Measurement Strategies for Nanomaterials in Air

Michele L. Ostraat, PhD
June 21, 2011
Agenda

- Brief Introduction to Nanotechnology
  - Implications for Aerosolized Nanomaterials

- Challenges and Considerations in Aerosol Nanomaterial Measurements

- Strategies Being Implemented and Developed
• Nanotechnology is not an industry but is an enabling technology used across broad industries
  • Nanotechnology research and applications are extremely diverse

▪ Assessing health implications and biological/environmental interactions of nanomaterials is challenging and complex

▪ Multiple interactions occur between nanomaterials and biological and environmental systems
  – Systems in question, i.e. fresh water, pond water, marine water,...
  – Diverse and often nonstandardized test methods, protocols, and assays are used to determine these interactions

▪ Nanomaterial characterization is impacted by many factors, including
  – Measurement protocols
  – Assays that alter nanomaterial characteristics
  – Availability of necessary instrumentation
  – Lack of standard protocols and instrumentation
ISO/TC229 Nanotechnologies:
Standardization in the field of nanotechnologies that includes either or both of the following:

- Understanding and control of matter and processes at the nanoscale, typically, but not exclusively, below 100 nanometers in one or more dimensions where the onset of size-dependent phenomena usually enables novel applications.
- Utilizing the properties of nanoscale materials that differ from the properties of individual atoms, molecules, and bulk matter to create improved materials, devices, and systems that exploit these new properties.

Diagram:
- DNA: 2 nm (Nature, 1953)
- AIDS Virus: 65 nm
- Visible Light: 400 – 700 nm
- Red Blood Cell: 6 - 8 μm
- Human Hair: ~20-100 μm
What are Aerosols?

- Aerosols are ensembles of
  - Solid particles suspended in a gas
  - Liquid particles suspended in a gas
  - Multi-phase solid/liquid particles suspended in a gas

- In contrast to colloidal particles, aerosol particles can not be made to be stable as a function of time
  - Colloidal particles can be stored
  - Aerosol particles can not be stored

- Time frame of aerosol stability varies from particle system to particle system
  - Aerosol particles change as a function of time

- Aerosol particles are characterized by their particle size distribution
Special Issues with Aerosol Nanoparticles

- Low charging efficiency
- Extremely high diffusivity
  \[ D = \frac{kTC_e}{3\pi\mu D_p} \]  
  Stokes-Einstein Relation
- High rate of coagulation/agglomeration losses with larger particles
- Negligible particle mass
  - Very long sampling times
  - Mass based detection often inaccurate due to negligible particle mass

<table>
<thead>
<tr>
<th>Particle Diameter (nm)</th>
<th>Distance Fallen Due to Gravity (um)</th>
<th>Distance Moved Due to Diffusion (um)</th>
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<tr>
<td>10</td>
<td>0.2</td>
<td>200</td>
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<td>100</td>
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<td>20</td>
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<td>1000</td>
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Phoretic Effects

- Inducing directional preference in diffusion due to gradients
  - Impart differences in momentum to particles by molecules

- Thermophoresis
  - Thermal gradients that cause net migration of particles from higher temperature to lower temperature regions of gas

\[ F_T = \frac{3\pi \mu^2 D_p}{C_c \rho T} \left( - Th \frac{dT}{dx} \right) \]

- Photophoresis
  - Nonuniform heating of particles exposed to light

- Diffusiophoresis
  - Presence of gradient of vapor molecules that are either heavier or lighter than surrounding gas molecules
Electrophoresis
- Charged particles follow electric field lines
- Collect charged particles onto substrates

Thermophoresis
- Particles move from hot to cool
  - Hot gas molecules have higher kinetic energy and momentum
    - More frequent collisions impart more energy and momentum to particle
  - Cool gas molecules have lower kinetic energy and momentum
    - Less frequent collisions impart less energy and momentum to particle
### Aerosol Particle Coagulation - Nanoparticles

- **Brownian Coagulation Coefficient** $K(D_{p1}, D_{p2})$
  - Nanoparticles
    - High diffusivity - move quickly and often
    - Insignificant collision cross-section
  - Larger particles
    - Low diffusivity - move slowly
    - Large collision cross-section
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Engineering and Technology

Broad Challenges

- Lack of instrumentation/experimental automation
  - In-line/real-time
  - Lack of standard methods and protocols

- Existing dose metrics potentially not suitable for nanomaterials
  - Mass – Surface Area - Number
  - Current Occupational Exposure Limits (OELs) are mass-based

- Differentiation between background and engineered sources
  - Natural - Incidental - Engineered
  - Temporal and spatial variations
Instrumentation not yet developed for robust, cost-effective occupational and/or environmental field testing

- Sensitivity to nanomaterials
- Differentiation between background and engineered nanomaterials
- Real-time measurements
  - Off-line instruments are slow and expensive
- Aerosol based instrument are more advanced, but are still in prototype development stage
- Biological and environmental matrices cause additional challenges
## Engineering and Technology

### Challenge: Aerosol Instrumentation

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Number, Surface Area, and Mass

- **Number:**
  - 97.4% < 100 nm
  - 2.6% > 100 nm
Number, Surface Area, and Mass

- **Number:**
  - 97.4% < 100 nm
  - 2.6% > 100 nm

- **Surface Area:**
  - 62.0% < 100 nm
  - 38.0% > 100 nm

![Graph showing frequency vs. Dp (nm)]
Number, Surface Area, and Mass

- **Number:**
  - 97.4% < 100 nm
  - 2.6% > 100 nm
- **Surface Area:**
  - 62.0% < 100 nm
  - 38.0% > 100 nm
- **Mass:**
  - 27.6% < 100 nm
  - 72.4% > 100 nm
Nanoparticles Have Almost No Mass

Edge of a single 10 micron particle

Relative size of 10 nanometer particles for comparison

A 10 μm particle weighs the same as one billion 10 nm particles

Large particles will bias filter weight
Source of Nanomaterials

- Naturally Occurring
- Incidental
- Engineered
These environments are not “new”
- Have been around from before the growth in nanotechnology

Background and incidental nanoparticles are found in occupational environments that do not necessarily handle or process nanomaterials

Photo by Keith Pohs
### Minimal Information About Nanomaterials

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<td>Octanol-Water Partition Coefficiency</td>
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- Characteristics perceived to be relevant to biological and/or environmental activity
- Analysis of aerosols can access only a few of these characteristics
Most nanomaterials are characterized by their ensemble properties.

Depending upon the sample, this can be trivial to complex.

Change over time and in different environments.
Agenda

- Brief Introduction to Nanotechnology
  - Implications for Aerosolized Nanomaterials

- Challenges and Considerations in Aerosol Nanomaterial Measurements

- Strategies Being Implemented and Developed
Information being shared on handling of nanotechnology

For example:
- Effectiveness of PPE and Engineering Controls; Ron Shaffer, NIOSH; July 8, 2008
- National Nanotechnology Initiative Strategy Documents
Focus Areas

Well-controlled sources of aerosol nanomaterials
- Generate well-characterized aerosol nanoparticles of various chemistries
- Evaluate instrumentation to measure aerosol nanoparticles
- Characterize aerosol behavior as a function of time

Portable Aerosol Instrumentation
- Develop a portable air sampling method for daily monitoring of R&D and manufacturing settings

Verification and Measurement of PPE
- Develop test method to measure filtration efficiency of filter media to aerosol nanoparticles
- Measure filtration efficiency of commercially available filter media to specific engineered nanoparticles
### Current Approaches

#### Approaches being used in occupational environments
- Comprehensive Exposure Assessment
- Control Banding
- Workplace Controls and PPE
- Nothing

#### Equipment being used to protect workers
- PPE
  - Gloves
  - Respirators and face masks
- Secondary containment
  - Laminar flow hoods
  - Glove boxes
- HEPA vacuums/filtration
- Others

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**Engineering and Technology**

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<tr>
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<th>C</th>
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**Exposure Index**
- "Dustiness"
- Amount Used

**Impact Index**
- Bulk hazard
- Surface Area
- Surface Activity
- Shape
- Size

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**Maynard; 2007 Ann Occ Hyg 51(1)**

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Objective

- Develop portable instrument to monitor air quality for nanomaterials to enable individual practitioners to evaluate workplace controls and determine their relative effectiveness
  - Detect and measure aerosol nanoparticle concentrations
  - Classify aerosol particles based upon particle diameter

Desired instrument features include

- Low cost
- Limited size resolution - 2 to 5 distinct size bins < 100 nm
- Simple to operate
  - Minimal training to collect and interpret data
  - Minimal maintenance and routine calibration
- Robust and reliable in wide variety of operating environments
  - High/Low particle concentrations
  - Broad particle chemistries
Nano-ID™ Nanoparticle Spectrometer

- Particle Measuring Systems
  - Particle size distributions from 5 nm to 500 nm
  - Operator-selectable dual function Particle Counter Mode - operates as 5 nm portable particle counter
  - Non-radioactive particle charging source
  - Fast scan speeds giving reliable results in as low as 30 seconds
  - Uses non-toxic, organic working fluid - provides 2,000 hours of operation between refills
  - Fast warm-up; begin sampling in 90 seconds
  - Large touch-screen user interface
  - Portable and self-contained, weighs only 7 kg
  - On-board data processing

http://www.pmeasuring.com/particleCounter/nanoParticleSamplers/particleCharacterization/NanoIDNPS500
Nano-ID Select Wide Range Aerosol Sampler

- **Particle Measuring Systems**
  - Particle Size: 2nm - 20 µm
  - Number of Sizing Channels: 12
  - Flow rate: 20 LPM
  - Size-resolved samples are not altered, permitting compositional analysis using ICP-MS, AAS, and SEM/TEM
Nano-ID Mass Reader MR250

- Particle Measuring Systems
  - Seven channels of resolution in the microparticle range of 250 nm to 20 µm, with mass sensitivity of 10 ng
  - Sample Targets: Polished microscope slides, nominal dimensions 76 x 26 x 1.1 mm
  - Calibration: User-selectable: Atmospheric Aerosol (Canterbury England), Arizona Test Dust, Carbon Nanotubes, Titanium Dioxide, user-specific calibration curves
  - Battery: 10 hour operation, charge time approx. one hour
- Determine suitability of current filtration methodology to nanoparticle filtration performance

- Develop test method to reflect industrially relevant conditions
  - Particle chemistry
  - Charged and uncharged particles
  - Relative humidity

- Collaboration with NIOSH

![Graphs showing filtration efficiency over time and particle size distribution.](image-url)
- Determine suitability of current filtration methodology to nanoparticle filtration performance

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- Collaboration with NIOSH
Current State of Science

- Inconclusive
- Lack of dose metrics
- Lack of OELs
- Publishing standards
  - Exciting gets published
  - Null results get little attention – why publish?
  - Minimal information about nanomaterials
  - Detailed description of protocols and methods
- Lack of standards
  - Conflicting results
  - Interlaboratory comparisons
- Who should generate data?
  - Academics – want to get published
  - Industry – want to sell products
Summary

- Challenges in nanotechnology are daunting - opportunities are endless
- The interest and investment in nanotechnology will expand
- Significant advances in nanotechnology will continue to drive investment and research
- Already seeing major impact
- Need to simultaneously assess occupational and environmental implications of nanotechnology if the promises are to be ultimately successful

*Materials Today June 2004. Zhong Lin Wang, Georgia Institute of Technology*
Thank You
Background Measurements

Michele L. Ostraat, PhD
June 21, 2011
Characterize background for temporal and spatial distributions
  - Daily...seasonal...
  - Determines measurement duration and frequency

Ability to resolve nanomaterials from non-nanomaterials

Measuring impact of nanomaterials, not artifacts

Diversity in backgrounds

Limitations of instrumentation and detection

Strategies being implemented and developed
Source of Nanomaterials in Occupational Environments

Naturally Occurring

Incidental

Engineered
These environments are not “new”
- Have been around from before the growth in nanotechnology

Background and incidental nanoparticles are found in occupational environments that do not necessarily handle or process nanomaterials
Occupational Environments that Contain Nanomaterials

Engineered
Challenge: Instrumentation

Biological and environmental systems are complex

Challenge: How do you find engineered nano-TiO$_2$ in mud?

Challenge: How do you track carbon nanomaterials throughout cellular processes?

Possible Solution: Radiolabelled nanomaterials

Challenge: How do you know the radiolabelled entity remains attached to the nanomaterial?
Challenges: Background Differentiation

- Dissolved materials
- Differentiation from non-nano forms
- Differentiation from naturally occurring nanomaterials
- Robust Instrumentation
- Spatial and Temporal Distributions
When assessing background, need to be able to differentiate nanomaterials from:

- Dissolved materials, i.e. metal salts
- Incorporated materials, i.e. within a crystal structure
- Non-nano forms, i.e. bulk materials
- Differentiation from naturally occurring nanomaterials
Particle Characteristics Change

<table>
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<tr>
<th>Sample</th>
<th>Solution</th>
<th>Average aggregate size in solution (nm)</th>
<th>% distribution</th>
<th>Surface charge (mV)</th>
<th>Aggregation state</th>
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<tr>
<td>Carbonyl iron</td>
<td>Water</td>
<td>564.5</td>
<td>47.8</td>
<td>-60.52</td>
<td>Mild</td>
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<tr>
<td></td>
<td>PBS</td>
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<td>80.3</td>
<td>-51.29</td>
<td>Mild</td>
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<td></td>
<td>F-12K media</td>
<td>578.9</td>
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<td>Crystalline silica</td>
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<td>Amorphous silica</td>
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<td>Nano-ZnO</td>
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<td>372.4</td>
<td>45.2</td>
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</tbody>
</table>

- Particle characteristics change depending upon the method, protocol, or assay used
- Also change in the presence of an environment

Assessing Toxicity of Fine and Nanoparticles: Comparing In Vitro Measurements to In Vivo Pulmonary Toxicity Profiles

Christie M. Sayes, Kenneth L. Rentz, and David B. Weatherill
Particle Characteristics Change

- Particle characteristics change depending upon the method, protocol, or assay used.

- Also change in the presence of an environment.

Assessing Toxicity of Fine and Nanoparticles: Comparing In Vitro Measurements to In Vivo Pulmonary Toxicity Profiles

Christie M. Sayers, Kenneth L. Reid, and David R. Waterfill
Liquid spray pyrolysis – common method for synthesizing particles for various applications

Ideal for well-controlled environments
Salt spray is a very common naturally occurring source of aerosol nanoparticles.

As Particle Dries
Size Decreases
Concentration Increases
Spray Formation

- Searching for nanoparticles in seawater...

As Particle Dries
Size Decreases
Concentration Increases
Spray Formation

- Becomes a challenge to differentiate between
  - Size
  - Composition
  - Other properties…
Differentiation Between Particles

- **Size**
  - Very subtle differences unless nanoparticle concentration >> concentration of salt water

- **Composition**
  - Very difficult unless composition of nanoparticles is distinct from composition of components in salt water
    - Ca, Mg, Na, Ag, ...

- **Other properties...**
  - Unique properties of nanoparticles could be used to identify presence and other characteristics of nanoparticles
    - Fluorescence, electrical, optical,…
  - However, this analysis would be unique to specific nanomaterials and their properties
  - Can not currently be designed as a “one size fits all” approach to nanoparticle detection
Given rate of diffusivity of nanoparticles
- Need to be able to resolve extremely small changes in aerosol particle size
  - Possible if working with very narrow particle size distributions
  - Environmental aerosols have a broader size distribution
  - Subtle differences in particle growth not discernible with current aerosol technology
  - Mass based measurements would not resolve increase due to nanoparticle mass
- Would need extremely fast response instruments to detect nanoparticles prior to collision with larger particles
  - Rate of particle agglomeration can be quite high
Aerosol Dynamics

- **Given rate of diffusivity of nanoparticles**
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Endotoxins are bacterial cell wall components
- Occur naturally in soil, water, and air
- Can contaminate other materials

Endotoxin exposure associated with respiratory symptoms, fever, septic shock, impaired organ function, and death

Endotoxin is a potential confounding factor in nanomaterial toxicity studies
Dispersing Nanomaterials

- How do these dispersion processes impact the physicochemical characteristics of the nanomaterial?

- How do additives that aid in dispersing and forming stable samples impact toxicological responses?

- How much of the “sample” is surfactant?
Objective
- Develop portable instrument to monitor air quality for nanomaterials to enable individual practitioners to evaluate workplace controls and determine their relative effectiveness
  - Detect and measure aerosol nanoparticle concentrations
  - Classify aerosol particles based upon particle diameter

Desired instrument features include
- Low cost
- Limited size resolution - 2 to 5 distinct size bins < 100 nm
- Simple to operate
  - Minimal training to collect and interpret data
  - Minimal maintenance and routine calibration
- Robust and reliable in wide variety of operating environments
  - High/Low particle concentrations
  - Broad particle chemistries
Interference from other Aerosol Sources

- Diesel engines known to be a high producer of nanoparticles
- Presence of a diesel generator 25 ft from a field instrument completely overwhelms background counts
Ability to “subtract” background requires several assumptions:

- Background is stable
- Temporal deviations are on a longer timescale than measurement timescale
Ability to “subtract” background requires several assumptions

- Background is stable
- Temporal deviations are on a longer timescale than measurement timescale

During Diesel Generator Operation
Average Total Concentration = 56,852 particles/cm³
Background Assessment

- Ability to “subtract” background requires several assumptions
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**Background Assessment**

- Ability to “subtract” background requires several assumptions
- Background is stable
- Temporal deviations are on a longer timescale than measurement timescale

![Diesel Emissions Graph](image)
- Depending upon measurement frequency, could misinterpret background measurements

  - Assume background counts high
  - Assume background counts low
Continuous/Long-Term Sampling

- Inexpensive devices to measure exposure to airborne contaminants

- Identify exposures characteristics
  - Duration
  - Temporal/spatial distribution

- Acute (real-time) and chronic monitoring (integrated filter)
  - Filter for off-line analysis
  - Field and environmental testing programs
**Bundling Ruggedized Instruments**

- **Ruggedize instruments for environmental studies**
  - Compare with laboratory tools under well-controlled environments

- **Multimedia sampling and analysis**
  - Instruments collect information real-time and collect samples for off-line analysis

- **Gather information on broad particle sizes for consistency with previous field studies**
  - Nanomaterials, PM$_{2.5}$, PM$_{10}$
Summary

- Background measurements must be conducted correctly

- Requires an understanding of the environment as well as the sources and sinks for nanomaterials
  - Temporal and spatial variations
  - Formation, fate and transport

- Current techniques require bundling instruments, expensive off-line characterization
  - Searching for that one piece of hay…

- Cheaper and more distributed instruments are being developed
  - No one size fits all approach yet
Thank You