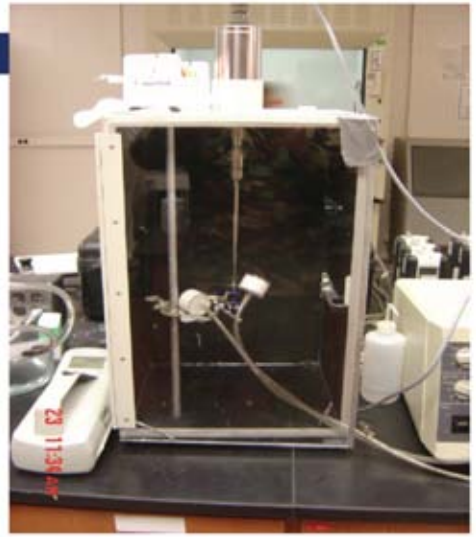
Filter sample at "source" for TEM analysis

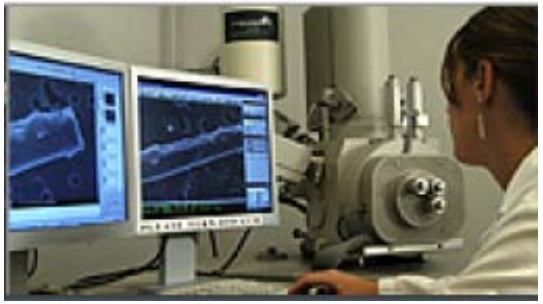
µm scale particle counter

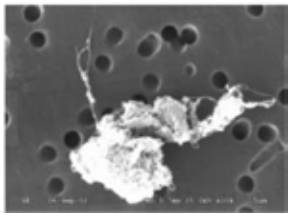
BZ filter collection for TEM analysis

Filter Sampling/TEM Analysis

Examples of Sampling Strategy

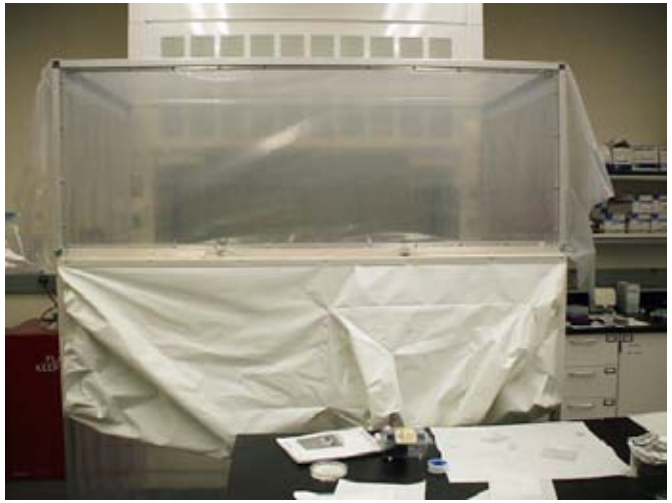






- Allows differentiation of ENP from background UFP
- Allows characterization of size, agglomeration, chemistry
- EXPENSIVE!

LBL: Eliminate Background UFP Interference



- We use zero background techniques to measure exposure to engineered nanoparticles
- This is a bottomless glovebox or hood antechamber with HEPA filtered air supply
- Run filtered fan to fill glovebox with particle-free air
- Repeat nano operation, while monitoring with direct reading instrument
- ~500x better sensitivity

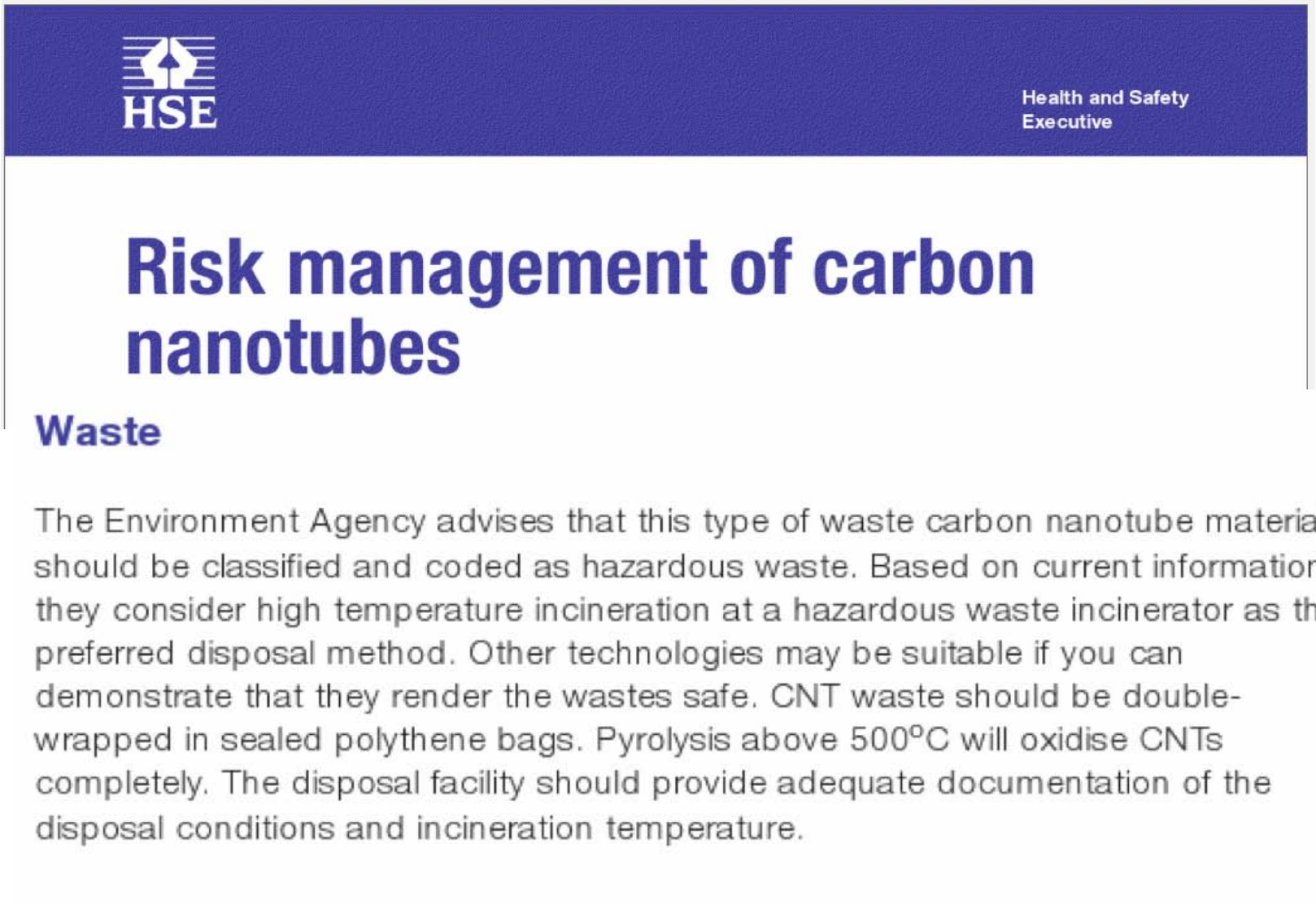
- If nothing detected, operation allowed to proceed without modification
- If exposure detected, work must be altered to eliminate exposure
- 80% of the time we don't see anything

Disposal of Waste Nanoparticles

Should I treat Nanoparticle-Containing Waste as Hazardous

- Not *explicitly* required under federal or California law
  - Although EPA rules now require some non-research users of CNTs to ensure that CNTs don't end up in US waterways
- DOE Consensus--Treat all waste containing engineered nanoparticles as if it were hazardous unless it ABSOLUTELY isn't (e.g. cured composite plastic with CNTs might not be treated as hazardous)
- Don't *call* it hazardous, just treat it as if it *were* hazardous

In UK, CNTs are Classified as Hazardous Waste



HSE

Health and Safety Executive

Risk management of carbon nanotubes

Waste

The Environment Agency advises that this type of waste carbon nanotube material should be classified and coded as hazardous waste. Based on current information, they consider high temperature incineration at a hazardous waste incinerator as the preferred disposal method. Other technologies may be suitable if you can demonstrate that they render the wastes safe. CNT waste should be double-wrapped in sealed polythene bags. Pyrolysis above 500°C will oxidise CNTs completely. The disposal facility should provide adequate documentation of the disposal conditions and incineration temperature.

Medical Surveillance or Monitoring

Should I offer Medical Exams for My Employees Exposed to Nanoparticles?

- No specific regulations
- No clear consensus, although many DOE labs now offer exams
- LBNL offers CNT workers a baseline exam and periodic follow-up "asbestos" medical examinations
  - —Medical tests are of low sensitivity, radiation risk from chest x-ray, etc
- See NIOSH Guidance Document for more thoughts (referenced later)

Effluent Scrubbing

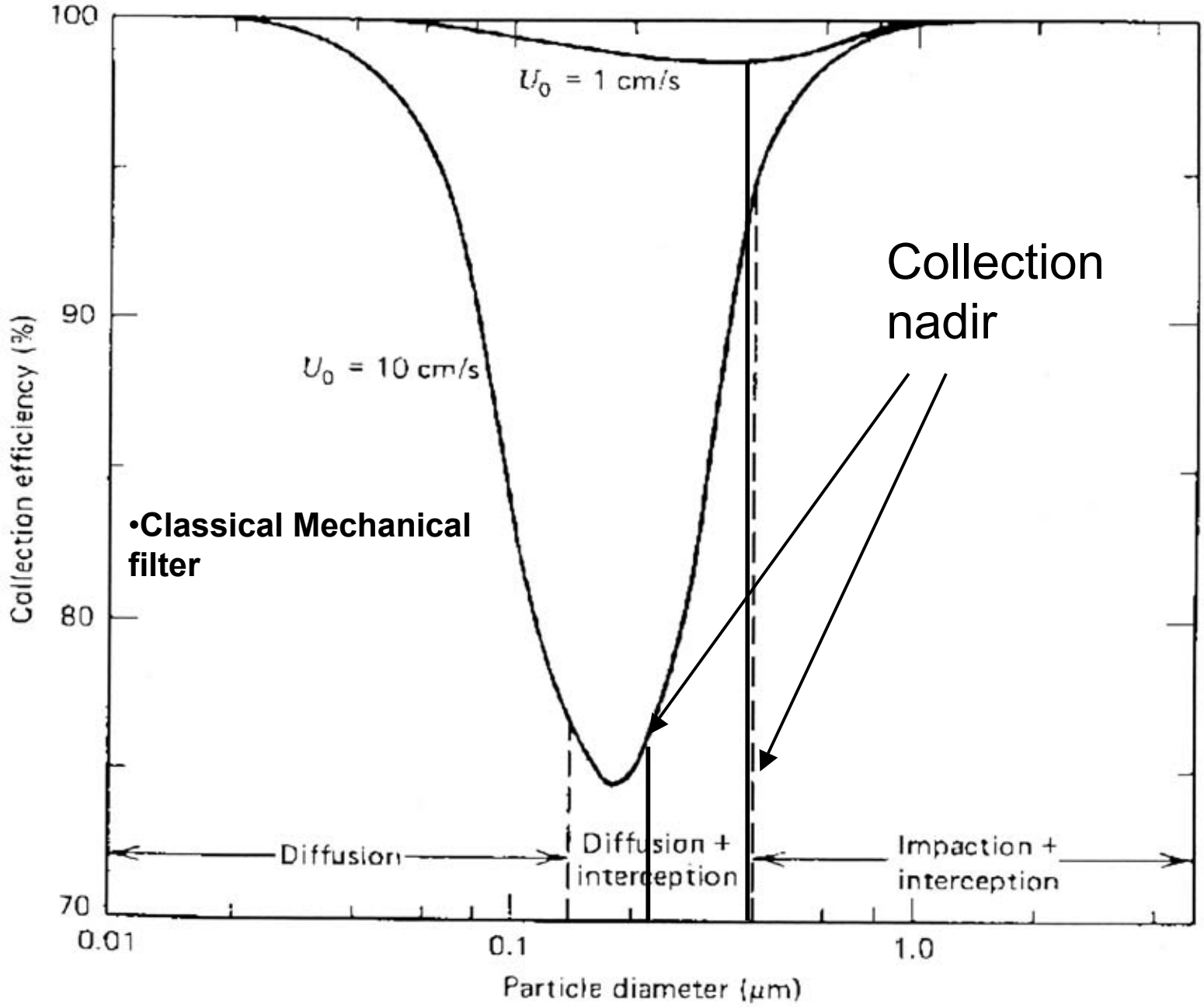
Should I Filter/Scrub My Exhaust Stack CNT Effluent?

- No legal requirement to do so
- Highly contentions issue
  - —Potential future liability
  - —Community relations
  - —Safety of maintenance workers
- Some companies are, some aren't

Engineered, Administrative and Personal Protective Controls

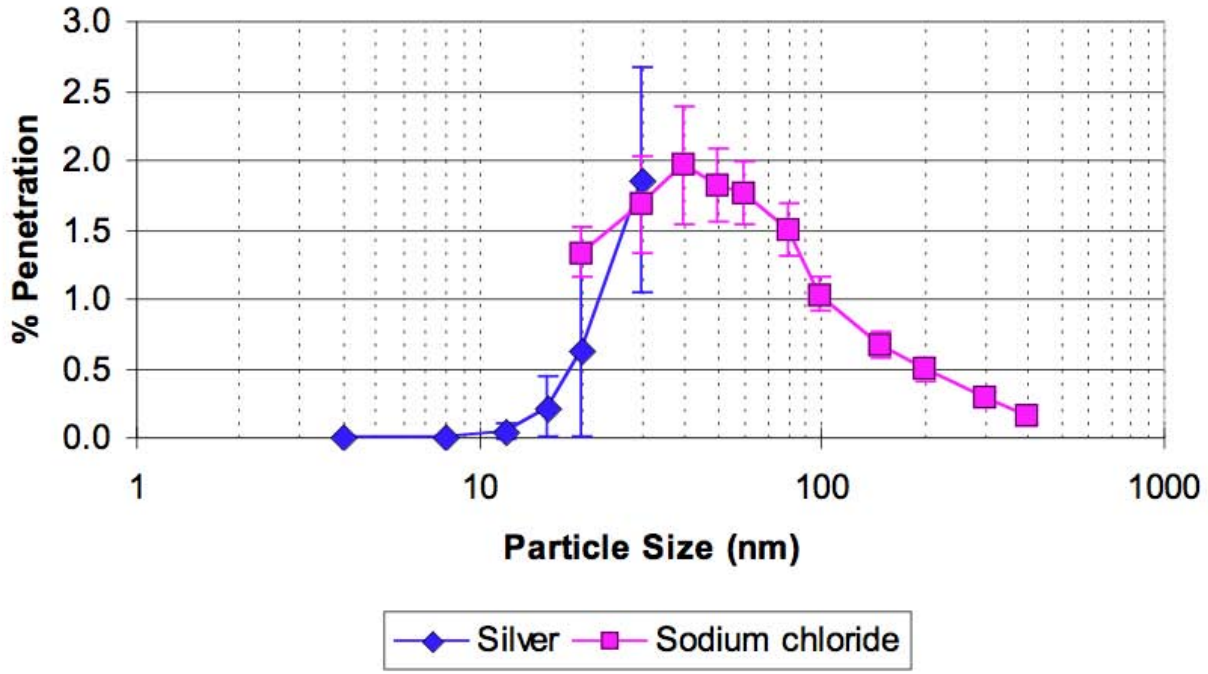
Will Safety Controls Work?

- Will air filters remove nanoparticles from air with the expected efficiency?
- Will respirators work effectively against nanoparticles?
- Will ventilation systems capture nanoparticles as they do for larger particles?
- Will gloves and coveralls keep nanoparticles off of the skin?


100
90
80
70
Collection efficiency (%)
U_0 = 1 cm/s
U_0 = 10 cm/s
Collection nadir
•Classical Mechanical filter
Diffusion
Diffusion + interception
Impaction + interception
0.01
0.1
1.0
Particle diameter (μm)

Do respirators and other filters work for nanoparticles?

Filtration Performance of a Typical NIOSH Approved N95 Filtering Facepiece Respirator



n = 5; error bars represent standard deviations
Sodium Chloride (TSI 3160); Silver (custom-built)
Flow rate 85 L/min

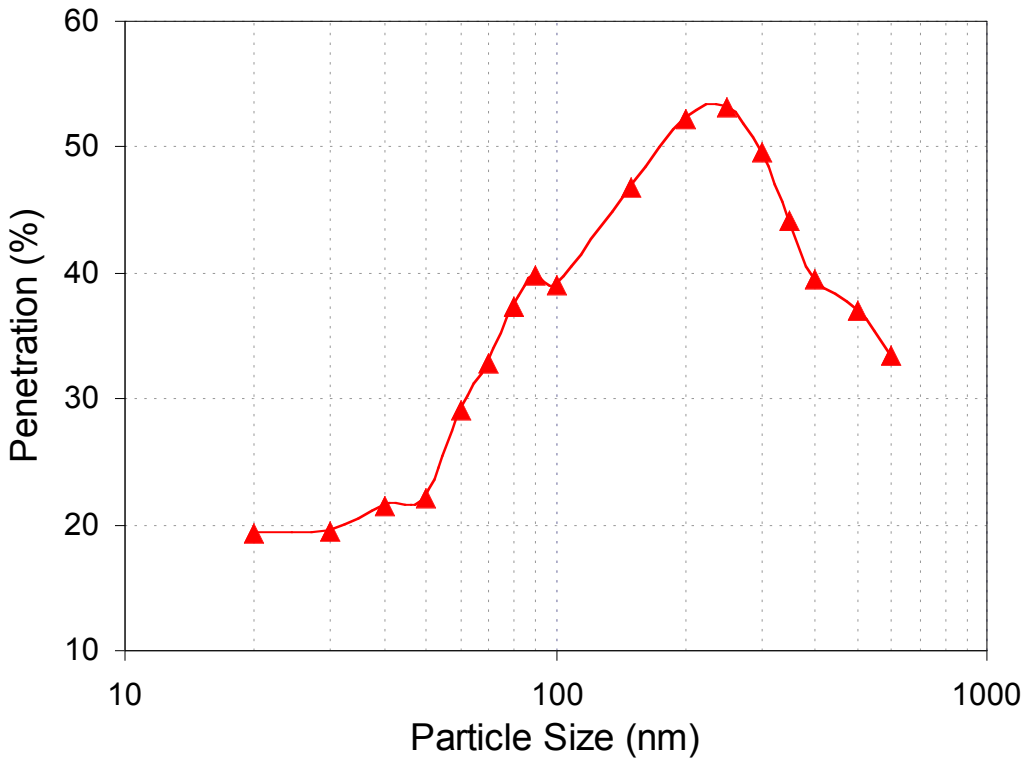
Filtration performance of NIOSH-approved N95 and P100 filtering facepiece respirators against nanoparticles, S. Rengasamy, WP King, B. Eimer and R. Shaffer, Journal of Occupational and Environmental Hygiene, In Press.

Summary : Percentage Penetration Results

Approval	Type	Polydisperse Aerosol Test (PAT) (%)	Monodisperse Aerosol Test (MAT) (%)	
			(40 nm)	(300 nm)
NIOSH	N95	0.61 - 1.24	2.0 - 5.2	0.20 - 1.56
NIOSH	P100	0.003 - 0.022	0.007-0.009	0.0006 - 0.001
CE	FFP2	0.27 - 0.50	1.45 - 2.22	0.69 - 0.84
CE	FFP3	0.009 - 0.014	0.155 - 0.164	0.06 - 0.07
FDA	Surgical Mask	1.58 - 88.06	8.98 - 72.51	2.14 - 88.95
N/A	Dust Mask	1.00 - 87.02	4.31 - 81.63	0.86 - 95.05

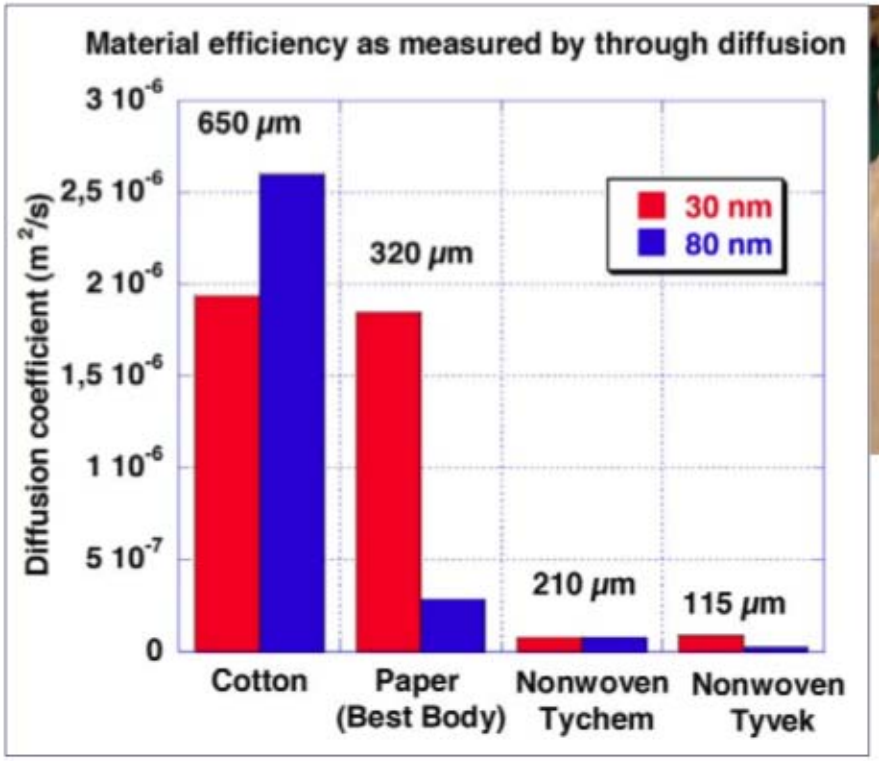
Particle Penetration Through Clothing

- Some fabric swatches behave like filter media
- Particle penetration driven by pressure differences
- Particle penetration is a function of the air permeability of the fabric
- FY09 NIOSH research project



10 cm diameter circular swatch
Single layer of needle-punched Aramid material
TSI 3160; Face velocity = 0.63 cm/sec; Flow rate 1L/min

Data from Nanosafe Consortium



Tests performed with graphite nanoparticles centred at 30 nm and 80 nm showed that high density polyethylene textile (Tyvek type) seems to be better than cotton and paper.

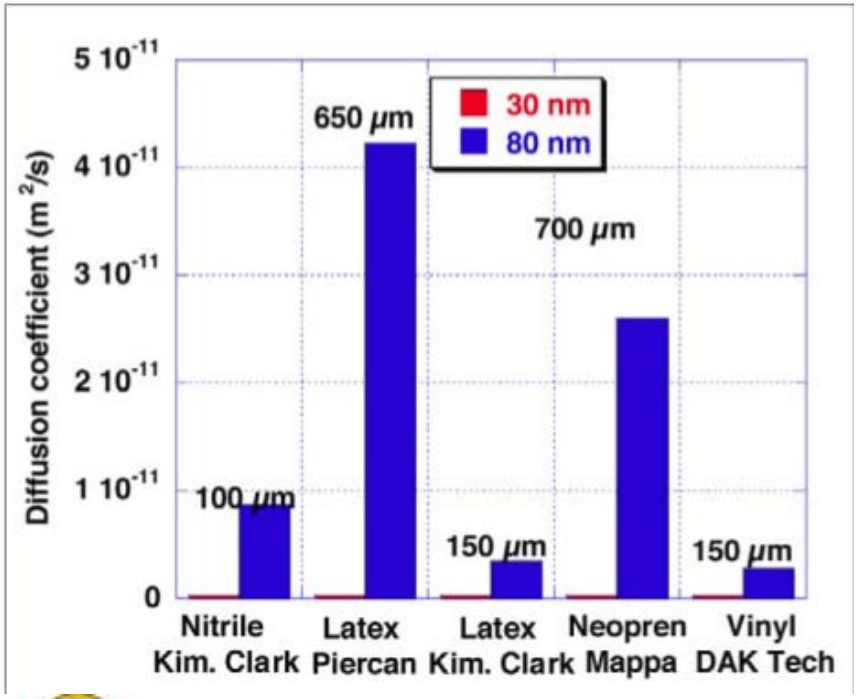
No Surprise: Nonbreathable materials are more impermeable to nanoparticles

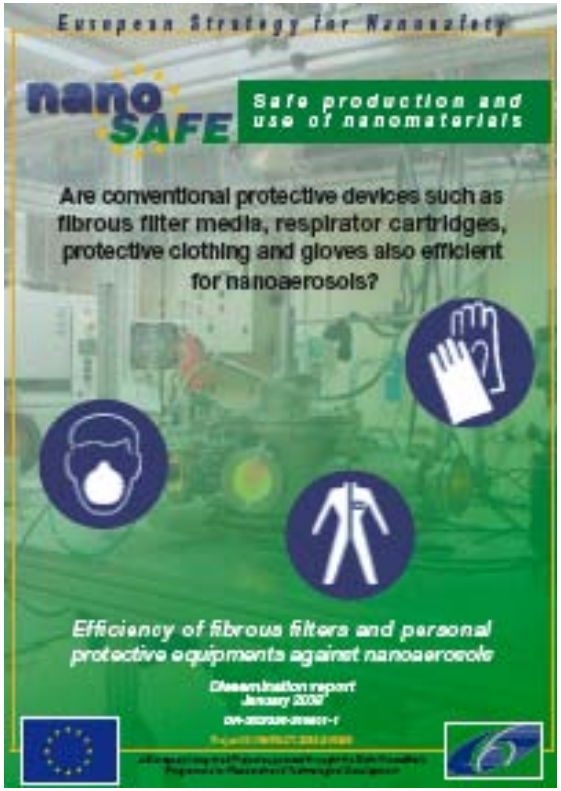
Gloves

- Glove contaminated with nanotubes
- Do gloves protect against nanoparticles?

Nanosafe Glove Findings

IV. Gloves performances





Warning: Nanoparticles may penetrate through commercially available gloves!

Advice: Use at least 2 layers of gloves.

Glove Penetration-Early Study

Dermal and Respiratory Protection in Handling Nanomaterials at the Center for High-Rate Nanomanufacturing (CHN)

Kwangseog Ahn and Michael J. Ellenbecker
Toxics Use Reduction Institute
Department of Work Environment
The University of Massachusetts Lowell

Surface Pores/Intrinsic Voids of Protective Gloves

- Latex and nitrile gloves have intrinsic voids in the micrometer size range
  - The voids do not appear to be going through the glove creating holes and causing the gloves to leak
  - These voids, however, might be vulnerable to the penetration of nanoparticles if the gloves are used under unfavorable conditions, such as in an elongated state or under a severe wear and tear situation
  - In addition, nanoparticles may be treated with special coatings to enhance their dispersion characteristics
  - When those coating materials and glove material are in close contact, the chance of particle penetration could potentially be increased
- There are wider gaps in between the cotton fibers in the cotton glove

Does Exhaust Ventilation Work?

Does Ventilation Work?

An Example from the Field

- **Average percent reduction from the use of a local exhaust ventilation unit was 96 +/- 6% based on particle counts and 88 +/- 12% based on mass**

portable fume hood extractor

Data and photos courtesy of Dr. Mark Methner, NIOSH Field Research Team.

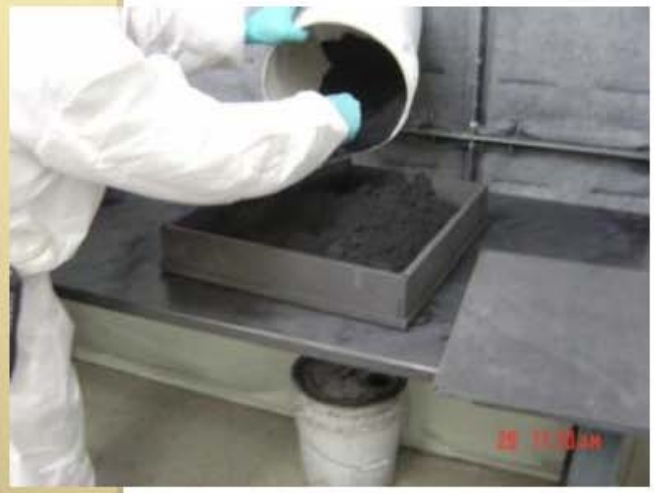
During reactor cleanout activities

Effectiveness of Local Exhaust Ventilation (LEV) in Controlling Engineered Nanomaterial Emissions During Reactor Cleanout Operation, M, Methner, Journal of Occupational and Environmental Hygiene, Vol. 5, June 2008, pages D63 - D69.

This Backdraft Ventilation is not Completely Effective

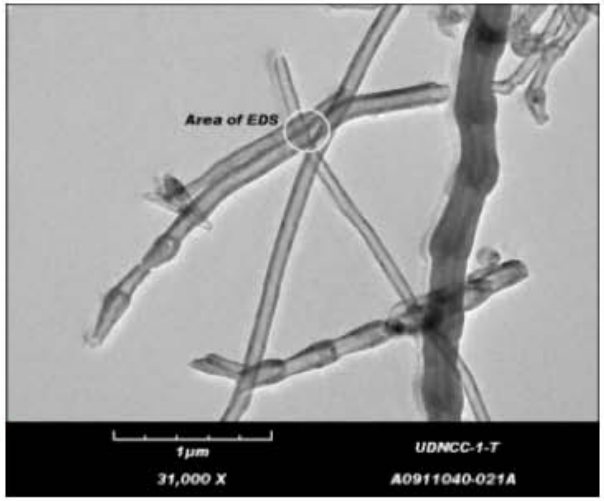
Two methods of clean up – HEPA vacuum and Leaf Blower

Darkened floor area due to grinding CNF into resilient floor tile with footwear



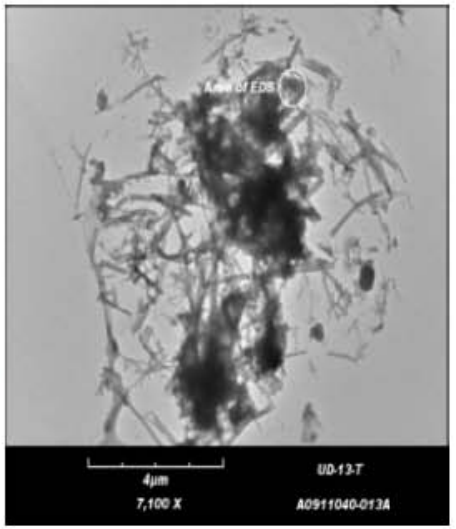
Loading tray w/ CNF's

PBZ



Poorly Designed Local Exhaust

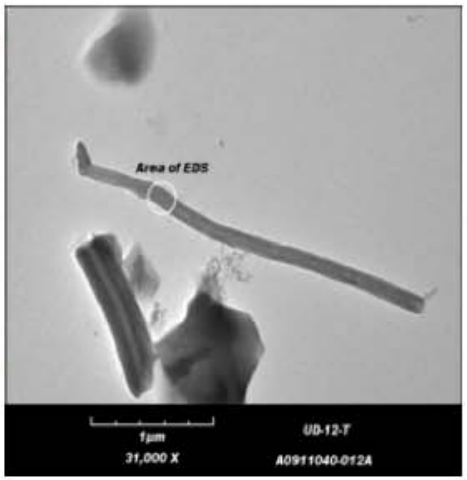
Surface grinding of CNF composite w/ LEV



PBZ during surface grinding w/ LEV

LEV inlet positioned 90 degrees from direction of plume exiting wheel – greatly reduced capture efficiency

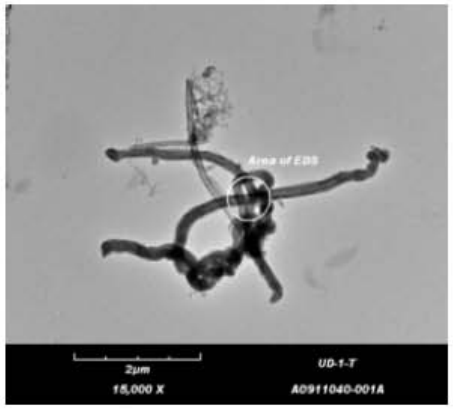
AS sample located just above LEV inlet – indicates less than optimum capture



At This Scale, Fume Hood Not Completely Effective

Weighing CNF's inside lab hood

PBZ indicates CNF's reach breathing zone and could escape and contaminate adjacent areas/entire lab



All Controls in Place

- Enclosure
- Ventilation
- Respirator
- Coveralls
- Gloves
- Air sampling

All required by the EPA!

Fully Enclosed, Ventilated

Manufacturing containment

Courtesy of Nanocomp Technologies, Inc.

Fully Enclosed, Ventilated

Courtesy of Nanocomp Technologies, Inc.

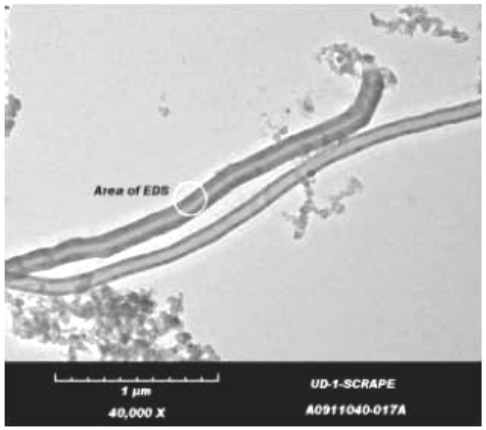
Limitations on Controls

Inadequate hand/wrist protection

Dermal exposure

Lab hood exhaust duct leakage

Took scraping of dark material and examined via TEM



Air Shower Decon

HEPA filtered "air shower" used to remove particulate resident on clothing. Interlock design ensures worker uses each time he enters/exits work area.

Contamination Control

Using HEPA vac to clean outer surface of trays of spilled material

Dark specs are clumps of raw CNF's that accumulate during tray loading

"Sticky mats" are used at the exit of the tray loading room – This mat was changed prior to transporting trays to the furnace area. This accumulation is due to 6 trips out to the furnace.

LBNL Rules for Engineered Controls

- Zero exposure to ENP
- Work that could (or does) generate an aerosol containing engineered nanoparticles must be conducted in a ventilated system such as fume hood, appropriate BSC, glove box or glove bag
    - Avoid HEPA filtered stand alone hoods or biosafety cabinets if not exhausted to the outside
    - NEVER use laminar flow hoods (clean benches)
- Test and maintain these systems

Spills

- Small spills cleaned up by lab personnel
- Large spills cleaned up by hazmat team
- Refer any people exposed in the incident for a medical review
- Clean up spill using wet methods/HEPA vacuuming
- Treat all clean up equipment as “contaminated”
- Dispose of waste appropriately

LBNL Administrative Controls

- Develop and implement a chemical hygiene plan specific to the scope of activities
- Housekeeping
  - —Clean surfaces after each shift if contaminated
    - Consider reactivity of material when selecting method
    - Dedicated HEPA Vacuum
    - Wet wiping
- Work practices
  - —Keep materials in closed containers except when inside ventilated systems

Posting and Labeling

- Post signs at entrance to work area warning of nanomaterials
- Label storage containers
- Label contaminated equipment

WARNING

Hood may be contaminated with nanoparticles.

Contact building manager prior to servicing

Materials Sciences Division

CAUTION

Building 67 Rooms 1201

MINIMUM REQUIRED PERSONAL PROTECTIVE EQUIPMENT:

Eye protection required within delineated area surrounding fume hood
Carry eye protection at all times in other parts of lab

APPLICABLE FORMAL WORK AUTHORIZATION DOCUMENTS:

None			

COMMENTS:

RESPONSIBLE INDIVIDUALS:

Name	Location	Work Phone #	Work Cell #	Home Phone #
Frank Ogletree	67-1210	(510)486-4862	(510)305-7908	(510)528-3502
Virginia Altoe	67-1212	(510)486-5173		(510) 559-7814
Miquel Salmeron	67-2111	(510)486-6704	(510) 234-3212	

BUILDING AND FACILITY MANAGER:

Name	Location	Work Phone #	Work Cell #	Home Phone #
Gil Torres	62-104A	(510) 486-5395	(510)289-5137	(925) 756-7255
Rick Kelly	67-3205	(510) 486-4088	(510) 457-8452	(510) 537-8391

LBNL: Worker Competency

- **Identify people potentially exposed to nanoparticles**
- **Provide appropriate nanosafety training**
- **Provide awareness-level training to guests (users)**

•You can take the LBNL awareness class on line (use "non-LDAP log in) at:
http://ehswprod.lbl.gov/coursebuilder/course/courselogin.aspx?cid=100&sid=1238 (non-LDAP log in)

MSDSs often of Little Use

MSDS for Nanomaterials: Effective?

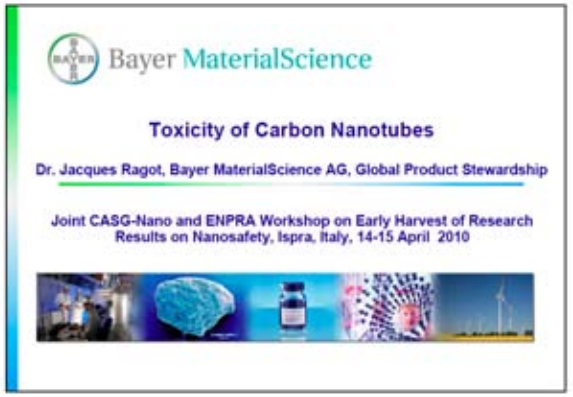
Case Study by NIOSH (AIHce 2009 Presentation)

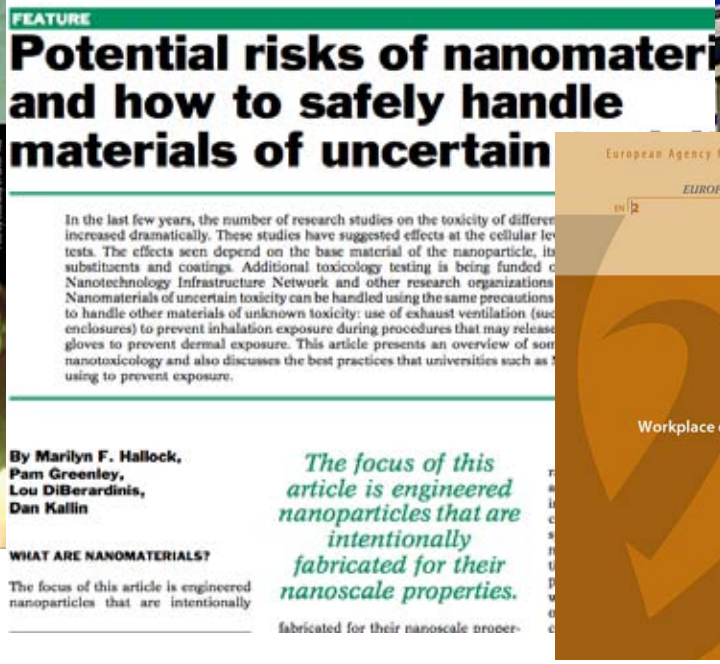
- 60 MSDS's for Nanomaterials reviewed.
- 58% referred to the PEL for bulk material
- 80% did not provide size information
- 87% did not contain toxicological data specific to the nanomaterial.

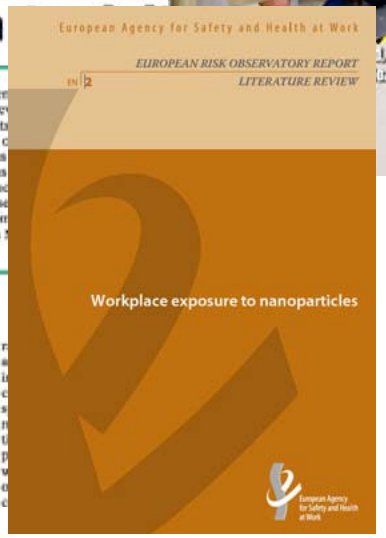
Detailed information was presented at AIHce

Work needed!

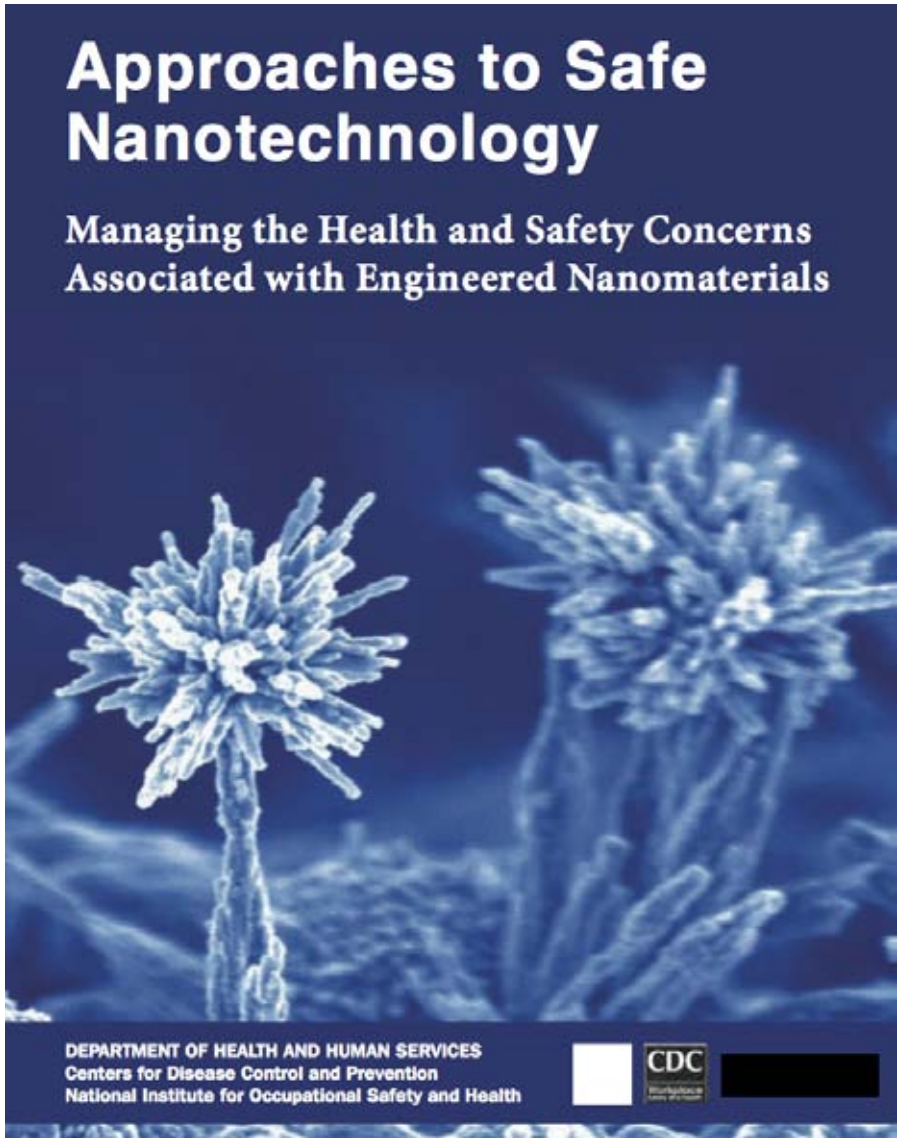
Everybody is Working On This!







Newest NIOSH Guide (3/2009)



- Update of prior guidance
- Some good information
- Doesn't change a whole lot over earlier editions

ASTM E 2535-07 (10/07)

Designation: E 2535 – 07

Standard Guide for Handling Unbound Engineered Nanoscale Particles in Occupational Settings[1]

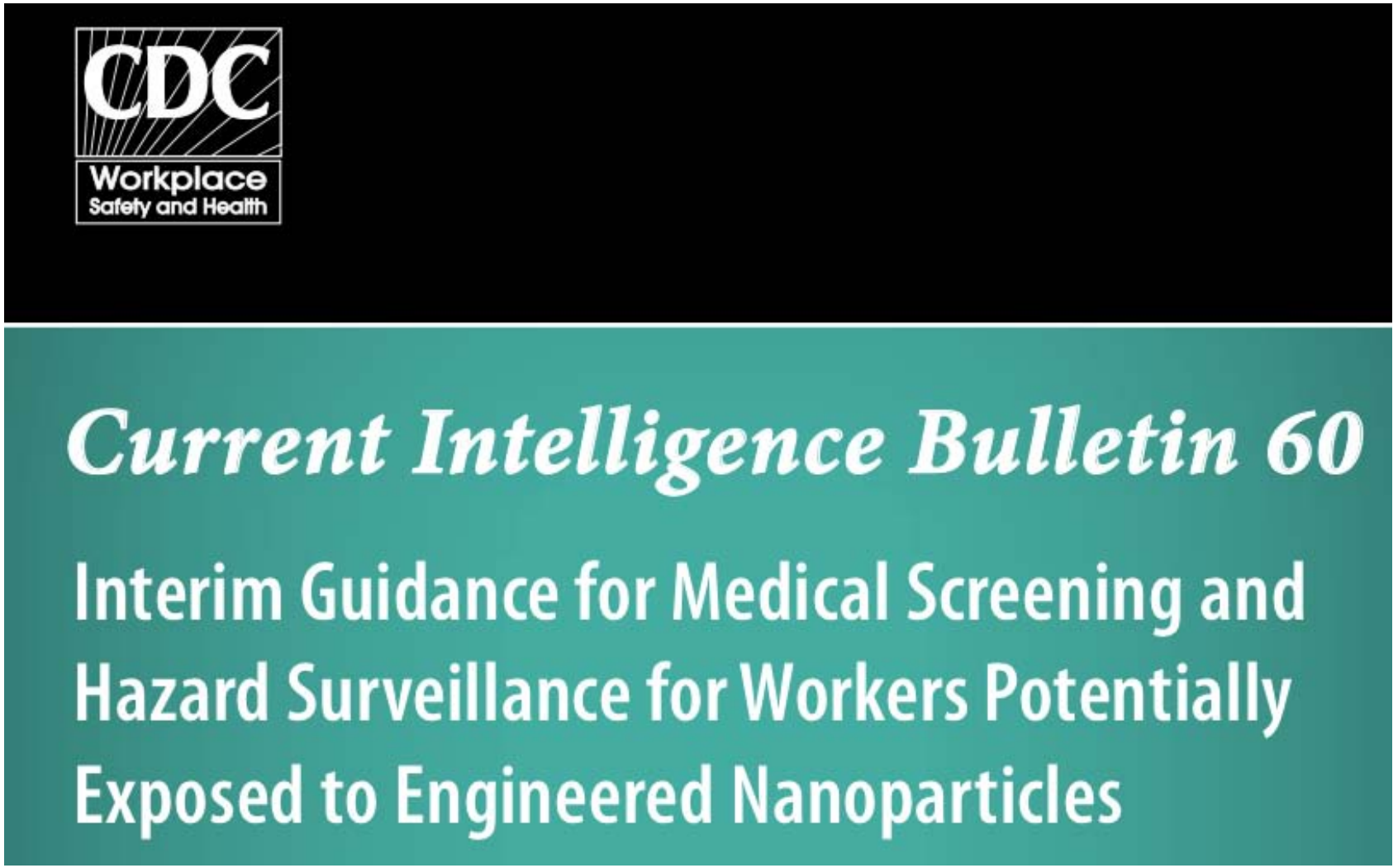
This standard is issued under the fixed designation E 2535; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

Nanometer-scale particles are encountered in nature and in industry in a variety of forms and materials. Engineered nanoscale particles as a class comprise a range of materials differing in shape, size, and chemical composition, and represent a broad range of physical and chemical properties. Workers within some nanotechnology-related industries and operations have the potential to be exposed to these engineered nanoscale particles at levels exceeding ambient nanoscale particle concentrations through inhalation, dermal contact and ingestion when not contained on or within a matrix (unbound). Occupational health risks associated with manufacturing, processing and handling unbound nanoscale particles, agglomerates or aggregates of nanoscale particles are not yet clearly understood. Dominant exposure routes, potential exposure levels and any material hazard are expected to vary widely among particular nanoscale particle materials and handling contexts. Additional research is needed to understand the impact of these exposures on employee health and how best to devise appropriate exposure monitoring and control strategies. Until clearer understandings emerge, the limited evidence available suggests caution when potential exposures to unbound engineered nanoscale particles (UNP) may occur.

DOE NSRC Safety Guideline

NIOSH Medical Surveillance Guide (2/2009)



ISO Technical Report 12885 (10/2008)

- Health and safety practices in occupational settings relevant to nanotechnologies
  - —Literature review
  - —Exposure assessment techniques
    - Air sampling
    - Dermal exposure assessment
  - —Risk assessment strategies
  - —Exposure control strategies
  - —Administrative controls
  - —Recordkeeping
  - —Waste management, fire and explosion control
  - —PPE

Early Nanotechnologist?