Use of Model Nanoparticles for Understanding Exposures in the Workplace

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Nanoscale Measurement Challenges

- Nano Reference Materials are needed for
  - Accurate characterization of minimum set of nanomaterial characteristics
  - Harmonized protocols for materials characterization (sample collection, handling, analysis)
  - Harmonized protocols for exposure assessment and toxicology testing
Types of Reference Materials

- National Institute of Standards and Technology (NIST)
  - Standard reference material (SRM®)
    - Certified value
    - Traceability to primary standards
    - Instrument calibration
  - Reference material (RM)
    - Reference value
    - Best estimate of true value
    - Instrument performance verification, method evaluation
Available nanoRMs

- NIST RMs
  - 3 sizes of nano Gold
  - TiO$_2$
  - 100 nm polystyrene latex spheres (SRM)
- ~20 nanoRMs available worldwide for EHS applications
  - [http://www.nano-refmat.bam.de/en/](http://www.nano-refmat.bam.de/en/)
- E. C. Joint Research Centre
  - 20 nm silica
Nano SRMs Under Development

- NIST SRM® 1898 TiO$_2$ nanopowder
- NIST SRM® 2483 CNT raw soot
- NIST SRM® 2482 CNT paper
- NIST SRM® 8281 Length sorted SWCNT
  - Length sorted (~100, 400, and 800 nm)
  - Suspension
Case Study: Ultrafine (<100 nm) Titanium Dioxide (TiO$_2$)

- Degussa P25 TiO$_2$ (Evonik Aeroxide)
  - Reference Material
  - Average Nano Particle Size : 21 nm
  - Specific Surface Area : $\sim$50 m$^2$/g
  - $\sim$80% Anatase, 20% Rutile

Anatase

Rutile
P25 TiO$_2$ Research Applications at NIOSH

- Used for development of protocol for measuring surface area by gas adsorption
- Used to evaluate relationships among surface area by gas adsorption, diffusion charging and calculations from geometric mean
- Fully characterized for density, morphology, primary particle size, particle cluster size, and total surface area.
- Used for toxicological studies
Model NP TiO$_2$ Experimental Design

- **Objective**
  - Compare diffusion charger, nanoparticle surface area monitor, scanning mobility particle sizer, and a filter-based gas adsorption measures of surface area

- **Well-characterized animal inhalation chamber**

- **Two aerosol concentrations:** 2.8 and 10.1 mg/m$^3$
Animal Inhalation Chamber
(Chen et al. 2006)
Workplace Evaluations of Metal Oxide Exposures

- Characterize airborne metal oxide exposure metrics by job or process.
- Obtain quantitative estimates of exposure in workers to fine and ultrafine metal oxide particle sizes by relating the measured exposure metrics to worker exposure.
- Evaluate a strategy for measuring workplace exposure to fine and ultrafine particles.
How relevant are the model NP to recommending industrial hygiene practices?

- NIOSH Draft Current Intelligence Bulletin 62, Occupational Exposure to Titanium Dioxide
  - REL of 2.4 mg/m$^3$ for fine TiO$_2$
  - REL of 0.3 mg/m$^3$ for nano TiO$_2$
- Workplace studies demonstrated ability to control and measure at these concentrations.
Importance of model nanoparticles for workplace exposures

- Use in toxicology studies
- Develop improved sampling and analytical methods that more closely align with the health endpoints observed in animals studies
- Use to conduct round robin of workplace exposure measurement techniques
- Use to assist microscopists
- Use to create a network of labs
  - proficiency tests
Additional Reference Material Work (2011)

- **NanoGo.** A round robin study of TiO$_2$ nanospheres and nanowires: raw, purified and functionalized MWCNT

- **International Alliance for NanoEHS Harmonization (IAHN)** planning a similar round robin in vivo study for 2011 with well characterized nanoparticles.

- **NIOSH Round Robin** study of NIST RM gold nanosphere particle sizing by TEM
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Measurement Methods for Workplace Sampling of Nanomaterials
Filter Based Samples

- Chemical analysis and electron microscopy
- Full Shift and Task Personal Sampling
  - Document tasks
- Full Shift and Task Based Area Sampling
- Background
  - Sample throughout day
  - Indoor and outdoor
Issues in the microscopic analysis of engineered nanomaterials

- Lack of a standard protocol
- Lack of standardized model NP material for comparison.
Microscopic evaluation of nanomaterials (TEM, SEM)

- Morphology
  - Comparison to bulk, qualitative loading
- EDS (EDAX) of particles for chemical composition
- Images from different representative areas of grid (same magnification)
- Count
  - (#particles/structures per #grid openings)
- Sizing
  - Length, diameter