# Exposure Assessment: Air Sampling Study

**Safe Handling of Engineered Nanoscale Materials Conference**
**Argonne National Laboratory**
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# Overview

- Background
- Measurement Techniques
- Sampling Strategy
- NSRC Industrial Hygiene Sampling Protocol
- Importance of Background Measurements
- Results of Air Sampling
- Other Instrumentation

# Background

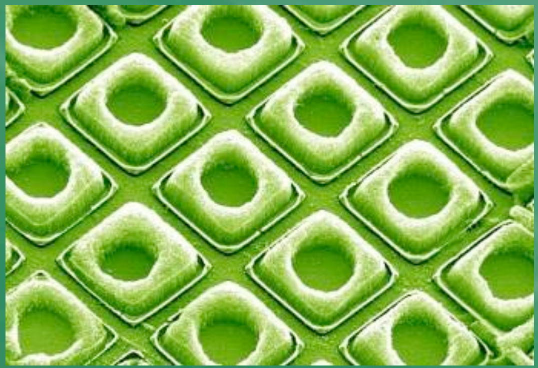
Department of Energy (DOE) Nanoscale Science Research Centers (NSRC) developing *Approach to Nanomaterial ES&H*

- Center for Nanophase Materials Sciences at Oak Ridge National Laboratory
  - Linda Horton, Director
  - Randy Ogle and Scott Hollenbeck, ES&H
- Materials Science and Technology Division
  - Steve Zinkle, Director
  - Kennie Edwards, ES&H

- *Applying industrial hygiene to nanoscale materials*

# Definition of Nanoscale Materials

- Freely engineered materials that have at least one dimension 1 – 100 nm
  - Several definitions
- Ultrafine particles are those less than 100 nm, but created incidental to process



**Carbon nanotube pattern-square-circle**

**Image provided by Zhengwei Pan**

**Oak Ridge National Laboratory**

# Summary of Health Effects

- Nanoscale particles exhibit different characteristics than larger materials with same chemical composition
- Particle characteristics such as mass, solubility, shape, surface area and chemistry, coatings and number may be important to measure for toxicological outcomes
- Nanomaterials must be handled using the *precautionary principle*, "acutely toxic in the short run and chronically toxic in the long run"

# Occupational Exposure Guidelines

- Currently there are no OSHA, NIOSH, or ACGIH standards or guidelines for employee exposure to “nanomaterials”
- Development of standards is hampered due to:
  - Limited toxicological data
  - Understanding if count, mass, surface area is correct measurement
  - Presence of dopants, often heavy metals, that may complicate toxicological studies (Arsenic, nickel)
  - Explosive nature of research and manufacturing processes integrating nanoscale materials

# Sampling Strategy

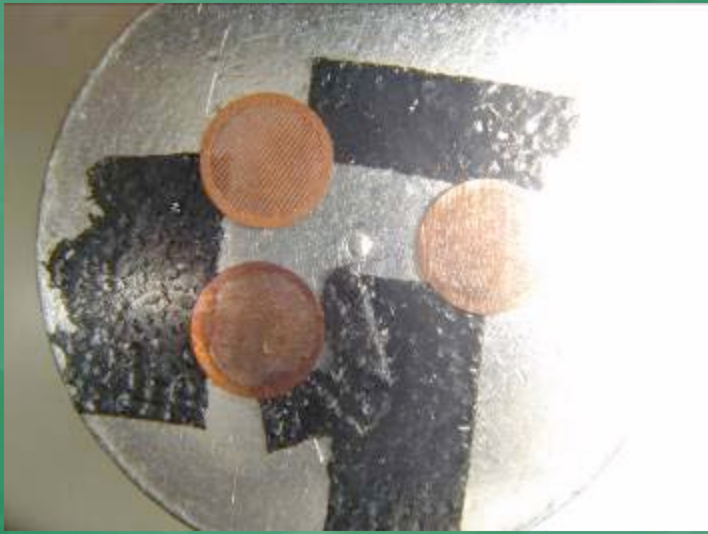
- So…
  - New definition
  - Toxicological outcomes under study
    - Different materials / target organs
  - Unsure what to measure due to uncertain health effects
  - No occupational exposure guideline
- How are we going to apply industrial hygiene?
  - Back to basics, art and science……

# Measurement Techniques

- Total and respirable dust
  - Sampling pump with filter (total) or cyclone (respirable), ug/m$^3$
- Particle count
  - Condensation Particle Counter, counts/cc
- Particle size distribution
  - Scanning Mobility Particle Sizer (SMPS)
  - Electrical Low Pressure Impactor (ELPI)

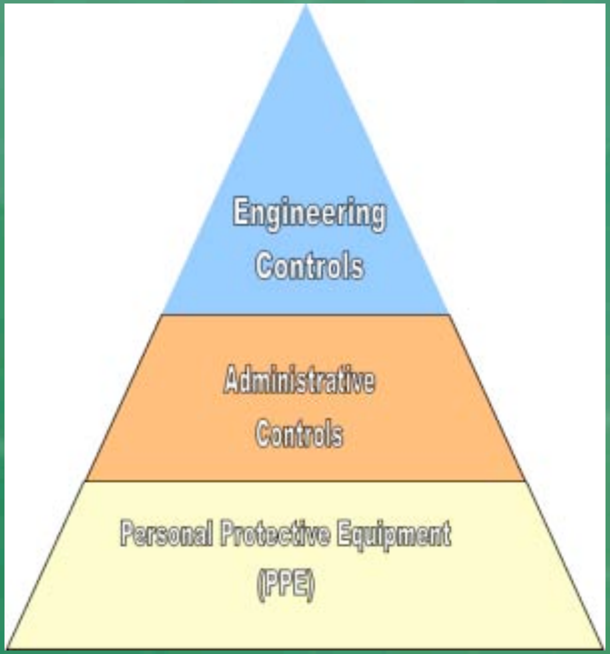
# Measurement Techniques

- Surface area
  - Direct reading portable aerosol diffusion chargers
- SEM / TEM



# Sampling Strategy

- Traditional industrial hygiene sampling focuses on determining employee exposure and using a hierarchy of controls to reduce exposure



# Sampling Strategy

- NSRC *Approach to Nanomaterial ES&H* stated employee exposure should be kept "as low as practicable in the research environment" (p. 10)
  - Attachment 1
- Two pronged sampling strategy
  - Determine if nanoscale materials are controlled at the source
  - Provide more detailed data into nanoscale materials that may be released and affect researchers
    - Characterize the aerosol

# IH Sampling Protocol

- Determine if nanomaterials are <u>controlled at the source</u>
  - Use of Condensation Particle Counter, TSI 3007

# IH Sampling Protocol

- Provide more detailed data into nanomaterials that may be released and affect researchers
  - CPC
  - GRIMM Aerosol Spectrometer
  - High volume air sampling pump with 0.1 um nucleopore filter
  - Passive air monitor (SEM / TEM stub)
  - SEM / TEM stub

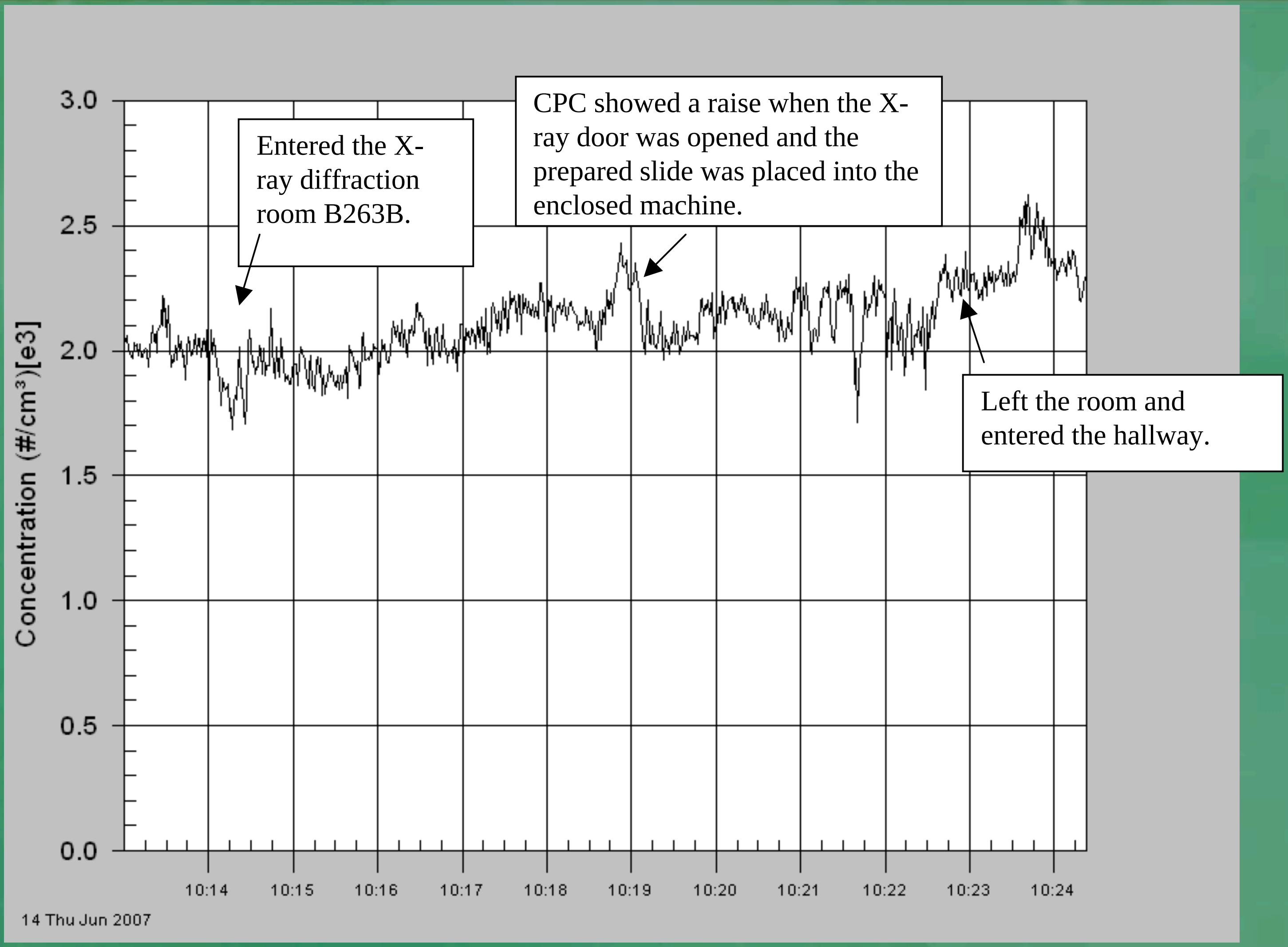
# Air Sampling Studies

- ORNL Physical Sciences Directorate
- Researchers working with nanomaterials
  - Synthesis, harvesting, other research processes
  - Not all met strict definition of “freely engineered nanomaterials”
- Numerous background samples in buildings or labs where nano work is/will take place

# Importance of Background Measurements

| Building | Location | Range (p/cc) | Mean | Standard Deviation | Time (s) |
|---|---|---|---|---|---|
| 1 | Ground floor – main entrance | 6330-8260 | 7360 | 413.2 | 571 |
| 1 | First floor | 484-6830 | 1270 | 889.9 | 8318 |
| 1 | First floor in empty research lab | 2750-4390 | 3700 | 272.8 | 9706 |
| 1 | Second Floor | 665-3200 | 1530 | 413.3 | 10328 |
| 1 | Third floor | 673-3250 | 1710 | 583.9 | 20512 |
| 2 | First floor – XRD Lab | 1174-1327 | 1243 | 29.7 | 171 |
| 2 | First floor TEM lab, in laminar flow hood | 4-897 | 399 | 199 | 605 |
| 2 | First floor SEM lab | 4344-6182 | 5596 | 249.42 | 705 |
| 2 | First floor SEM lab | 7995-13051 | 10938 | 903.73 | 559 |

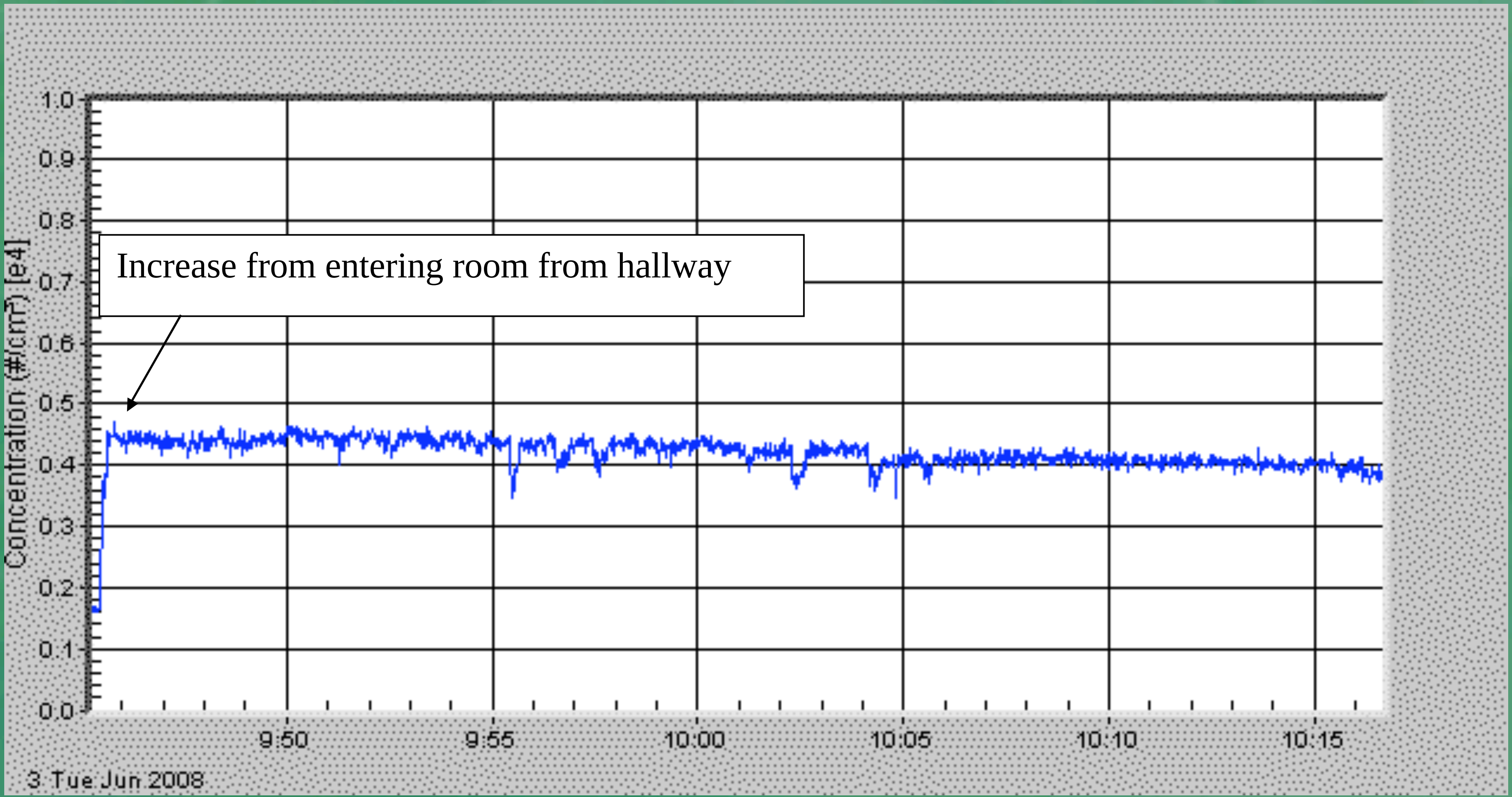
# Importance of Background Measurements



# Results of Air Monitoring

- Study 1: Weighing nanomaterials (2008)
- Study 2: Grinding nanomaterials (2007)
- Study 3: Synthesis and harvesting of nanohorns using laser ablation (2006)

# Results of Air Sampling #1

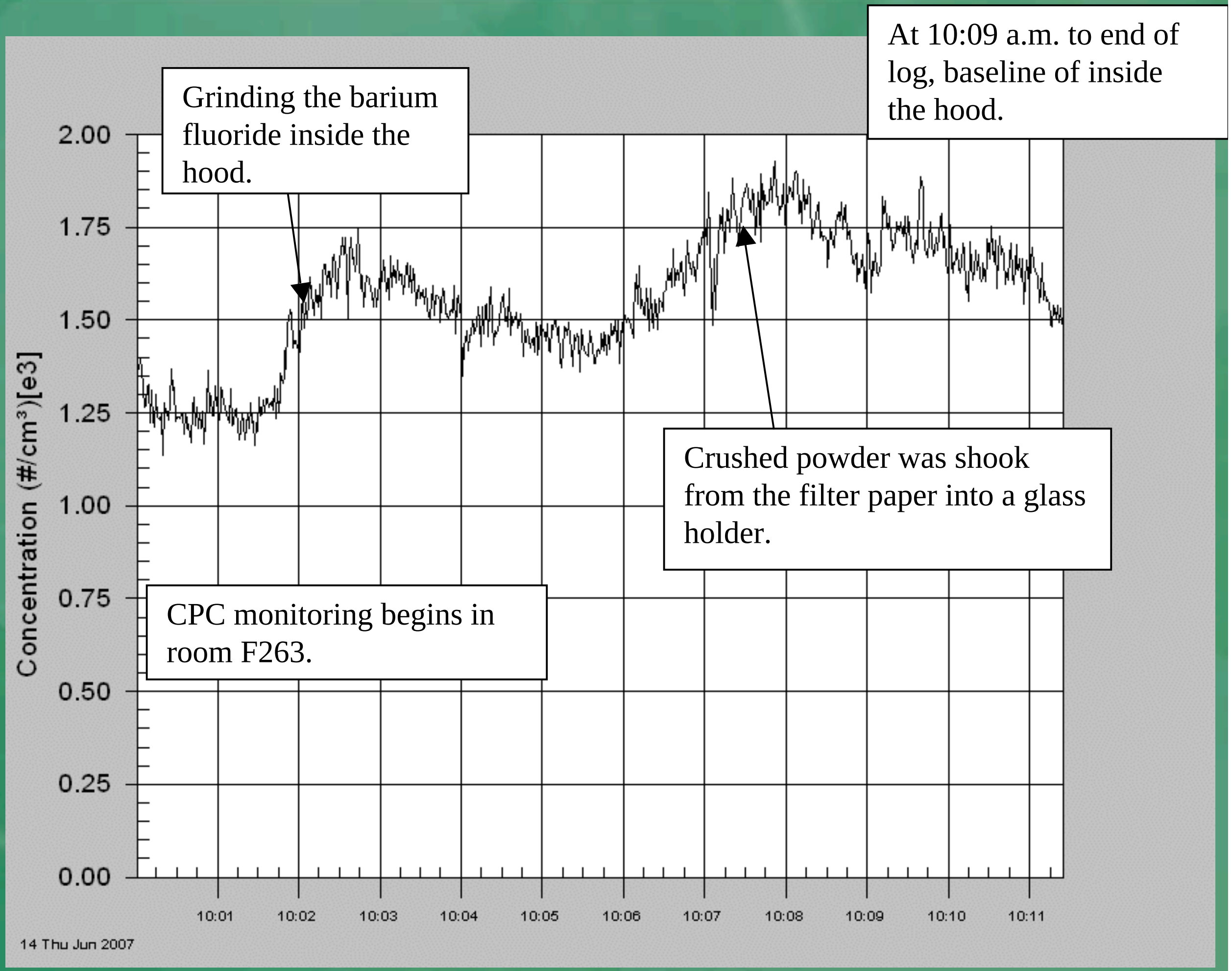


# Results of Air Sampling #1

Weighing of carbon nanotubes

| | Figure 1 – Background G-55 June 2 | Figure 2 – Background G-55 June 3 | Figure 3 – Weighing G55 June 3 |
|---|---|---|---|
| Mean (#/cm³) | 3400 | 4190 | 4360 |
| Min. (#/cm³) | 2750 | 1600 | 3990 |
| Max. (#/cm³) | 3750 | 4730 | 4740 |
| Std. Dev. (#/cm³) | 132.9 | 312.5 | 120.5 |
| Sample Time (secs) | 656 | 1886 | 806 |

# Results of Air Sampling #2



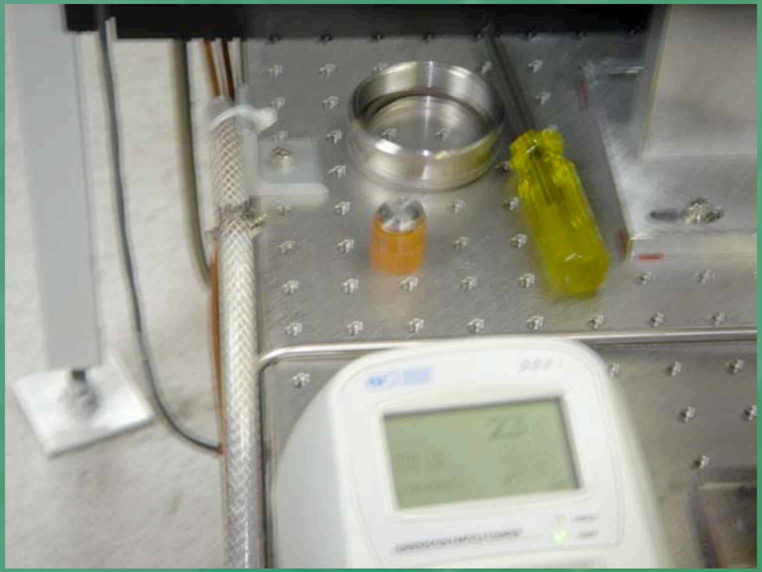
# Results of Air Sampling #2

| Activity / Materials | Range (p/cc) | Mean (p/cc) | SD | Time (s) |
|---|---|---|---|---|
| Room background | 970-1344 | 1214.19 | 50.58 | 426 |
| Grinding 1g BaF in hood | 1161-1929 | 1580.73 | 164.38 | 540 |
| Hood background | 1481-1887 | 1665.16 | 78.83 | 145 |

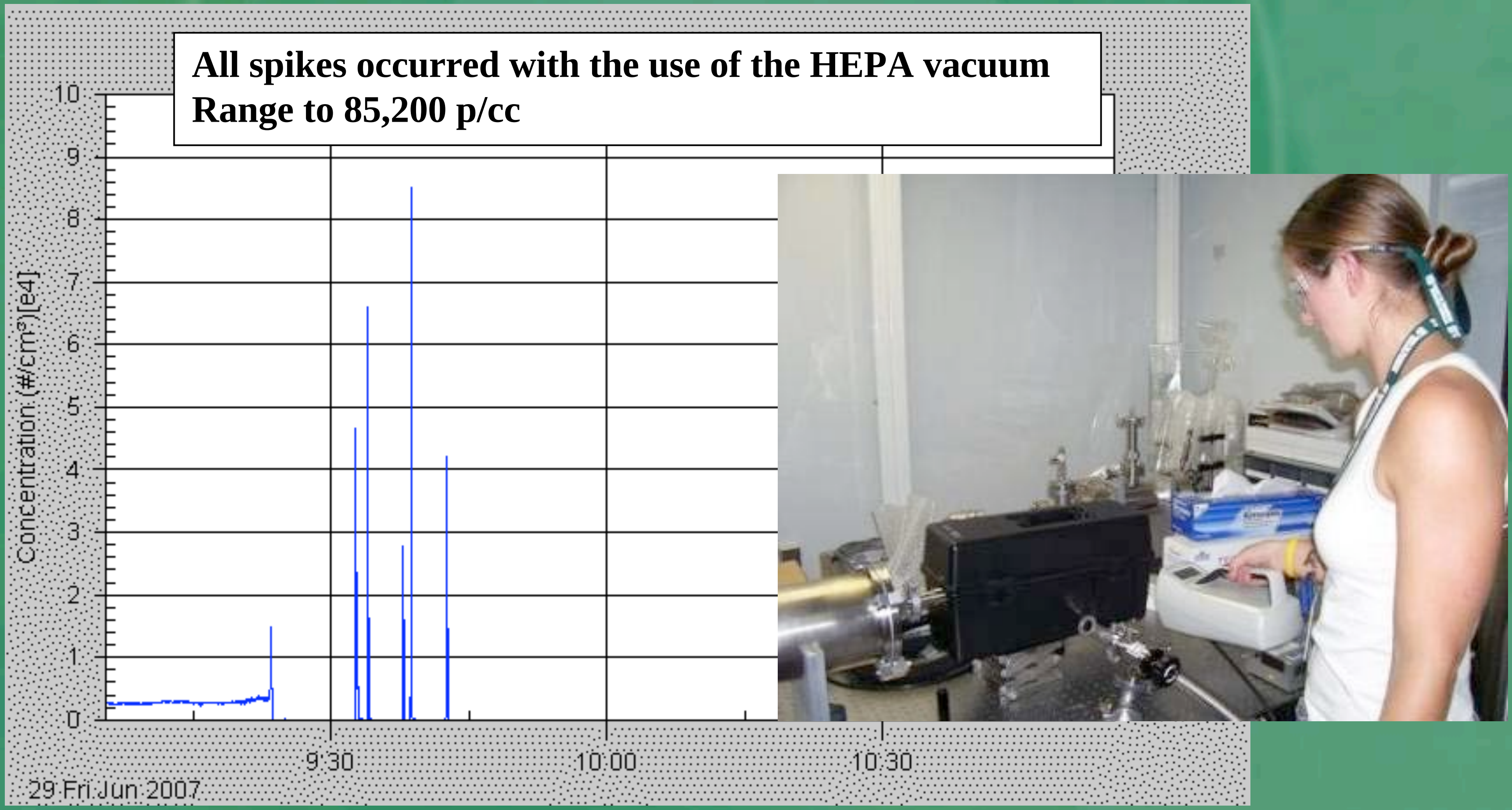
# Results of Air Sampling #3


Laser ablation to create carbon nanohorns

# Results of Air Sampling #3



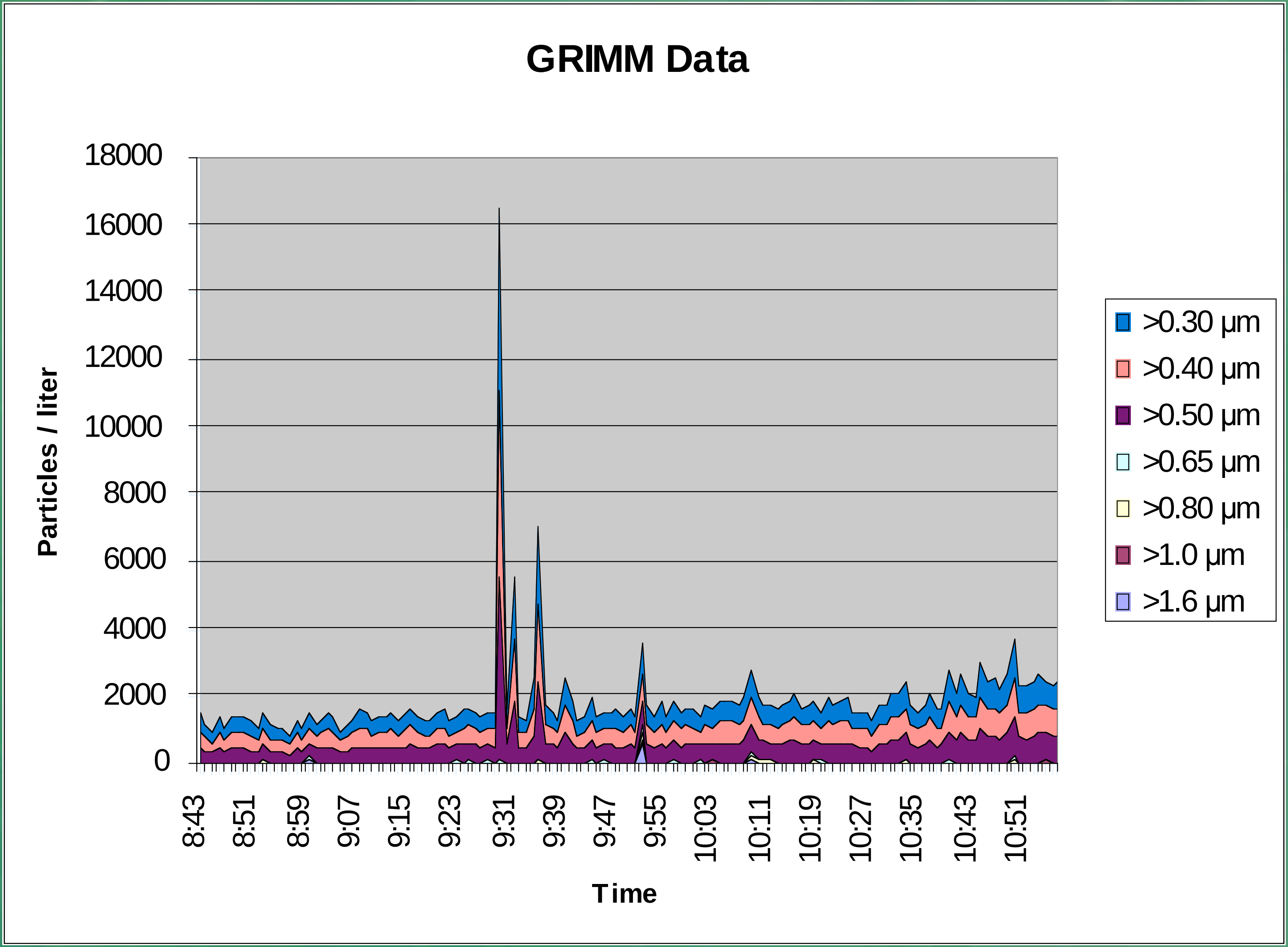
# Results of Air Sampling #3



# Results of Air Sampling #3

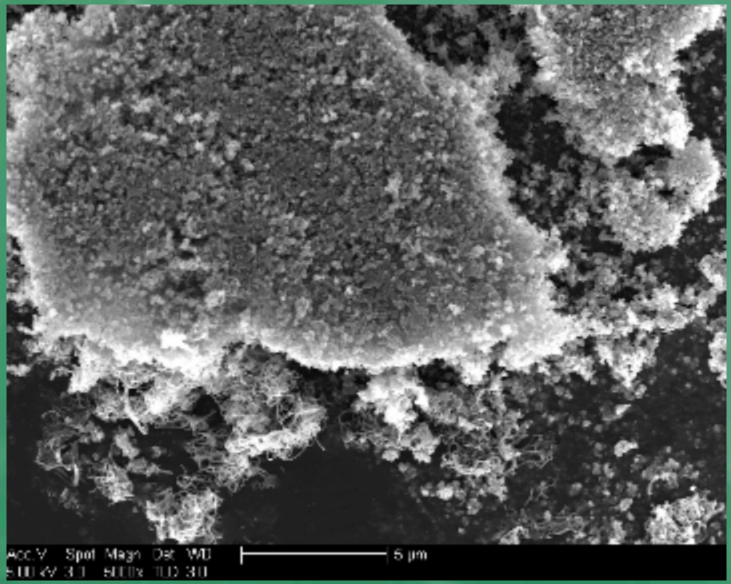
| Activity / Materials | Range | Mean | Median | SD | Time |
|---|---|---|---|---|---|
| Cleanroom area of room 217, room background | 0-53 | 5.33 | 2 | 10.08 | 60 |
| Dismantling enclosure, removing robot (quartz tube containing nanohorns is closed) | 0-105 | 26.17 | 27 | 15.79 | 300 |
| **Quartz tube opened on one end, nanohorns scraped from sides and HEPA vacuum used at other end to force material into collection chamber (HEPA filter)** | **6-85185** | **1312.2** | **26** | **6114** | **840** |
| Using Nilfisk HEPA vacuum and methanol soaked Kimwipes to clean quartz tube and other parts | 0-49 | 26.25 | 27 | 8.71 | 900 |
| Removing collection chamber which contains nanohorns on a HEPA filter | 5-36 | 16.21 | 15 | 6.14 | 180 |
| Cleaning parts used to connect collection chamber to quartz tube using MeOH Kimwipes and Nilfisk HEPA vacuum | 8-46 | 26.54 | 23 | 7.64 | 480 |
| Placing collection device, tools, and container in glove bag (takes place in laminar flow hood) | 6-35 | 19.53 | 17 | 5.85 | 240 |
| Glove bag sealed, harvesting nanotubes takes place in glove bag, in laminar flow hood | 4-51 | 28.13 | 29 | 6.37 | 1200 |
| Glove bag opened, as items removed they are wiped with MeOH soaked Kimwipe and Nilfisk vacuum | 10-242 | 36.82 | 26 | 23.49 | 300 |
| Glove bag taped shut and final clean up takes place | 6-171 | 26.11 | 17 | 14.37 | 660 |

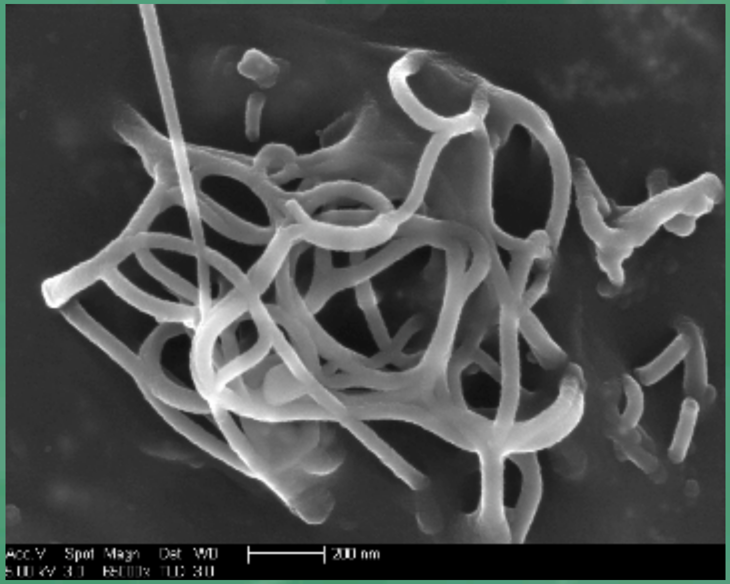
# Results of Air Sampling #2



# Results of Air Sampling

- “Bulk” from cold finger inserted into quartz tube where ablation occurred

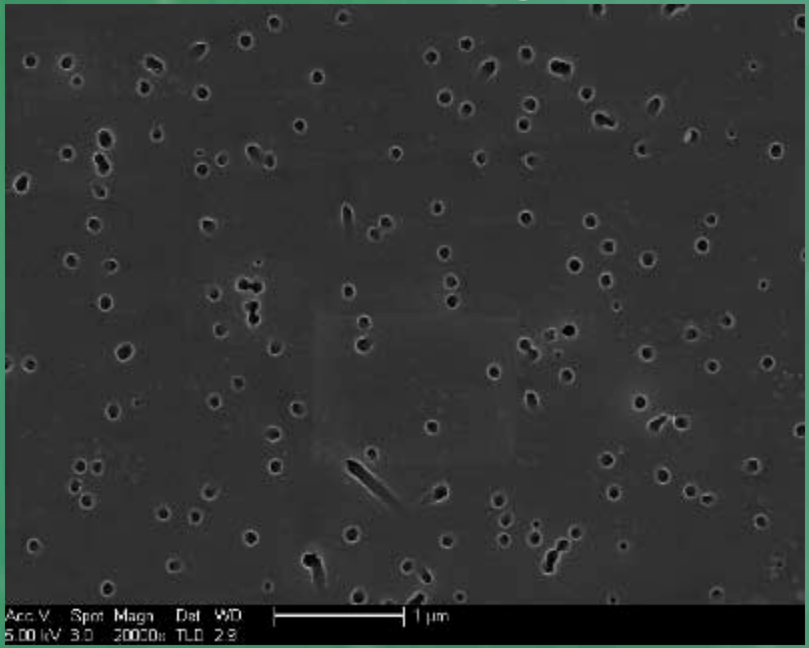


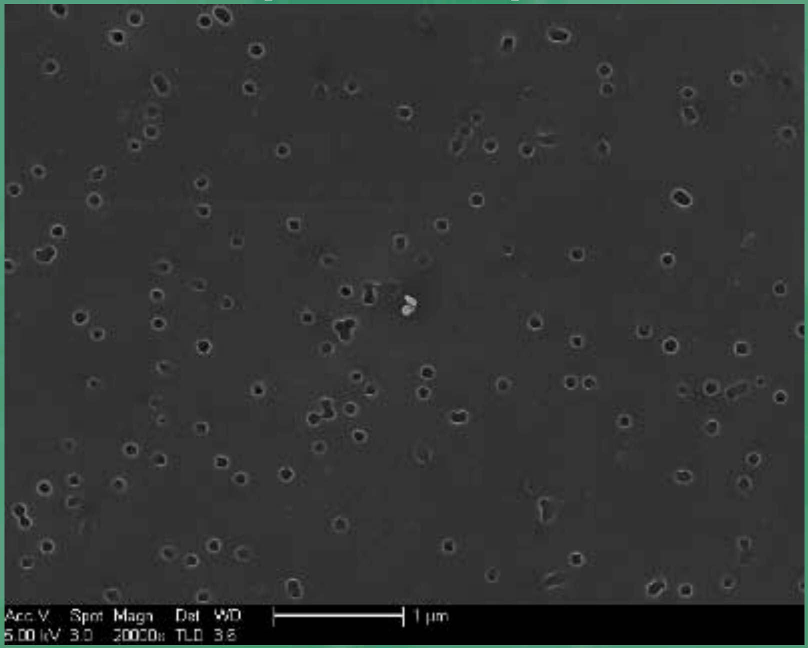

Micrographs courtesy of RJ Lee Group

# Results of Air Sampling

- Blank and High Volume Pump Samples




Blank




Active Sample

Photomicrographs courtesy of RJ Lee Group

# Discussion


- Use of CPC
  - Extremely effective to use to identify background levels and spikes due to particle generating processes in the research environment
    - Spikes may not be nanomaterials!
    - Spikes seen due to doors opening/closing, heating processes (furnace), other equipment (vacuum and heat exchanger)
  - Must carefully monitor instrument, collect detailed task level data correlated with time
  - Two person task
  - Background levels crucial to data interpretation
  - Not effective to collect employee exposure samples
  - Not effective to characterize aerosol, or less than 10 nm

# Discussion

- Use of Aerosol Spectrometer
  - Provides particle size distribution
    - May need to dilute sample
  - Did not measure particles less than 300 nm
    - Agglomeration of discrete nanomaterials
  - Particle size distribution can help predict lung deposition and potential health effects, as well as control methodologies
  - Stationary instrument, affected by movement and surrounding processes

# Discussion

- Active and passive air samples analyzed with SEM/TEM
  - Can provide confirmation of particle size distribution, morphology, chemistry and count
  - Time/resources required to analyze samples
  - Placement of samples
- Synchronize instrument times for ease of data analysis
- Spatial and temporal issues

# Discussion

- Particle spikes found due to equipment issues:
  - HEPA vacuum
  - Heat exchanger on laser enclosure
- Controls and work practices appeared effective overall:
  - Work in hoods
  - Wet methods
  - Closed systems / enclosures
  - Consistent use of PPE

# Instrumentation

**(Not an endorsement of any equipment or manufacturer)**

- TSI
  - CPC 3007

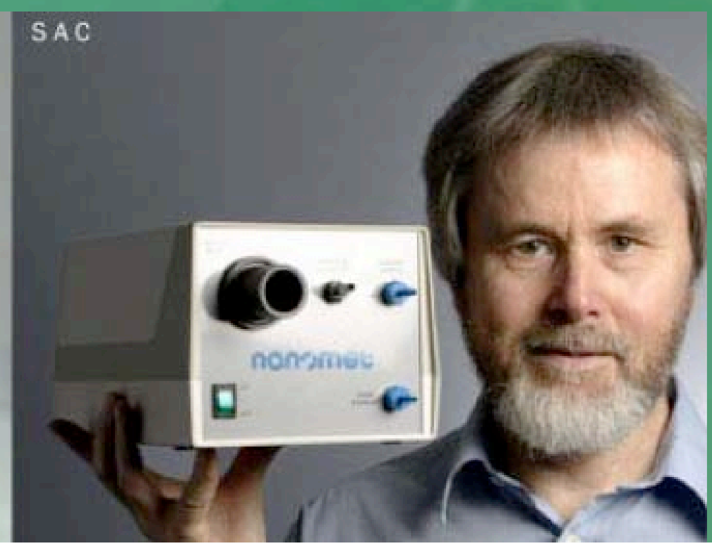
    - Particle size range of 0.01 to >1.0 µm
  - P-Trak 8525
    - Particle size range 0.02 to 1 µm
  - AEROTRAK 9000 Nanoparticle Aerosol M

    - Surface area equivalent dose of particles in th range of 10 to 1000 nanometers
    - Reported as those that deposit in tracheobronchial or alveolar regions of the lung

# Instrumentation

**(Not an endorsement of any equipment or manufacturer)**

- Naneum
  - SAC 1
    - Hand-held size-selective device (1nm to 100 nm in up to 20 separate size bands)
  - WRAS 1 (Wide range aerosol spectrometer)
    - Collects and sizes ultra-fine and nanoscale particles
    - Can be analyzed chemically and characterized physically (AA, MS, SEM, TEM)

# Instrumentation

**(Not an endorsement of any equipment or manufacturer)**


- GRIMM
- Aerosol Spectrometer 1.108
  - Particle Sizing in 16 channels, 0.30 - 20 µm
  - Allows for use of 47 mm filter for later analysis
- Wide Range Aerosol Spectrometer
  - Add CPC and DMA (electrostatic classifier)
  - Complete WRAS system covers the range from 0.005 to 20/30µm

# Recommendations

- Continued development of air sampling protocol, toxicological studies, and employee exposure guidelines
- Continued collaboration between DOE facilities, NIOSH and others to create sampling strategy and meaningful data collection and analysis
- Questions?