

# Nanoparticle Exposure Assessment

Finding a needle in a haystack

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Department of  
Environmental and Radiological Health Sciences

1

3/18/09

Colorado  
State  
University



June 2006

A nanometer is one-billionth of a meter.  
That's like comparing the size of a marble to the size of Earth.  
Welcome to the world of **nanotechnology**.



**A tsunami is unnoticeable in the open ocean—a long, low wave whose power becomes clear only when it reaches shore and breaks...**

**Nanotechnology has been around for two decades, but the first wave of applications is only now beginning to break. As it does, it will make the computer revolution look like small change.**

**Jennifer Kahn**  
**National Geographic**



# What is Nanotechnology?

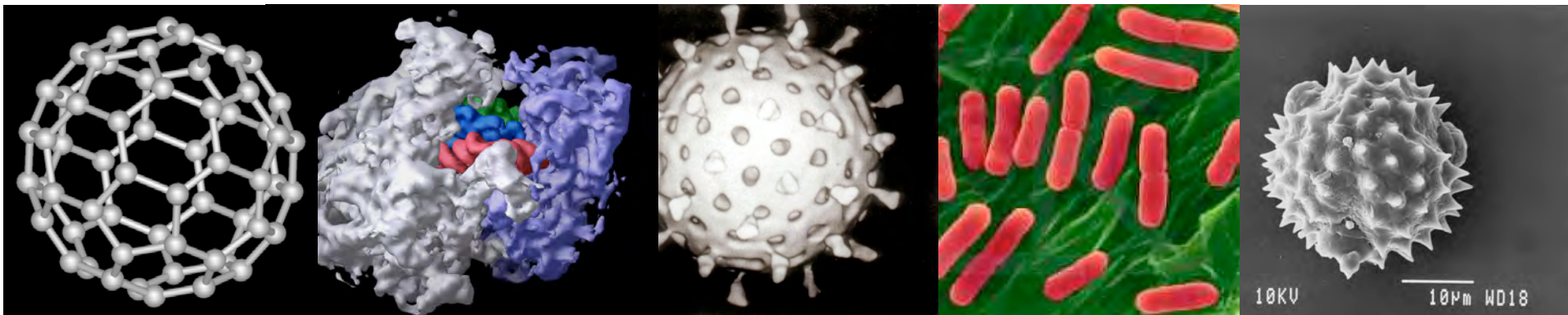
**Nanotech is building stuff that does stuff at the nanoscale**

**Richard Smalley**

**Nanotechnology will let us build computers that are incredibly powerful. We'll have more power in the volume of a sugar cube than exists in the entire world today.**

**Ralph Merkle**





Fullerene

Ribosome

Virus

E. Coli

Pollen

Engineered particles/structures  
with length scale from 1-100 nm



Particle Size, nanometers

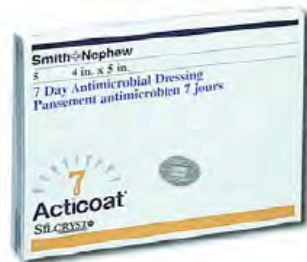
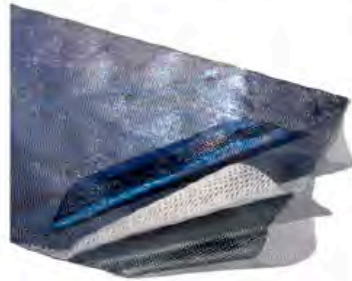
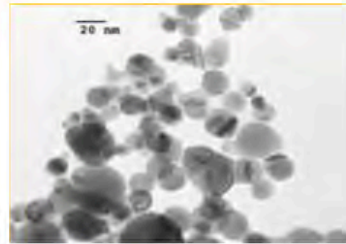




# Nanomaterials in Consumer Products



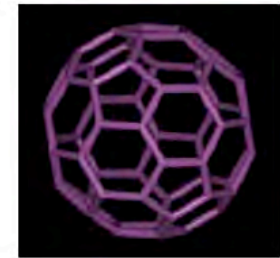
*Nanoclays and nanoclay composites, used in automotive applications like the Hummer H2's running boards*



*Silver nanoparticles used for antimicrobial effect in wound dressings and consumer products*



*Single-walled nanotubes are becoming realistic for memory chips in devices like cell phones*



*Fullerenes' electronic properties also make them strong antioxidants*



## Science News

Share Blog Cite

### New Nanotechnology Products Hitting The Market At The Rate Of 3-4 Per Week

*ScienceDaily* (Apr. 25, 2008) — New nanotechnology consumer products are coming on the market at the rate of 3-4 per week, a finding based on the latest update to the nanotechnology consumer product inventory maintained by the Project on Emerging Nanotechnologies (PEN).

See also:

#### Matter & Energy

- Nanotechnology
- Materials Science
- Thermodynamics
- Physics
- Technology
- Engineering

#### Reference

- Nanomedicine
- Nanorobotics
- Nanoparticle
- Nanotechnology

One of the new items among the more than 600 products now in the inventory is Swissdent Nanowhitening Toothpaste with "calcium peroxides, in the form of nano-particles." Today, in testimony before the Senate Commerce Committee, PEN Project Director David Rejeski cited Ace Silver Plus--another of the nine nano toothpastes in the inventory--as an example of the upsurge in nanotechnology consumer products in stores. The hearing marks the start of U.S. Senate debate on the future direction of the annual \$1.5 billion federal

investment in nanotechnology research and development (R&D).

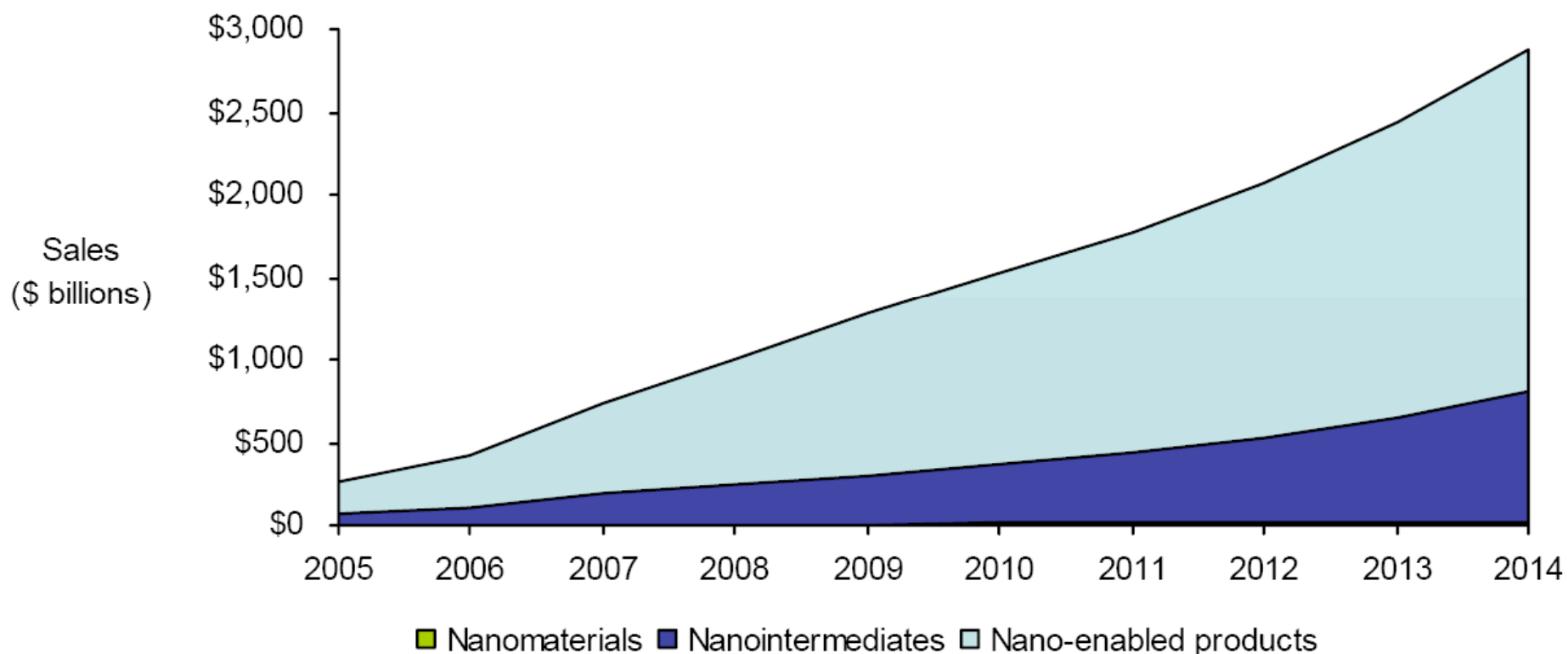
The number of consumer products using nanotechnology has grown from 212 to 609 since PEN launched the world's first online inventory of manufacturer-identified nanotech goods in March 2006. Health and fitness items, which includes cosmetics and sunscreens, represent 60 percent of inventory products.



Nano Silver Toothpaste, purchased in a store in Washington D.C. (Credit: 2008 - Alex Parlani, Project on Emerging Nanotechnologies)



## Sales of products incorporating nanotechnology, 2005 to 2014



Source: Lux Research Report "Sizing Nanotechnology's Value Chain"



# Nanomaterials in Research

- Medicine:
  - Targeted drug delivery/therapy
  - Diagnostic imaging
- Energy:
  - Pollution control catalysts
  - Improved batteries, solar cells
- Other Tech:
  - Memory, display, transistors, processors



# Health Risk from Nanoparticles?

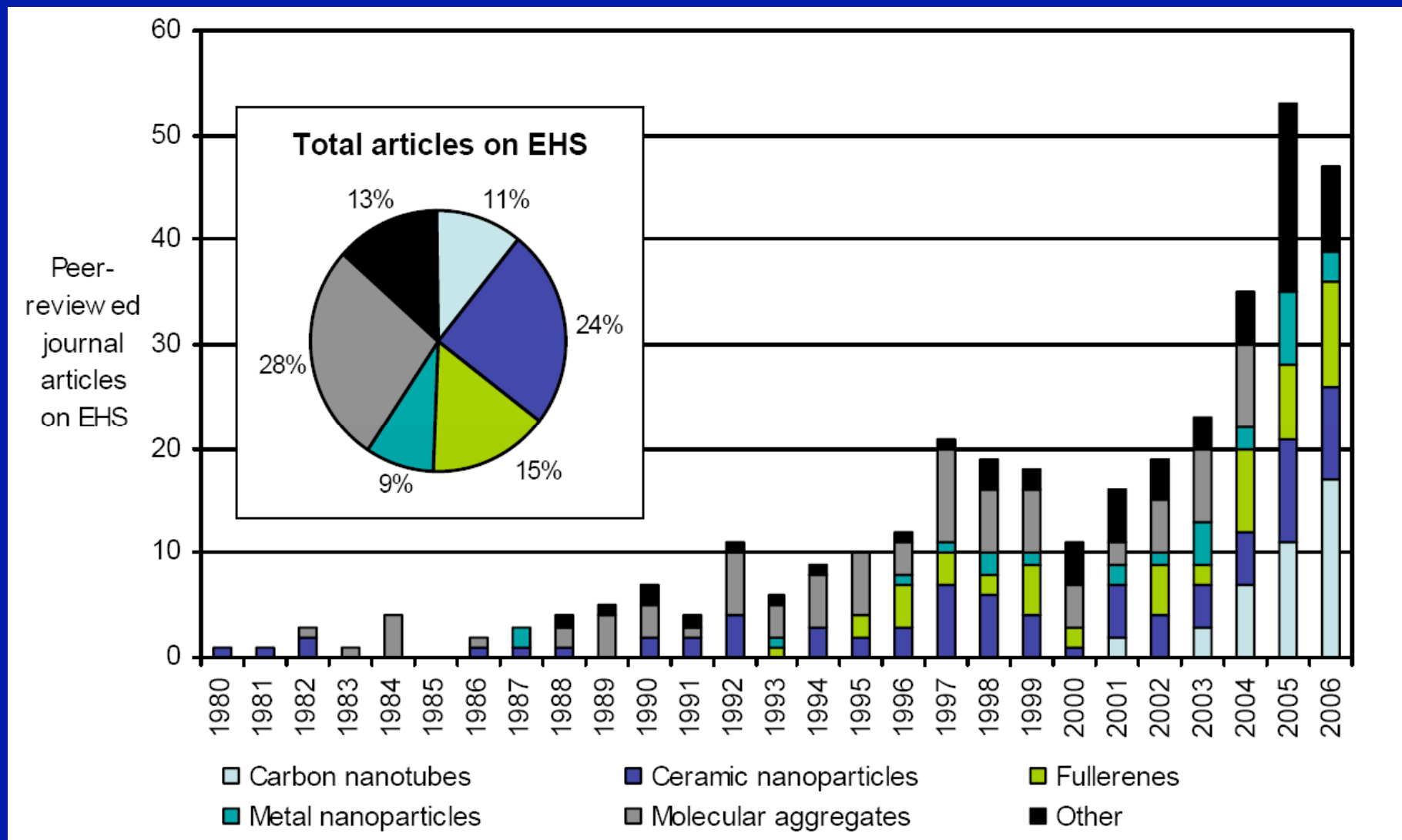
The same properties that make nanoparticles attractive:

- high reactivity
- ability to cross cell membranes

.....also could lead to adverse health effects.



# EHS Research Lags Nanoscience



Sources: Lux Research, ICON



# Questions That Need Answers:

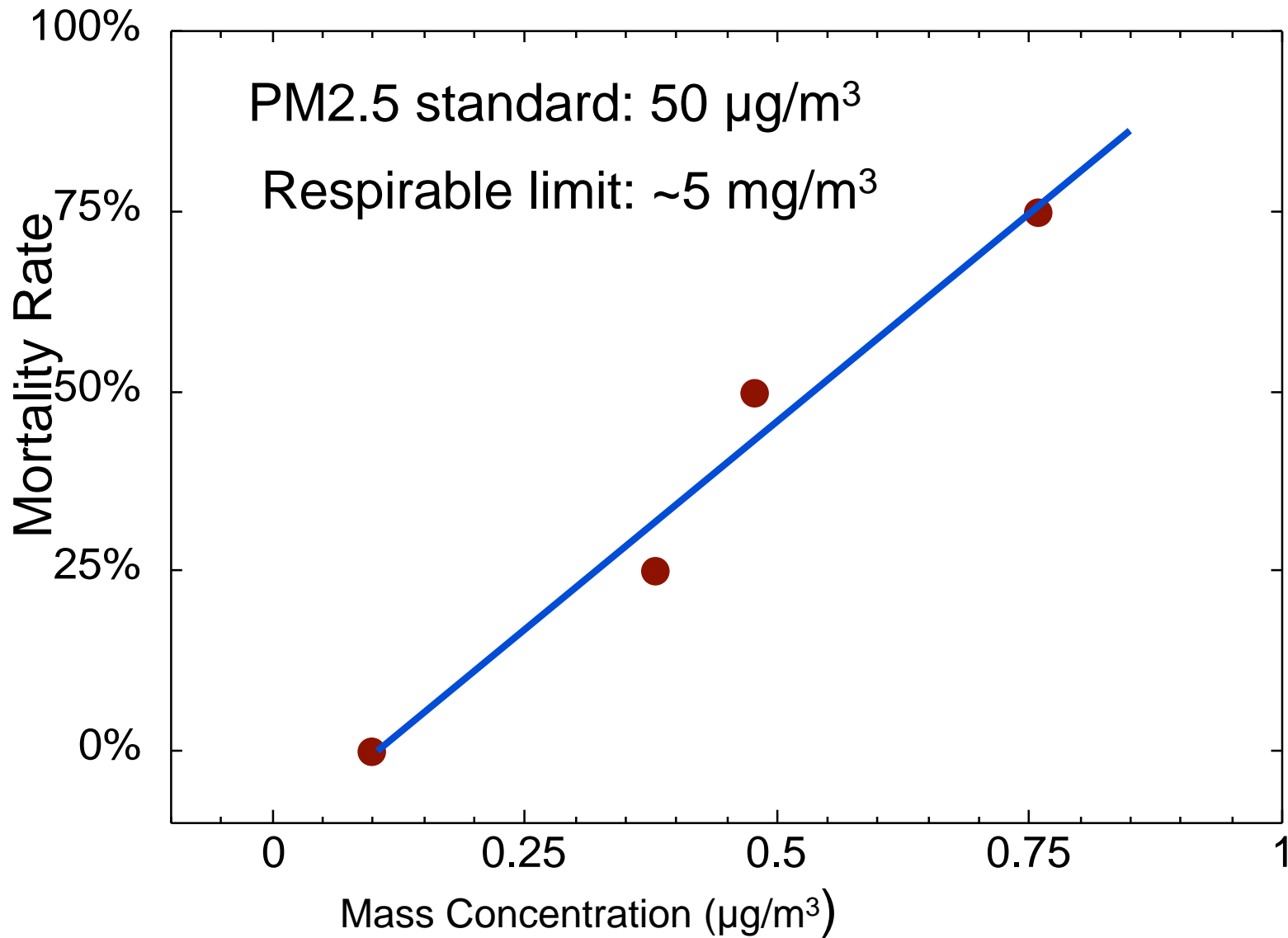
- Are nanoparticles hazardous?
- What are the routes of exposure?
- How do we assess and manage exposures?



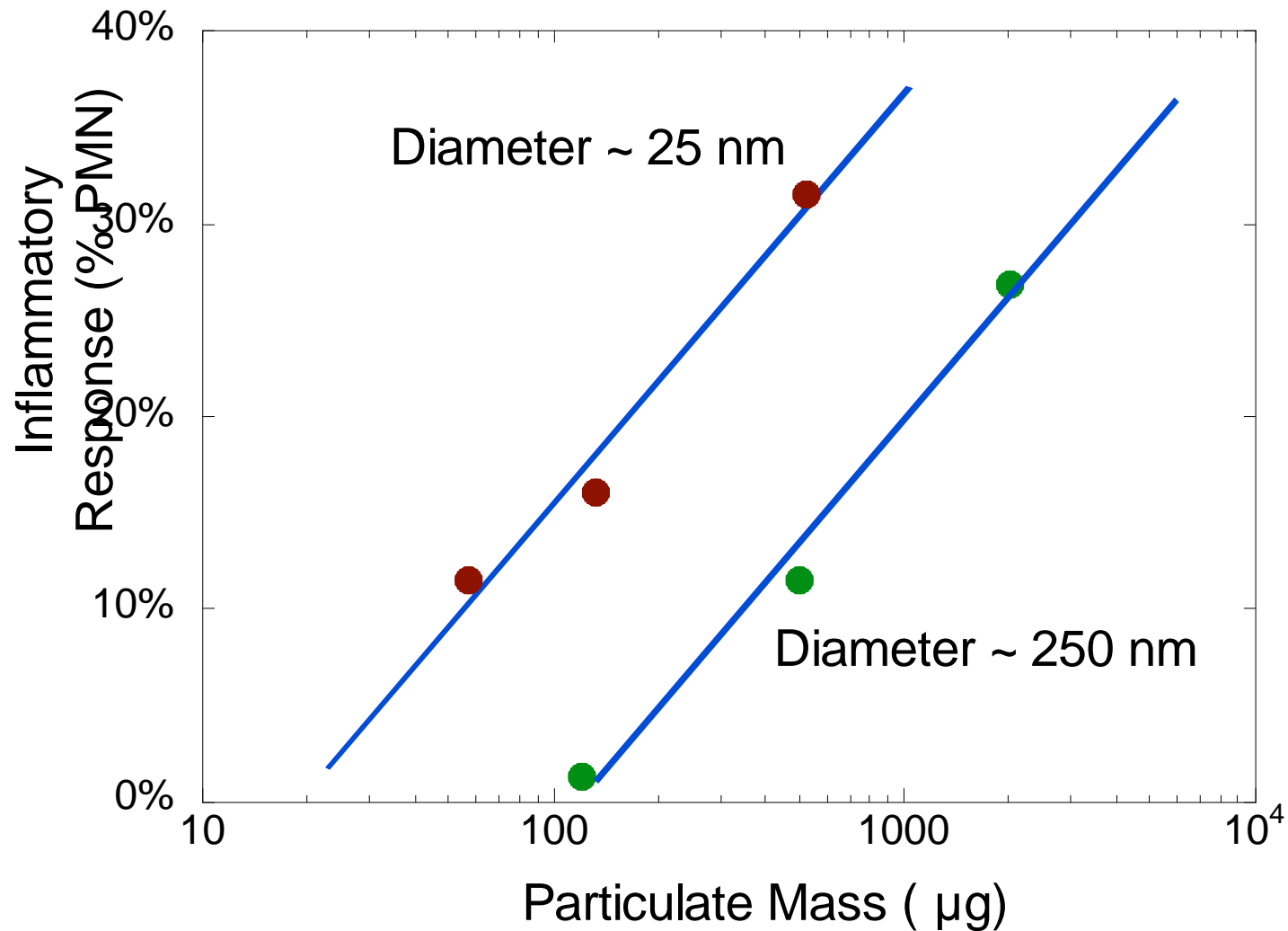
# Are Nanoparticles Hazardous?



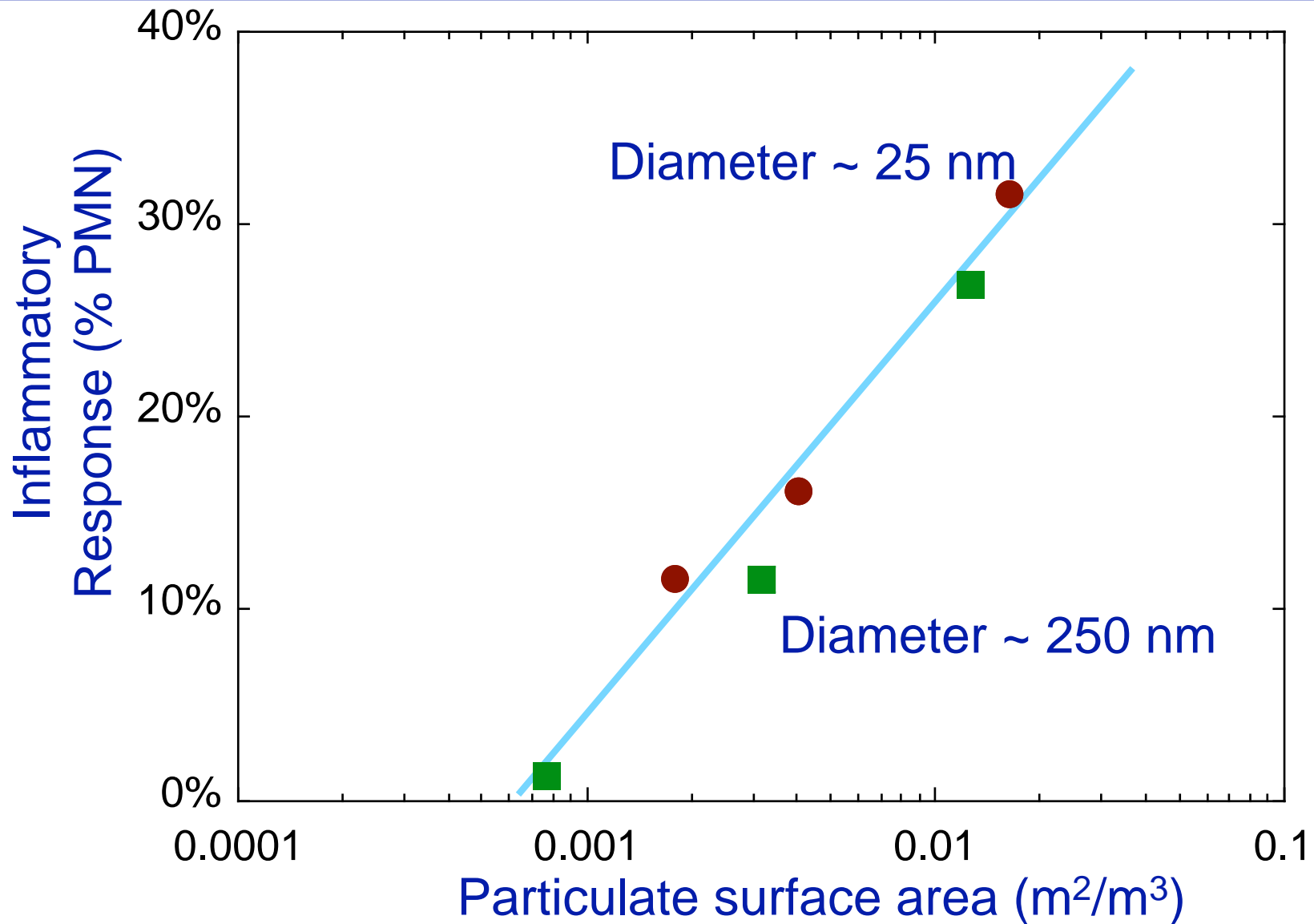
# Ultrafine PTFE inhalation (rats)



# TiO<sub>2</sub> instillation in rats - Oberdörster et al. (2000)

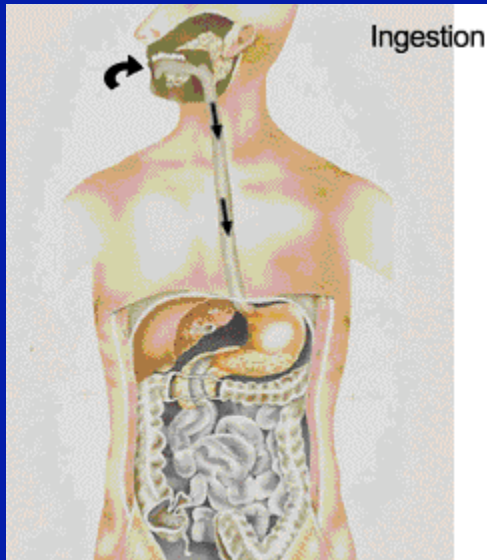


# TiO<sub>2</sub> instillation in rats

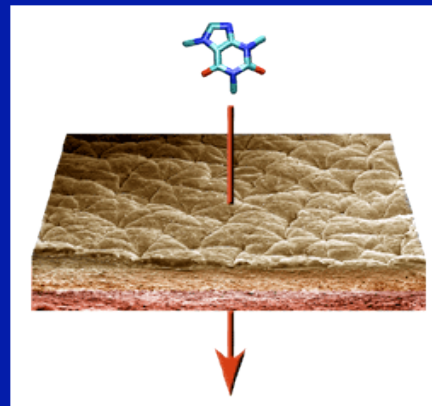


# What are the relevant exposure routes?

## Ingestion (injection)



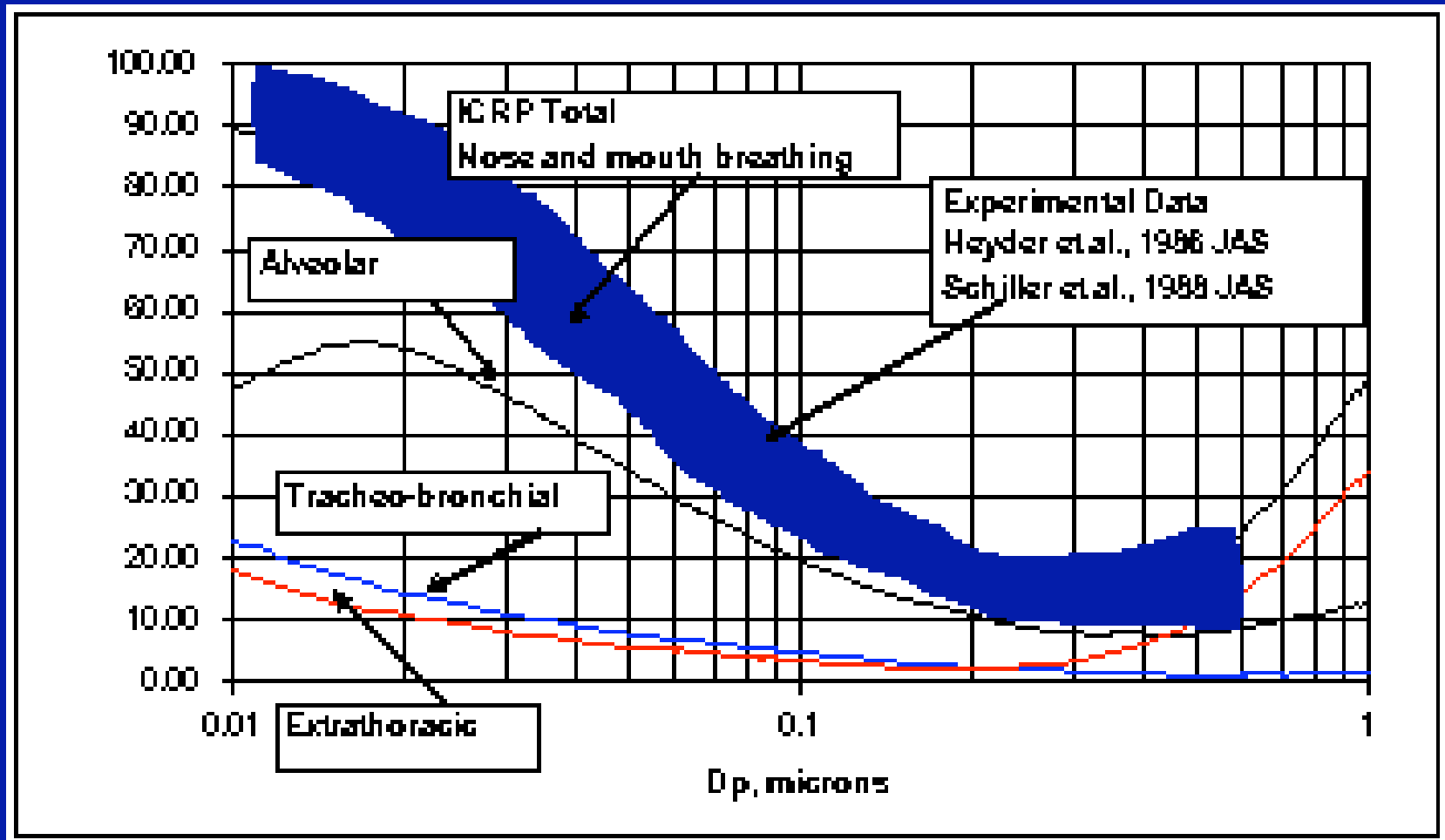
## Dermal absorption



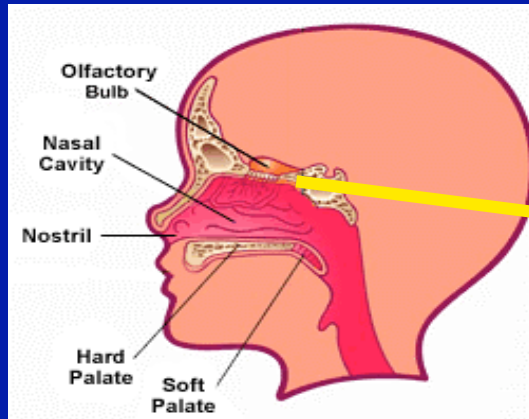
## Inhalation



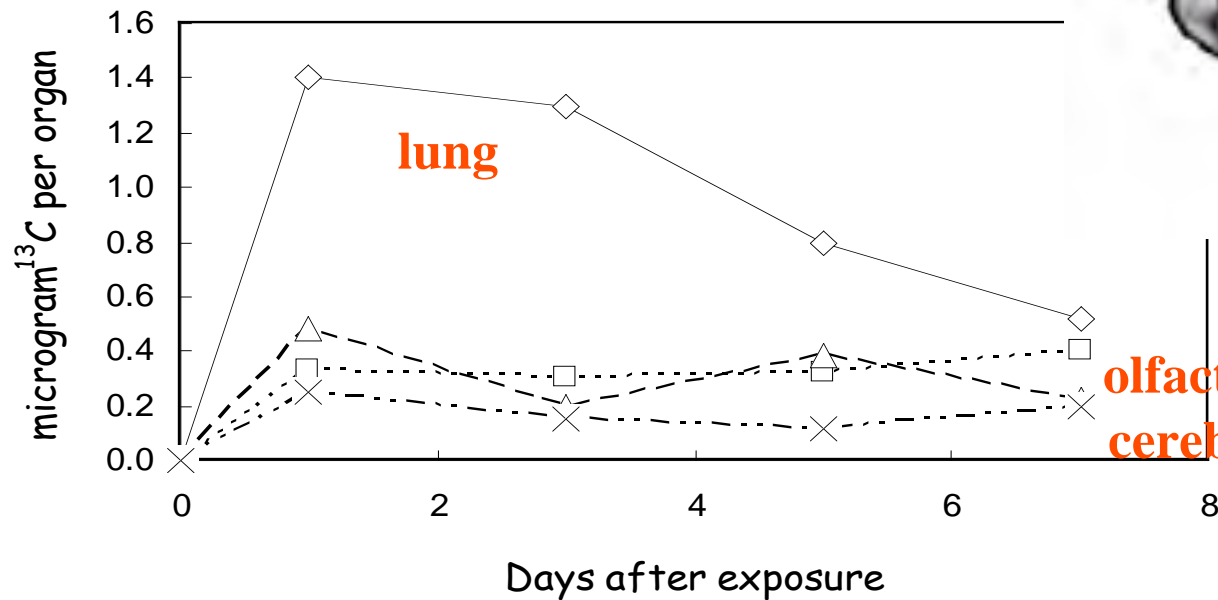
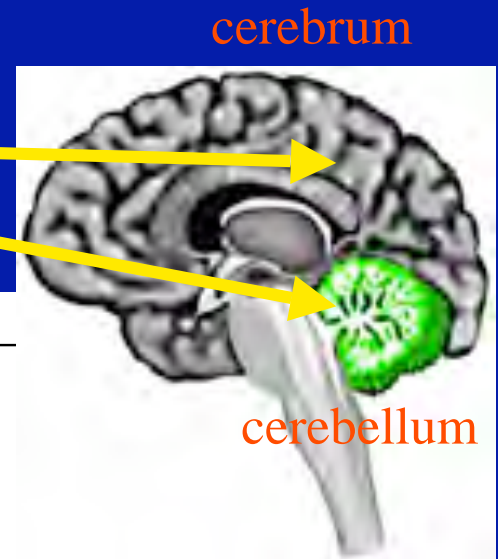
# Respiratory Deposition Efficiency



# Nanoparticles Can *Translocate* Because of Their Small Size



via olfactory nerve



Oberdörster *et al.*, 2004



# How do we assess (measure) nanoparticle exposures?



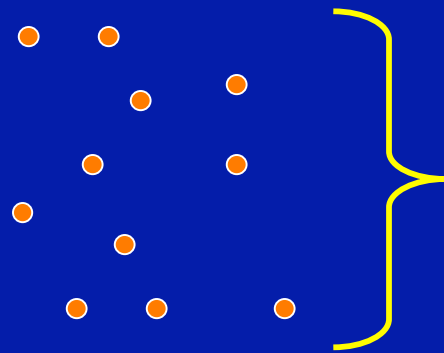
# More questions that need answers

- Are airborne nanoparticles present?
- At what concentrations?
- Where did they come from?



# Nanoparticles Have Almost No Mass

← Edge of a single 10 micron particle

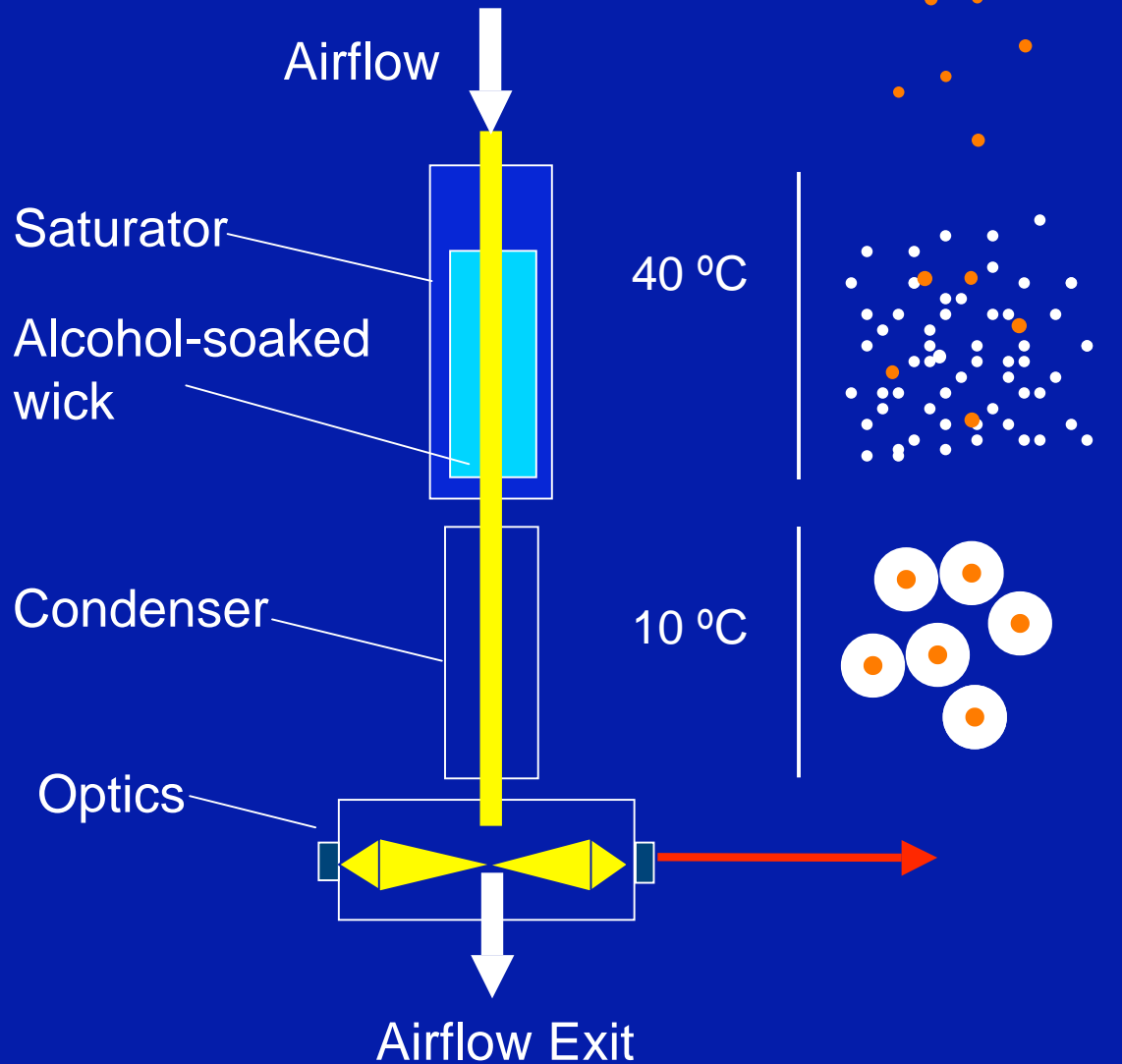


Relative size of 10 nanometer particles for comparison

A 10 micron particle weighs the same as one billion 10 nanometer particles

**Bottom Line: We cannot detect nanoparticles with traditional techniques:**  
filters, impactors, light scattering

# Condensation Particle Counter



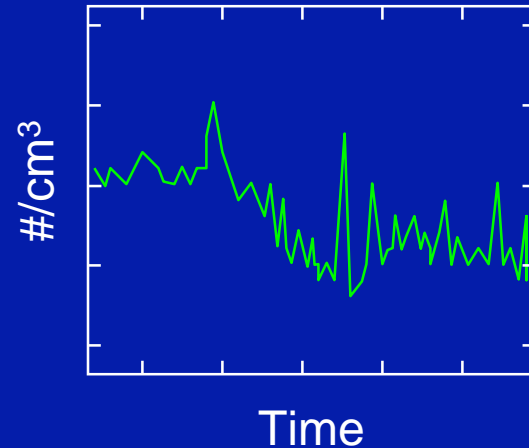
Nanoparticles are too small to be 'seen' by an aerosol photometer

1. Aerosol becomes saturated with hot vapors
2. Colder temp. causes vapor condensation and promotes particle growth
3. Large particles are easily counted



# Condensation Particle Counters

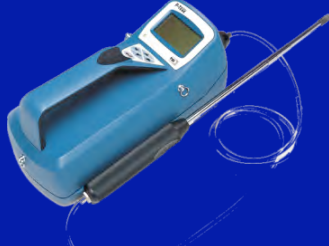



- Advantages:
  - Real-time output
  - Portable
  - Relatively inexpensive



- Disadvantages:
  - Not-size resolved
  - Non-specific detection
  - Lower size limit 10-20 nanometers

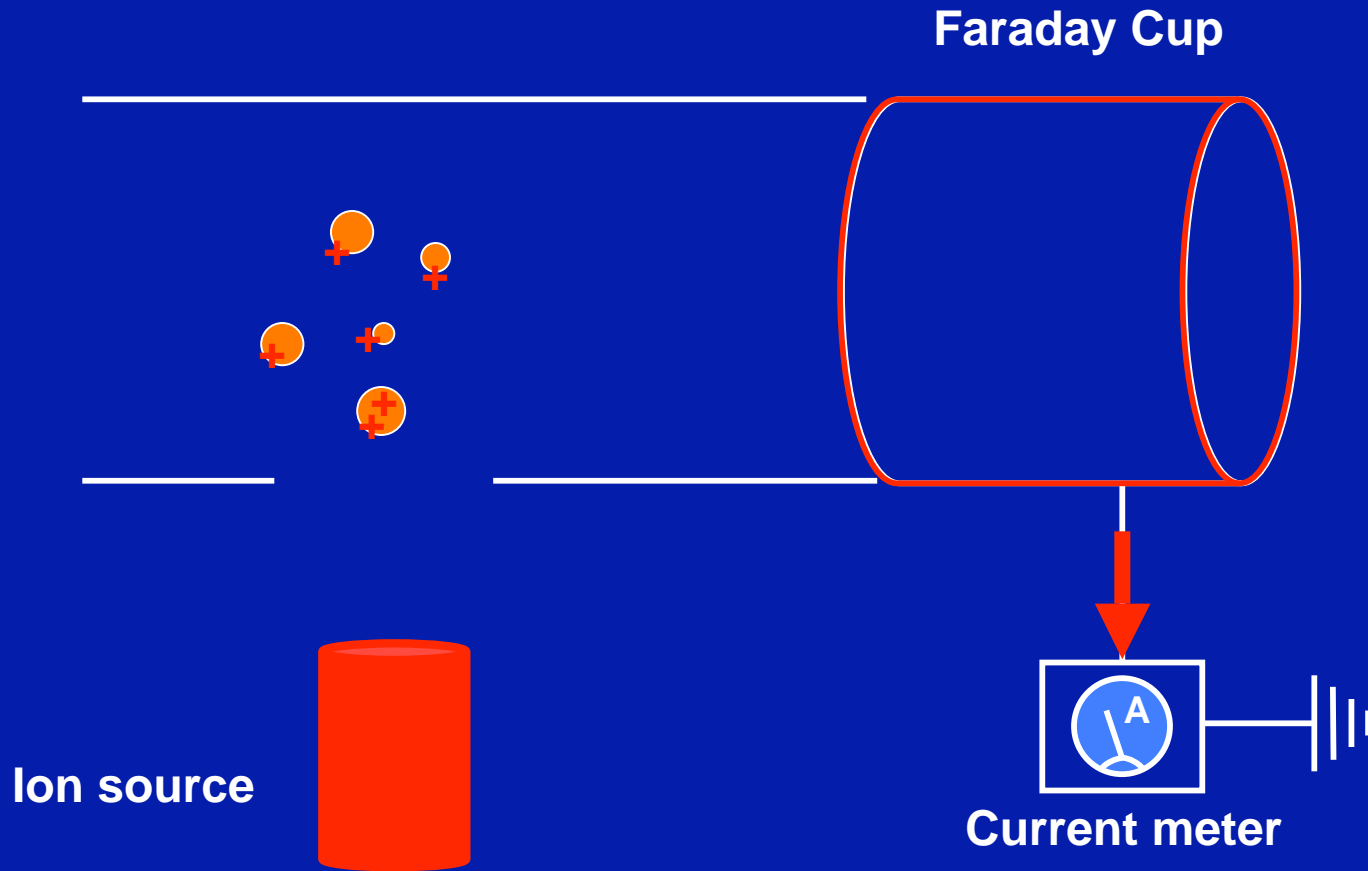


# Condensation Particle Counters (CPCs)

|                 |   |   |   |
|-----------------|---|---|---|
|                 | <p>P-TRAK</p>  <p><i>Courtesy of TSI</i></p> | <p>CPC 3007</p>  <p><i>Courtesy of TSI</i></p> |  <p><i>Courtesy of GRIMM</i></p>  <p><i>Courtesy of TSI</i></p> |
| Cost            | \$6K  | \$8K  | \$20k   |
| Size Range (nm) | 20 - 1000   | 10 - 1000   | 2 – 1000  |
| Max Conc.       | $5 \times 10^5$ p/cc  | $1 \times 10^5$ p/cc  | $1 \times 10^7$ p/cc  |



# Diffusion Charger: Principle of Operation



- # of ions attached ~ particle surface area

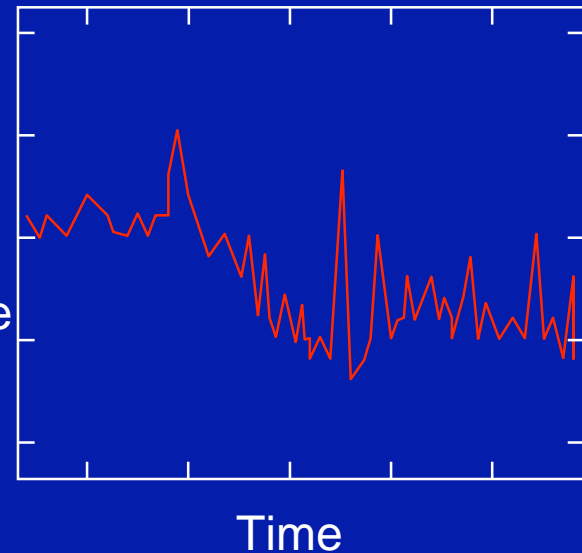


# Surface Area Measurement: Diffusion Chargers

- Advantages:

- Real-time output
- Portable
- Surface area may be relevant to health hazards

Surface Area  
Concentration  
Or  
Deposition Rate



- Disadvantages:

- Not-size resolved
- Non-specific detection
- Susceptible to bias from large particles (> 100 nm)

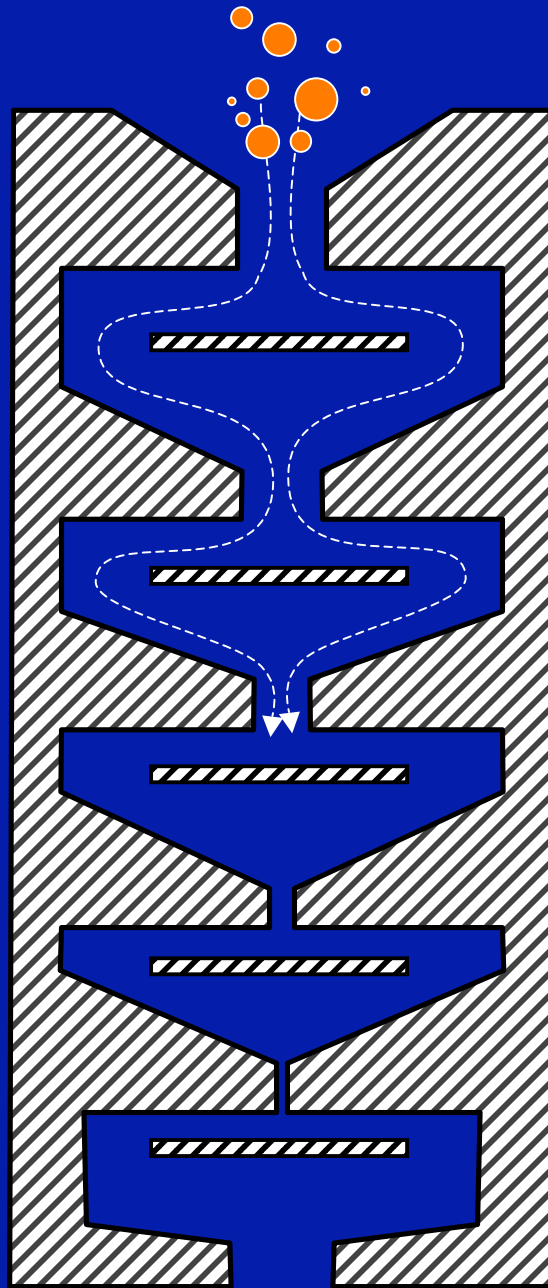


# Surface Area Measurement: Diffusion Chargers

|            | DC 2000 CE<br><br><i>Courtesy of EcoChem</i> | AeroTRAK 9000<br><br><i>Courtesy of TSI</i> | NSAM 3550<br><br><i>Courtesy of TSI</i> |
|------------|---|--|--|
| Cost       | \$10K   | \$10K  | \$16   |
| Size Range | 10 – 1000 nm  | 10 – 1000 nm   | 10 – 1000 nm   |



# Low-Pressure Cascade Impactor



- Separates particles by their 'aerodynamic diameter'
- Bottom stages are operated at low pressure
  - $\frac{1}{4}$  atmosphere of pressure
  - Reduced viscous drag
  - Nanoparticles can now impact

Low-pressure zone



# Low Pressure Impactors

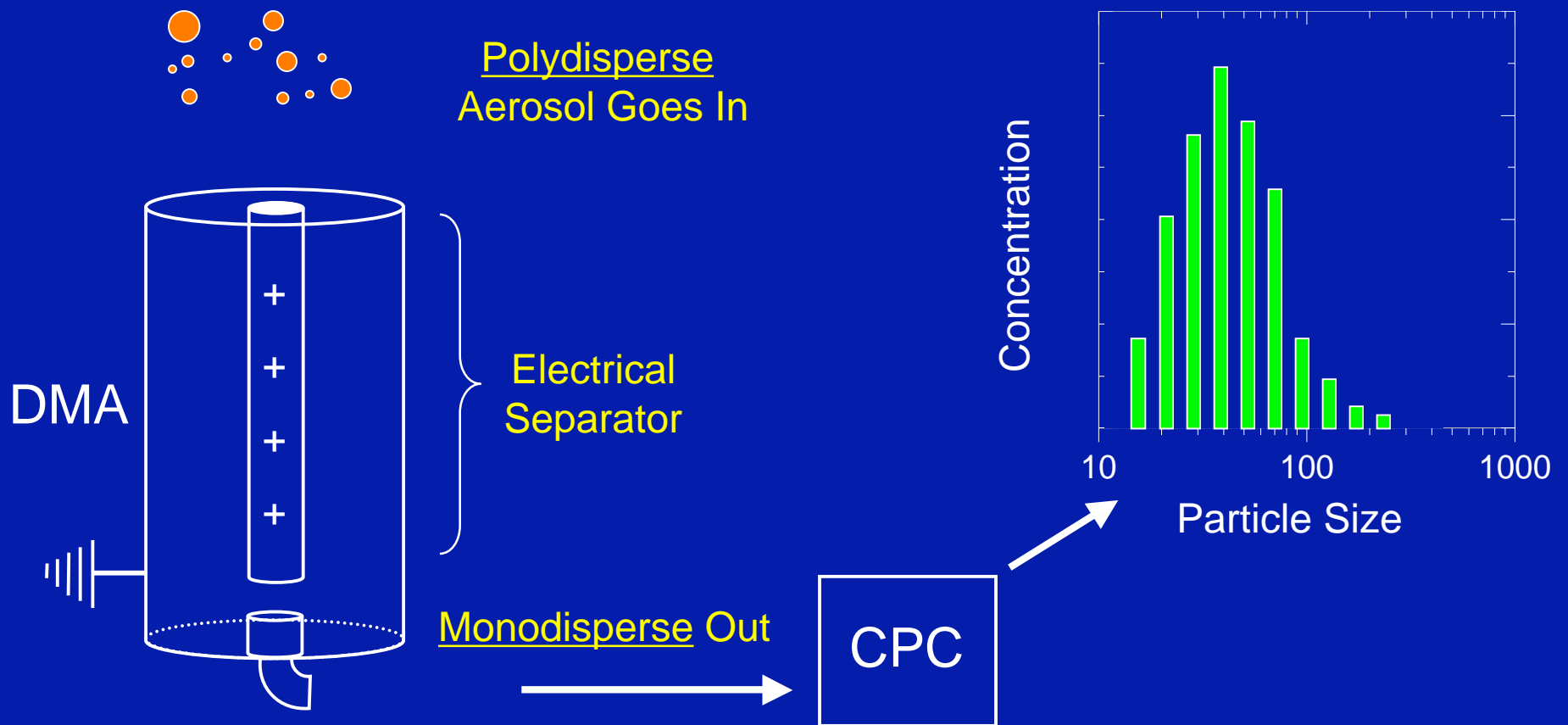
|                  | NanoMOUDI II<br><br><i>Courtesy of MSP</i> | DLPI<br><br><i>Courtesy of Dekati</i> |
|------------------|---|--|
| Cost             | \$30K   | \$20K  |
| Lower Size Limit | 10 nm   | 30 nm  |

- Advantages:
  - Size resolved
  - Secondary Analyses
- Disadvantages:
  - Cost
  - Time-integrated
  - Time-intensive



# The Scanning Mobility Particle Sizer (SMPS)

- Combination of Differential Mobility Analyzer (DMA) and Condensation Particle Counter (CPC)



# Scanning Mobility Particle Sizer

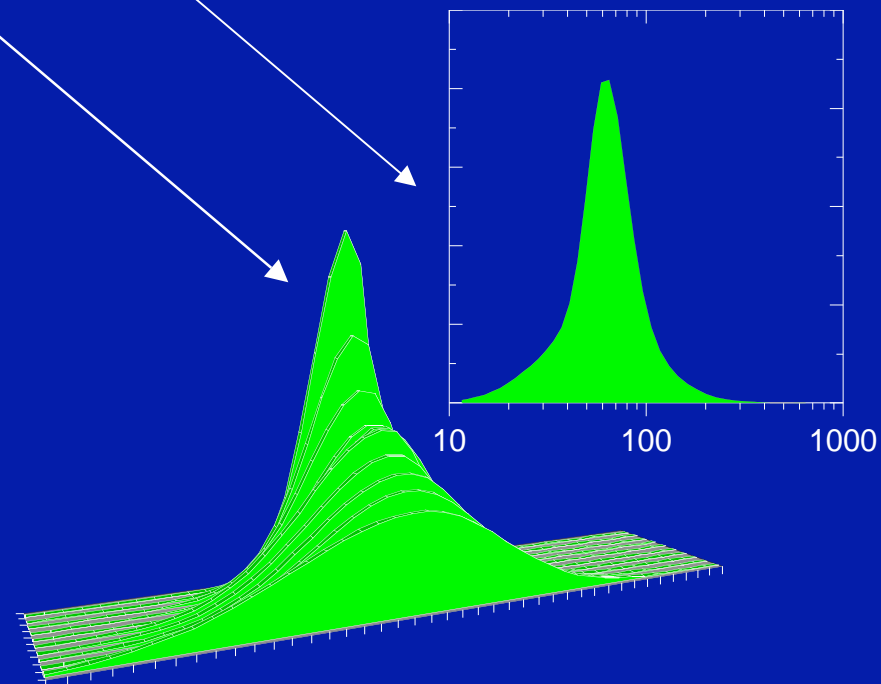
- Advantages:
  - Size, concentration measurement
  - Quasi-real-time (5 min scan)
- Disadvantages:
  - Cost: \$50 - \$80k
  - No specificity



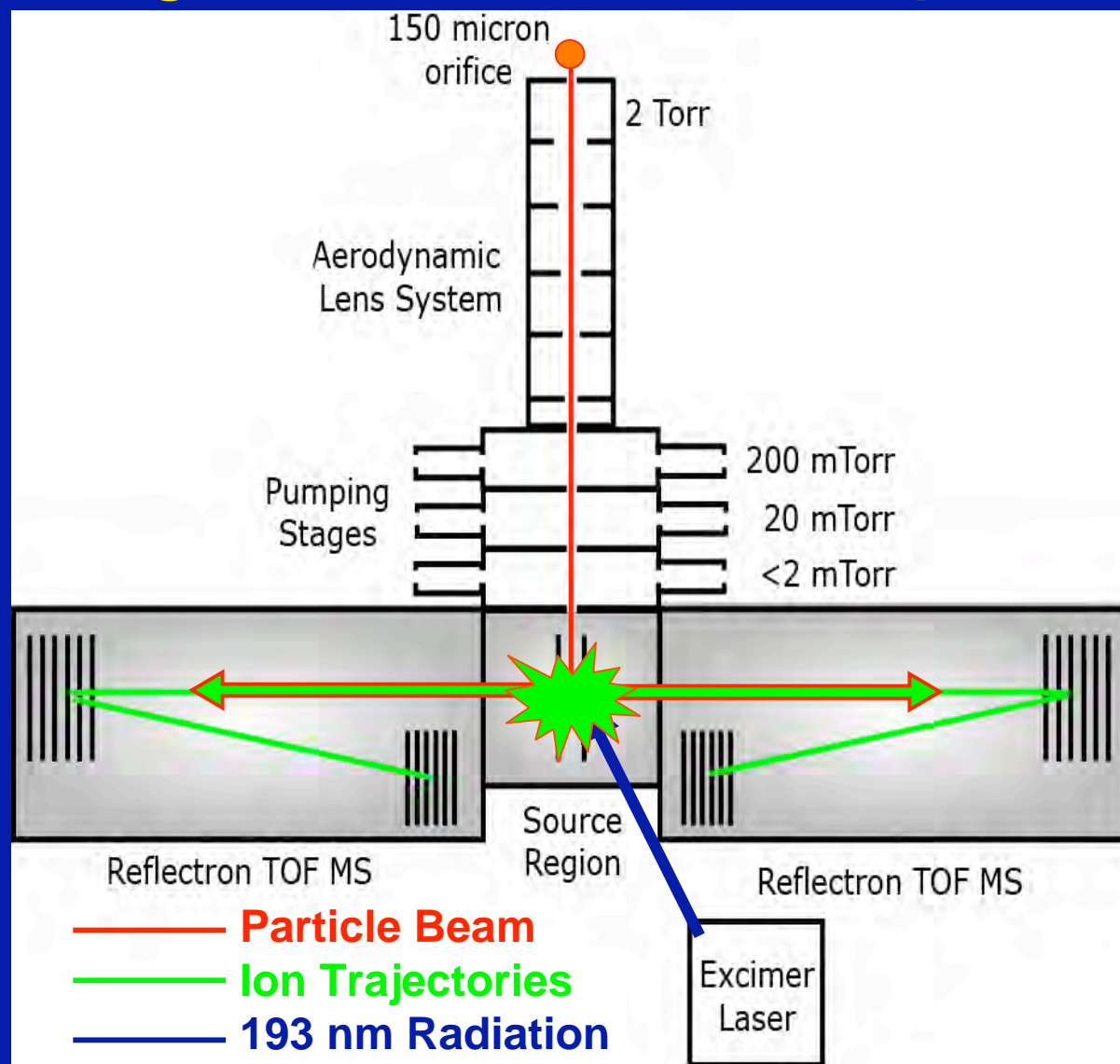
Courtesy of TSI



Courtesy of GRIMM



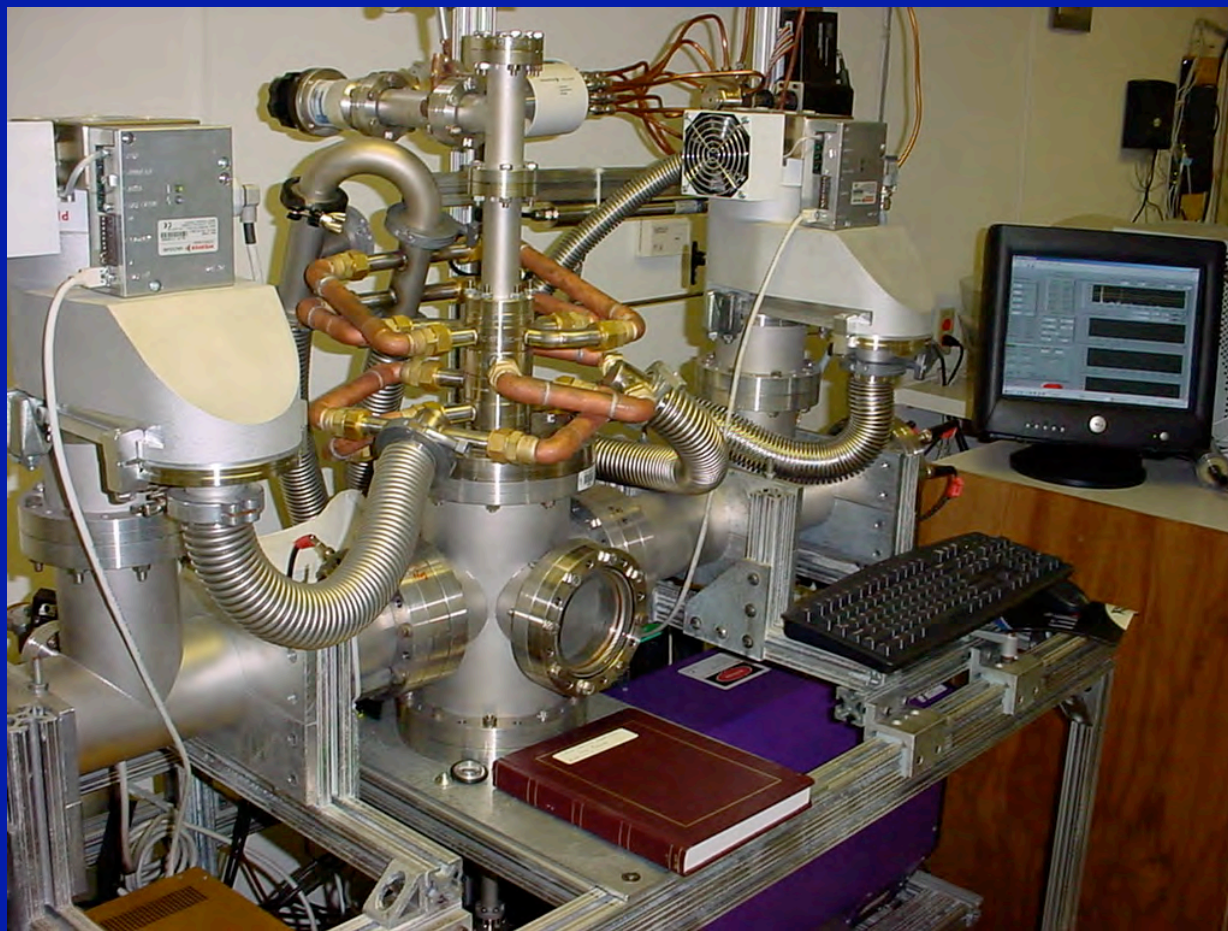
# Single Particle Mass Spectrometers



1. Focus particles into a narrow beam
2. Select a particular size
3. Pump to low pressure
4. Blast particles with high energy laser
5. Measure positive and negative ion fragments



# Single Particle Mass Spectrometers

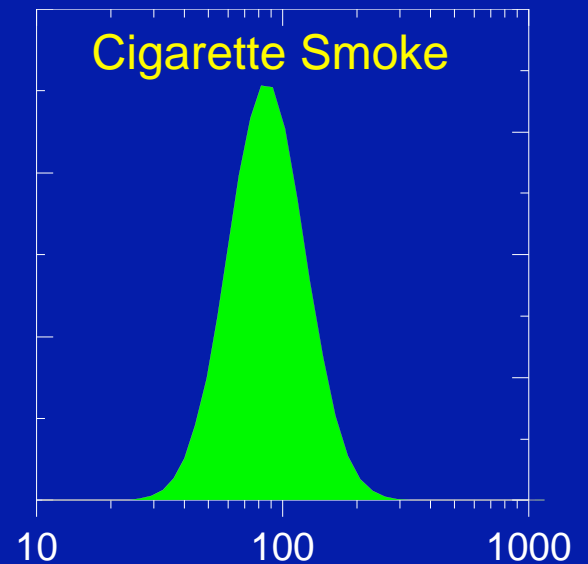
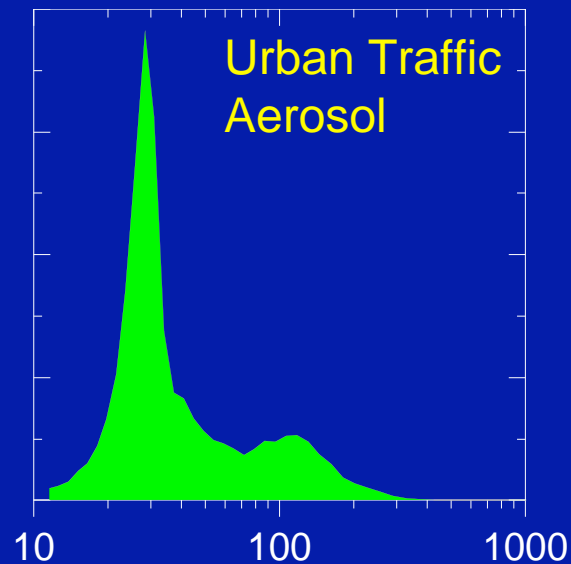
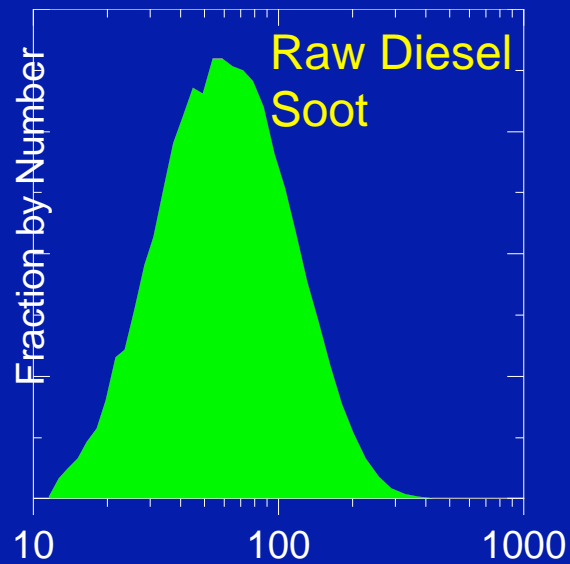


- Advantages:
  - Rapid measurement
  - Individual particles
  - Chemical composition
  - Somewhat portable
- Disadvantages
  - VERY expensive
  - Size limit: 30 nm
  - Need PhD to operate

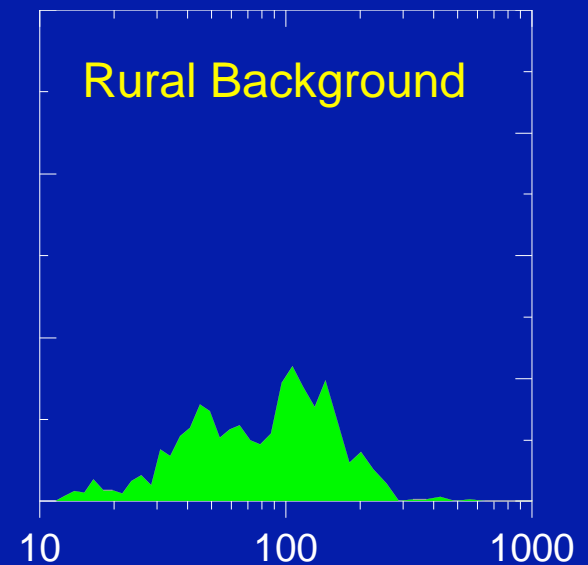
*Courtesy of M. Tolocka, LSU Dept. Chemistry*



# Combustion Aerosols Are also *Nanoparticles*



- NOT 'Engineered' nanoparticles
- We breathe them every day
- How to tell the difference?



# How do we distinguish *incidental* nanoparticles from *engineered* nanoparticles?

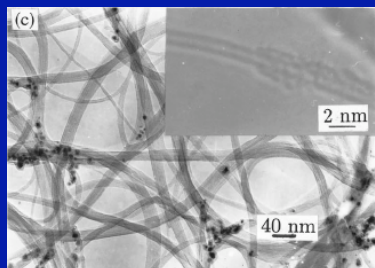
- Biogenic nanoparticles:
  - from natural sources:
    - fugitive dusts, sea spray, volcanic eruptions, forest fires
- Incidental nanoparticles
  - from normal industrial operations:
    - combustion → evaporation/condensation processes
- Engineered nanoparticles:
  - from nanotechnology operations
    - Carbon nanotubes, TiO<sub>2</sub> powder, fullerenes, etc.



# Engineered

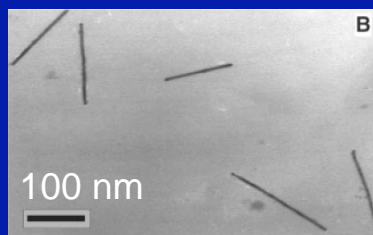
vs.

# Ambient



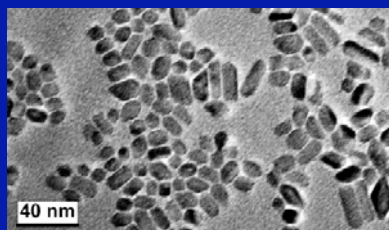
Carbon Nanotubes

Cheng, et al. *App. Phys. Lett.* (1998)



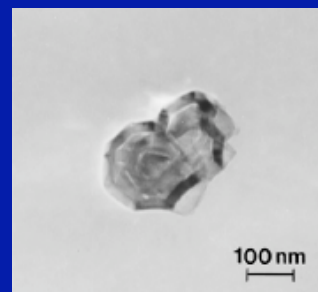
CdTe Nanowires

Tang, et al. *Science* (2002)

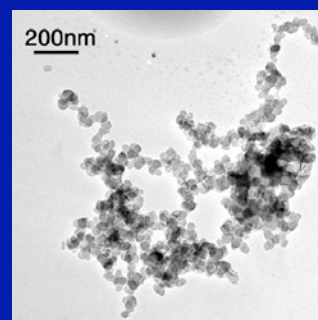


TiO<sub>2</sub> Crystals

T. Gao et al. *Mat. Letters* (2000)



Murr et al. *J. Nano. Res.*  
(2004)



Li, J. et al. *JGR* (2003)

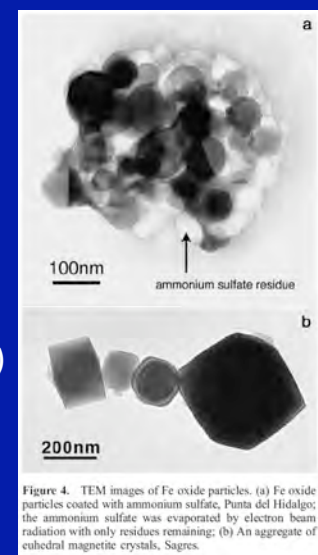
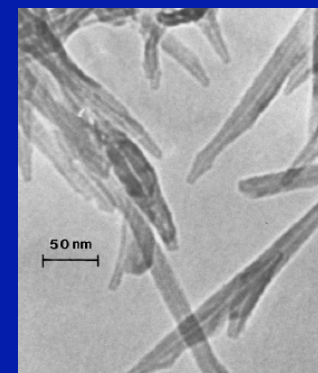
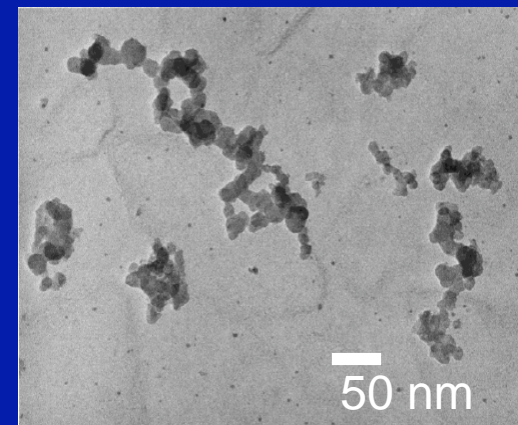


Figure 4. TEM images of Fe oxide particles. (a) Fe oxide particles coated with ammonium sulfate, Punta del Hidalgo; the ammonium sulfate was evaporated by electron beam radiation with only residues remaining; (b) An aggregate of cuboidal magnetite crystals, Sagres.



# The problem of specificity

- Counting all the airborne nanoparticles does not provide information on about *composition or source*
  - similar to the identification of asbestos fibers
- How do we determine the nanoparticle type/source?

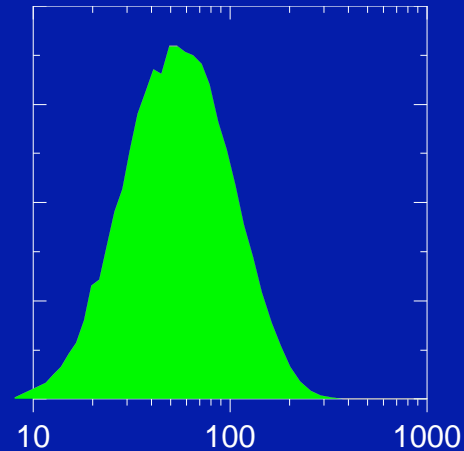
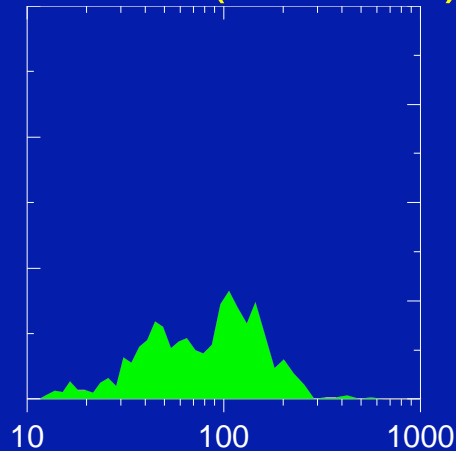


# How Real-Time Instruments Can Help

Ambient (outdoor)

vs.

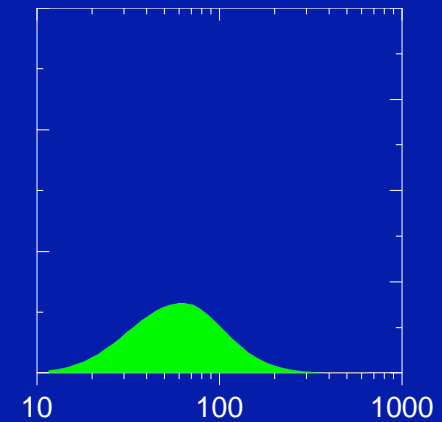
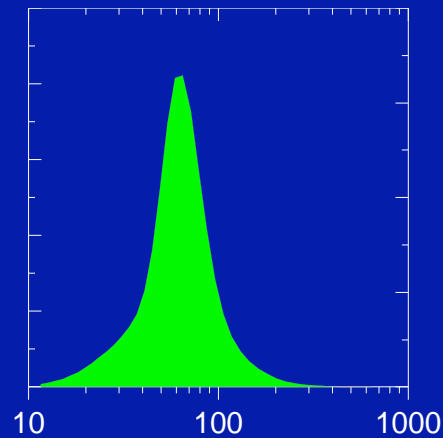
In-Plant



Weekday (Process On)

vs.

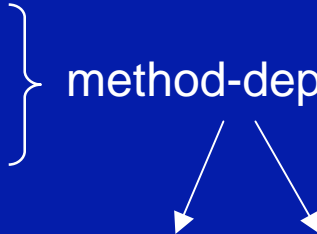
Weekend (Shutdown)



# Specificity:

## A How-to Guide for Nanoparticle Identification

### 1. **Capture** the particles on a flat, uniform surface

- Metal foil
  - Glass Slide
  - SEM or TEM grids
- } method-dependent
- 

### 2. **Image** the particles with SEM / TEM / AFM

- Sizing information
- Physical appearance

### 3. **Analyze** chemical characteristics of individual particles

- Spectroscopy (EDS, FE-AES, EELS)
- Particle identification

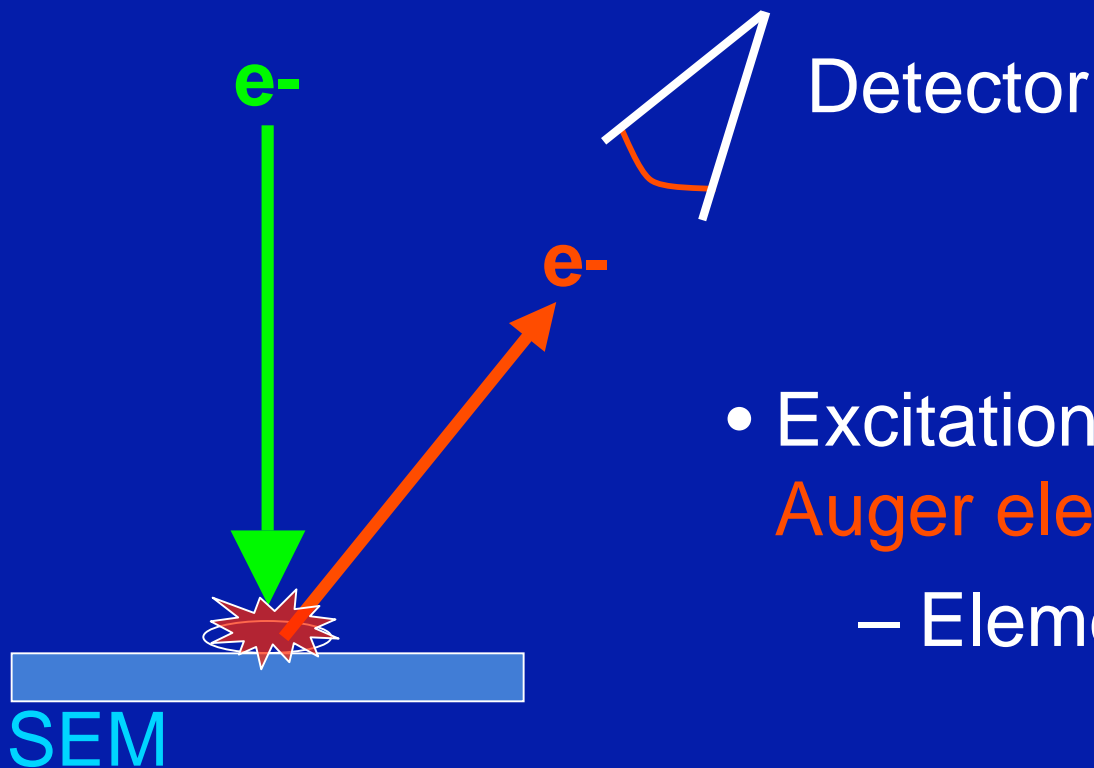


# Nano-Scale Spectroscopy Made Simple

1. Shoot energy (electrons) at the material
  2. Measure what comes off
    - Ejected x-rays (EDX)
    - Secondary Electrons (AES)
    - Scattered Electrons (EELS)
    - Ejected ions (SIMS)
- Consider:
    - Detection Limits (size, penetration depth, sensitivity)
    - Substrate (TEM vs. SEM)
    - Measurement (elemental composition, bonding state)



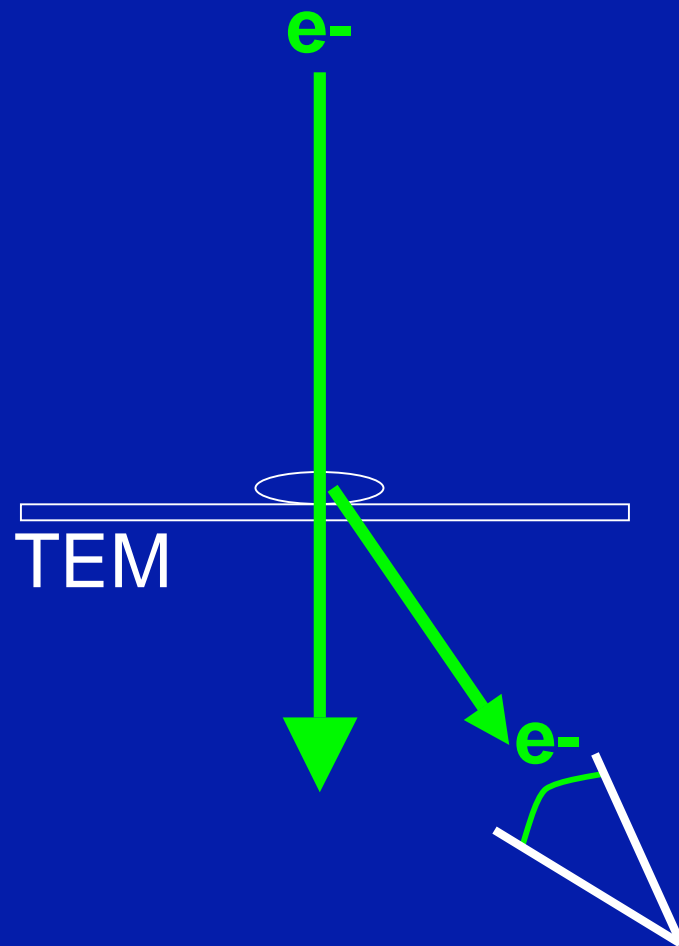
# Field-Emission Auger Electron Spectroscopy (FE-AES)



- Excitation causes emission of **Auger electrons**
  - Elemental identification
- Medium resolution: ~20 nm



# Electron Energy Loss Spectroscopy (EELS)



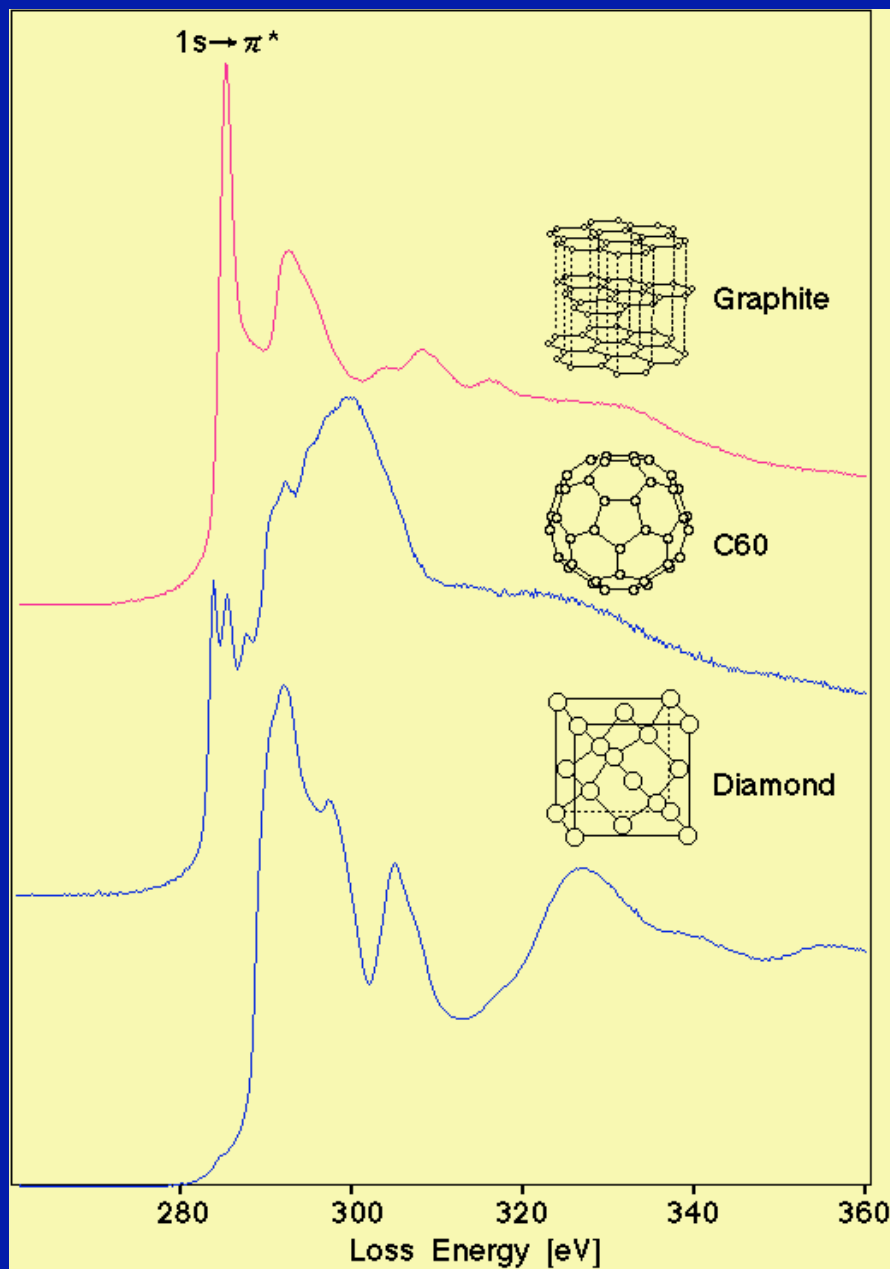
- Scattered electrons lose energy as they pass through material
  - Elemental identification
  - Bond Structure
- High resolution: 1 – 10 nm

Detector



# EELS Analysis

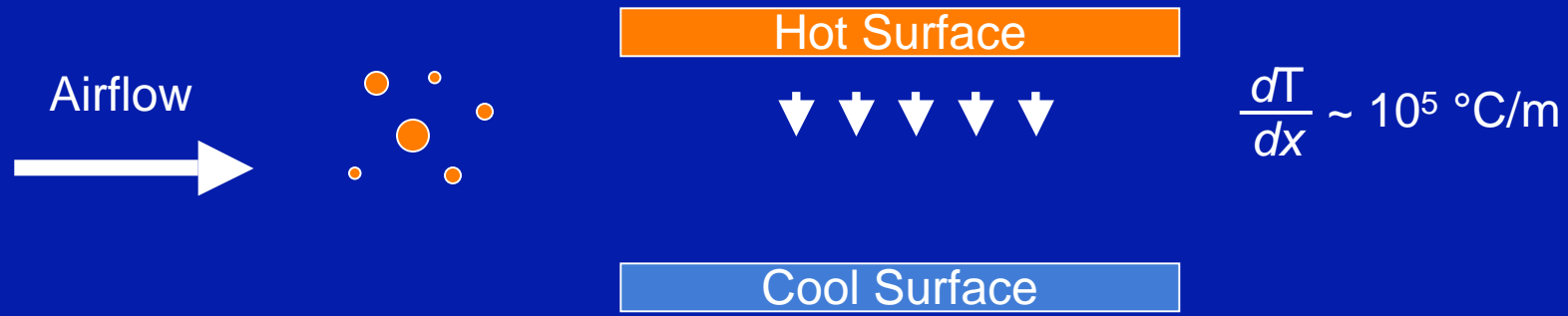
- Can identify different allotropes of carbon
- TEM with EELS:  
High-resolution  
elemental mapping



<http://eels.kuicr.kyoto-u.ac.jp/eels.en.html>



# Will Thermal Precipitators Come Back into Style?

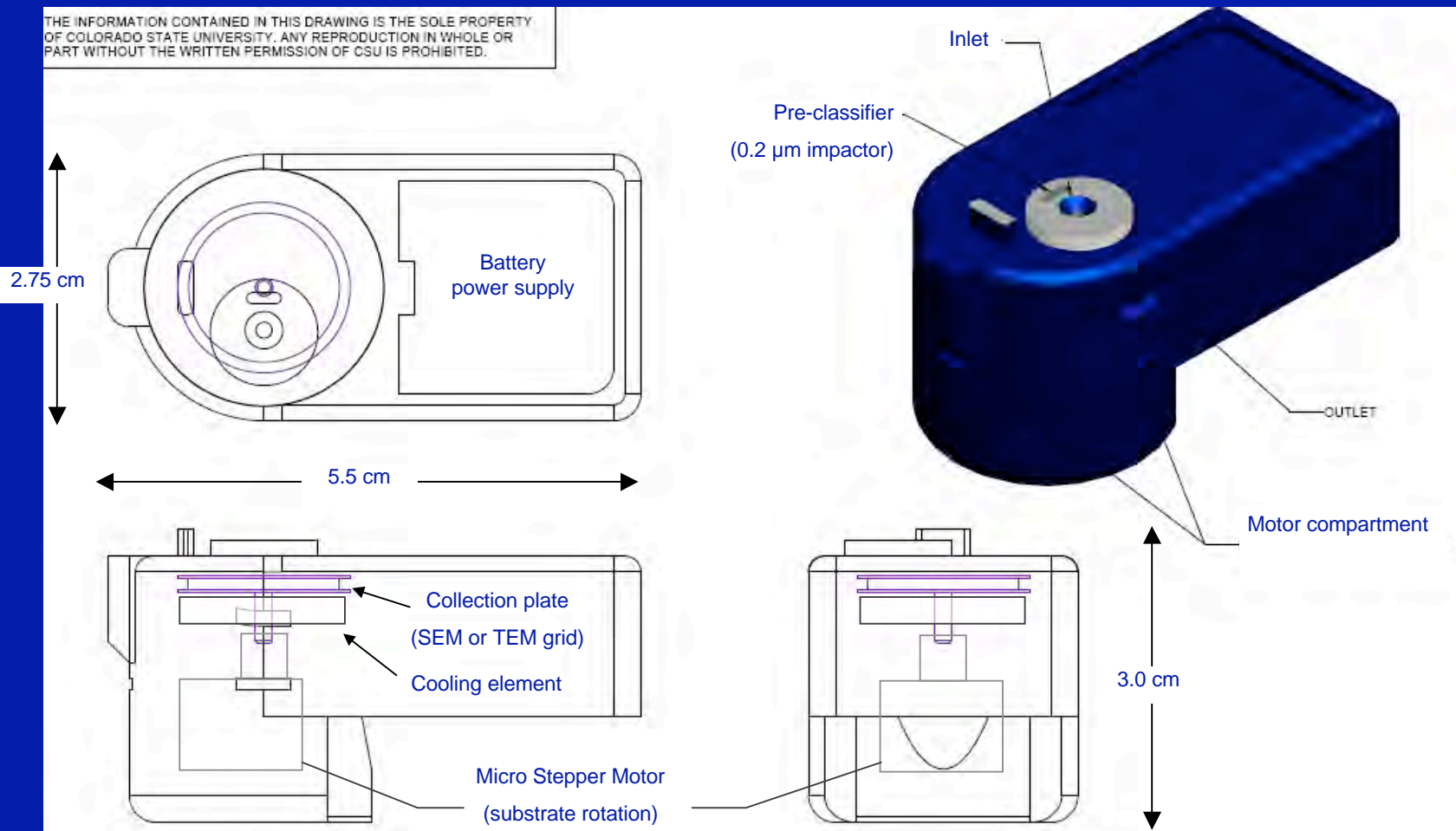


- Advantages
  - Non-destructive, 'gentle' collection technique
  - Can use TEM or SEM substrates as collection surface
    - Imaging
    - Secondary spectroscopic analyses
- Disadvantages
  - Not real-time
  - Few to no commercially available devices



# CSU Personal Thermal Precipitator

THE INFORMATION CONTAINED IN THIS DRAWING IS THE SOLE PROPERTY OF COLORADO STATE UNIVERSITY. ANY REPRODUCTION IN WHOLE OR PART WITHOUT THE WRITTEN PERMISSION OF CSU IS PROHIBITED.



# Questions that need answers

- Are airborne nanoparticles present?
  - Yes, almost always
- At what concentrations?
  - Usually higher than you think
    - Combustion → heating, transportation, welding, etc.
    - Outdoor penetration (urban background, rush hour effect)
- Where did they come from?
  - The \$1,000,000 question
  - Are they hazardous?



|  | Low Dustiness | Medium Dustiness | High Dustiness |
|--|---------------|------------------|----------------|
| <b>Hazard Group A</b>  |               |                  |                |
| Small  | 1             | 1                | 1              |
| Medium   | 1             | 1                | 2              |
| Large  | 1             | 2                | 2              |
| <b>Hazard Group B</b>  |               |                  |                |
| Small  | 1             | 1                | 1              |
| Medium   | 1             | 2                | 2              |
| Large  | 1             | 3                | 3              |
| <b>Hazard Group C</b>  |               |                  |                |
| Small  | 1             | 1                | 2              |
| Medium   | 2             | 3                | 3              |
| Large  | 2             | 4                | 4              |
| <b>Hazard Group D</b>  |               |                  |                |
| Small  | 2             | 2                | 3              |
| Medium   | 3             | 4                | 4              |
| Large  | 3             | 4                | 4              |
| <b>Hazard Group E</b>  |               |                  |                |
| For all hazard group E substances, choose control approach 4 |               |                  |                |

# Exposure Management Control Banding - Concept

## Parameters

Amount Used

Dustiness

Hazard Group (R-Phrase)

## Control Approach

- 1. General Ventilation
- 2. Engineering Control
- 3. Containment
- 4. Specialist Advice

# Questions?

