

# Use of Model Nanoparticles for Understanding Exposures in the Workplace

Laura Hodson, MSPH, CIH

Centers for Disease Control and Prevention  
National Institute for Occupational Safety and Health



*The findings and conclusions in this presentation have not been formally disseminated by the National Institute for Occupational Safety and Health and should not be construed to represent any agency determination or policy*



# Nanoscale Measurement Challenges

---

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

# Types of Reference Materials

---

## n National Institute of Standards and Technology (NIST)

### n Standard reference material (SRM<sup>®</sup>)

- n *Certified value*
- n Traceability to primary standards
- n Instrument calibration

### n Reference material (RM)

- n *Reference value*
- n Best estimate of true value
- n Instrument performance verification, method evaluation

# Available nanoRMs

---

- n NIST RMs
  - n 3 sizes of nano Gold
  - n TiO<sub>2</sub>
  - n 100 nm polystyrene latex spheres (SRM)
- n ~20 nanoRMs available worldwide for EHS applications
  - n <http://www.nano-refmat.bam.de/en/>
- n E. C. Joint Research Centre
  - n 20 nm silica

# Nano SRMs Under Development

---

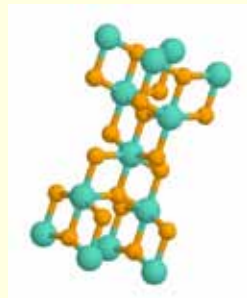
- n NIST SRM<sup>®</sup> 1898 TiO<sub>2</sub> nanopowder
- n NIST SRM<sup>®</sup> 2483 CNT raw soot
- n NIST SRM<sup>®</sup> 2482 CNT paper
- n NIST SRM<sup>®</sup> 8281 Length sorted SWCNT
  - n Length sorted (~100, 400, and 800 nm)
  - n Suspension

# Case Study: Ultrafine (<100 nm) Titanium Dioxide (TiO<sub>2</sub>)

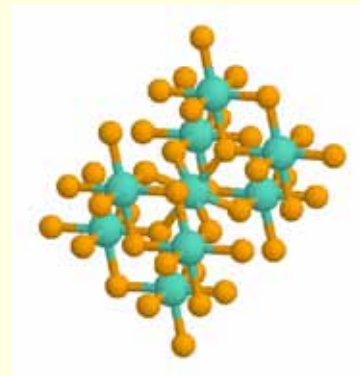
---

n Degussa P25 TiO<sub>2</sub> (Evonik Aeroxide)

- Reference Material
- Average Nano Particle Size : 21 nm
- Specific Surface Area : ~50 m<sup>2</sup>/g
- ~80% Anatase, 20% Rutile



Anatase



Rutile

# P25 TiO<sub>2</sub> Research Applications at NIOSH

---

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

# Model NP TiO<sub>2</sub> Experimental Design

---

## n Objective

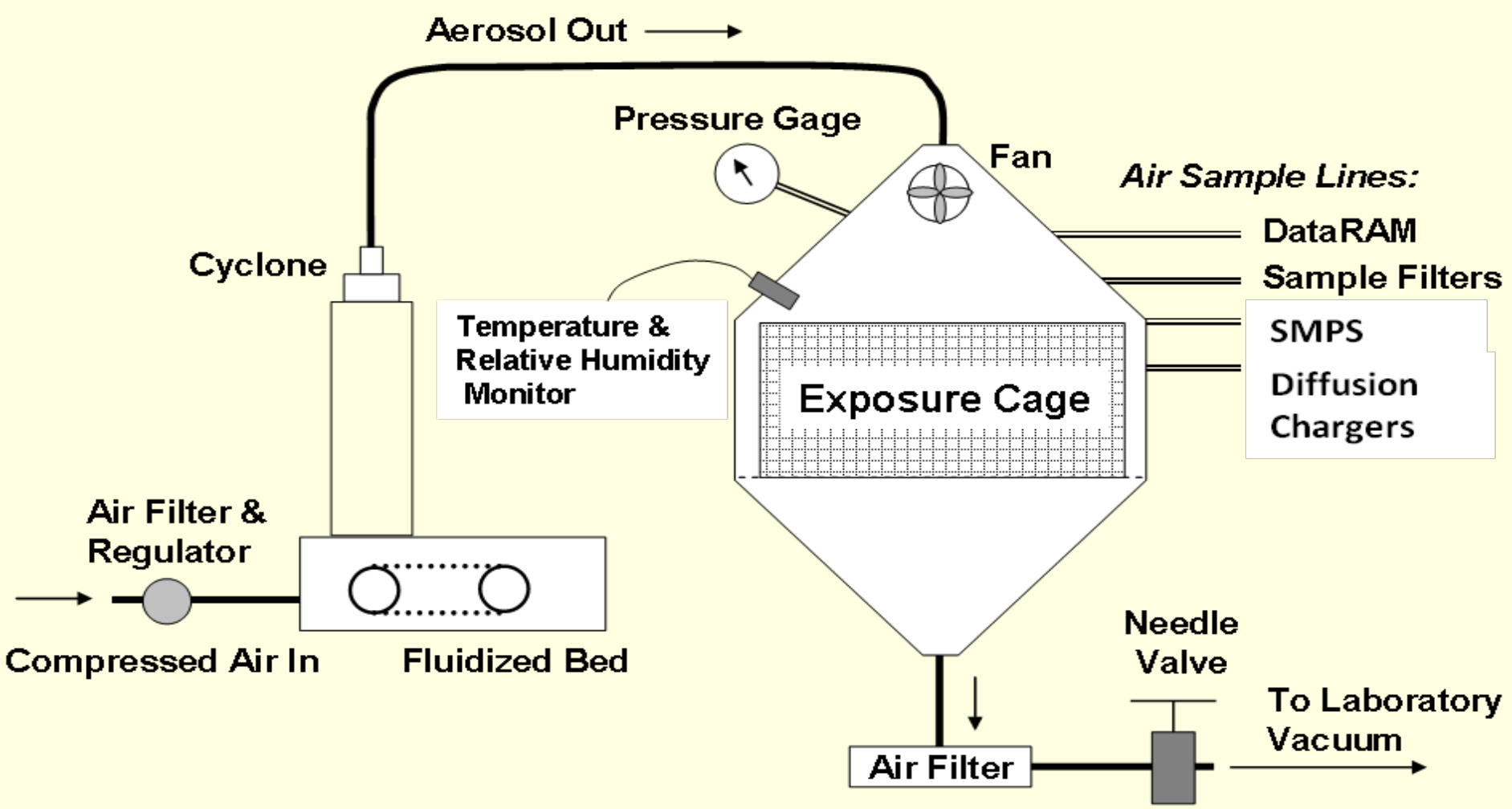
- n Compare diffusion charger, nanoparticle surface area monitor, scanning mobility particle sizer, and a filter-based gas adsorption measures of surface area

## n Well-characterized animal inhalation chamber

## n Two aerosol concentrations: 2.8 and 10.1 mg/m<sup>3</sup>



# Animal Inhalation Chamber (Chen et al. 2006)



# Workplace Evaluations of Metal Oxide Exposures

---

- n Characterize airborne metal oxide exposure metrics by job or process.
- n Obtain quantitative estimates of exposure in workers to fine and ultrafine metal oxide particle sizes by relating the measured exposure metrics to worker exposure.
- n Evaluate a strategy for measuring workplace exposure to fine and ultrafine particles



# How relevant are the model NP to recommending industrial hygiene practices?

- n NIOSH Draft Current Intelligence Bulletin 62, Occupational Exposure to Titanium Dioxide
  - n REL of 2.4 mg/m<sup>3</sup> for fine TiO<sub>2</sub>
  - n REL of 0.3 mg/m<sup>3</sup> for nano TiO<sub>2</sub>
- n Workplace studies demonstrated ability to control and measure at these concentrations.



# Importance of model nanoparticles for workplace exposures

---

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

# Additional Reference Material Work (2011)

---

- n **NanoGo**. A round robin study of TiO<sub>2</sub> nanospheres and nanowires: raw, purified and functionalized MWCNT
- n **International Alliance for NanoEHS Harmonization (IAHN)** planning a similar round robin in vivo study for 2011 with well characterized nanoparticles.
- n **NIOSH Round Robin** study of NIST RM gold nanosphere particle sizing by TEM

# Thanks to:

---

- n Charles Geraci, Jr. PhD, CIH Coordinator of the **NIOSH Nanotechnology Research Center**
- n Aleks Stefaniak, PhD
- n Ryan LeBouf, PhD
- n Bon Ki Ku, PhD
- n Brian Curwin, PhD

**Laura Hodson, [lhodson@cdc.gov](mailto:lhodson@cdc.gov)**



# Measurement Methods for Workplace Sampling of Nanomaterials



# Filter Based Samples

---

- n Chemical analysis and electron microscopy
- n Full Shift and Task Personal Sampling
  - n Document tasks
- n Full Shift and Task Based Area Sampling
- n Background
  - n Sample throughout day
  - n Indoor and outdoor

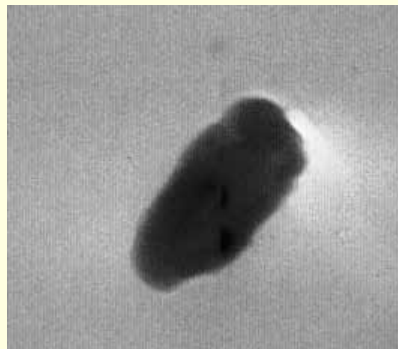
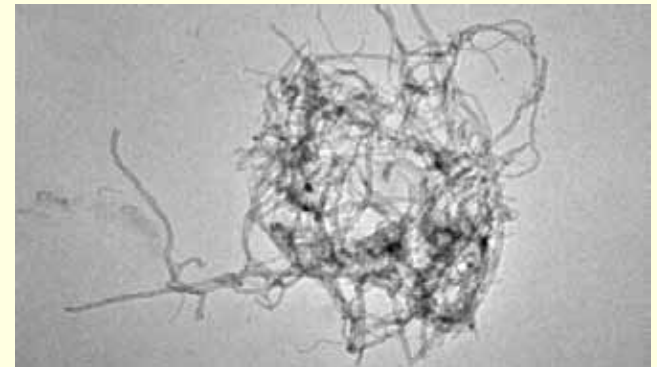
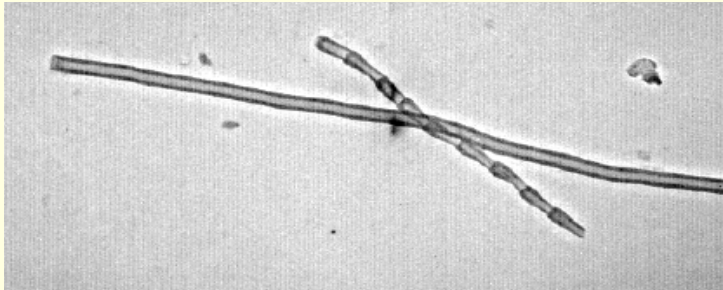




# Issues in the microscopic analysis of engineered nanomaterials

---

- n Lack of a standard protocol
- n Lack of standardized model NP material for comparison.



# Microscopic evaluation of nanomaterials (TEM, SEM)

---

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