# The Detection and Characterization of Nanoparticles in the Environment

## An Overview on Nanotechnology Detection and Analysis Methods

**John Scalera, U.S. EPA**
**Office of Environmental Information,**
**OIAA/ EAD**
**July 12, 2006**



## Areas to be Presented

- What Are You Looking For?
- Analytical Hurdles
- Unique Properties, Analysis, and Source Identification
- Environmental Analysis Methods
- Development of Standards
- Additional Information Sources

DISCALIMER: The identification of manufacture supplied information or their products as a part of this presentation is for information purposes only and should not be perceived as an endorsement by the EPA.

## What Are You Looking For ?

- **Manufacturer's Characterization Information:**
  - Organic versus inorganic structure/ chemical composition/molecular weight
  - Solubility
  - Type (fullerenes, single-walled nanotubes (SWNTs), ...m dots, dendrimers, complexed organics, contain a metal eleme...
  - Particle Size Distribution
  - Particle Surface Area
  - Zeta Potential
  - Use (pharmaceutical, gasoline additives, material properties enhancement, water purification)
  - Specific industries/locations involved in production



## What Are You Looking For ? (cont.)

- **Environmental Transformation:**
  - Degradation (biotic and abiotic)
  - Oxidation to a more complex state
  - Morphological changes
  - Agglomeration/coagulation
  - Aggregation

## Environmental Analysis Hurdles

- Trace levels of the nanoparticles of interest
- Other nanoparticles of non-interest (natural, incidentally formed)
- Particle size changes (agglomeration, aggregation, condensation)
- Chemical Impurities/Interferences
- Vaporization of Organics During Sample Preparation and Analysis

Mr. John Scalera
5 of37

## Environmental Analysis Hurdles

- Static charges
- Extraction Efficiencies (sequestration)
- Aquatic stability due to colloidal formations in the environment
- Lack of quality control reference materials/surrogates
- Lack of standard analytical methods
- Laboratory contamination/ background levels

Mr. John Scalera
6 of37

## Unique Properties, Analysis and Source Identification

- **Unique Physical Characteristics**
  - Particle Size
  - Diffusion Properties
  - Morphology

**Unique Chemical Characteristics**
  - Radioactive Isotope Ratios
  - Marker chemicals
  - Elemental Ratio Characterization
- **Unique Spectroscopic Properties**
  - Gold particle reflection at nano level
  - Fluorescence freq.varies with particle size.
- **Unique Quantum Effects**
  - Magnetic properties

*Mr. John Scalera*
*7 of37*

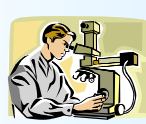
## Environmental Analysis Process

- Sample Collection

- Extraction

- Fractionation/Concentration/Cleanup

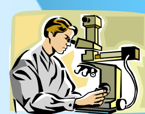
- Analysis



*Mr. John Scalera*
*8 of37*

## Environmental Analysis Method Types

- Real-time analysis
  - single-particle analytical techniques
  - ensemble analytical techniques
- Subsequent analysis
  - single-particle analytical techniques
  - ensemble analytical techniques



*Mr. John Scalera*
*9 of37*

## Aerosol: Bulk Sample Collection

- Mechanical Collectors
  - HEPA filters , ultra-low particle air filters (down to 5 nms)
- Aerodynamic Mobility Based Collectors
  - Cyclones (down to about 60 nms)
  - Impactors (down to about 60 nms)

*Mr. John Scalera*
*10 of37*

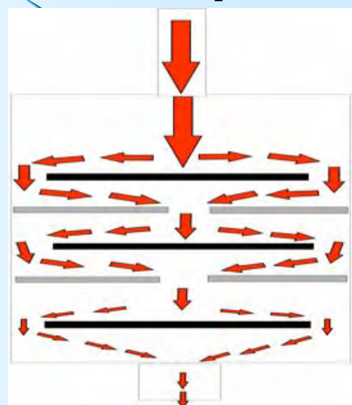
## Aerosols: Isolation of Nanoparticle Fractions- Aerodynamic Mobility

- **Inertia Impactors**
  - Particle size = "aerodynamic diameter"
  - Cascade impactor = multiple impactor plates in series
  - Nano- Micro-orifice uniform deposit impactor (MOUDI), 6 nm limit

- **Electrical Low Pressure Impacto (ELPI)**

  Real-time particle counts per size fraction
  - Incorporates multiple electrometers
  - Range 7 nms to 10 microns

Cascade Impactor



Mr. John Scalera
11 of37

## Aerosol: Bulk Sample Collection

- Electrostatic Collectors
  - Aerosol particles are charged in a chamber then electro-statically precipitated onto a collecting surface
  - Down to 5 nms

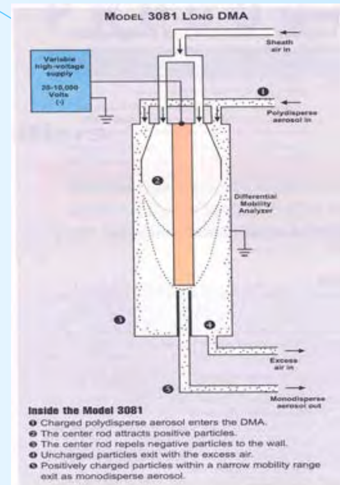
- Thermal Precipitators

Mr. John Scalera
12 of37

## Aerosols: Isolation of Nanoparticle Fractions-Electrical Mobility

- **Differential Mobility Analyzer (DMA)**
  - Particle size = "electrical mobility equivalent diameter"
  - 2 nm to 1micron
  - Alternate voltage to obtain various nanometer size fractions to outlet slit
- **Fast Mobility Particle Sizer (FMPS)**

  Real-time particle counts per size fraction
  - Incorporates multiple electrometers
  - Range 6 nm to 560 nm




TSI Model 3081 DMA

Mr. John Scalera
13 of37

## Aerosols: Particle Counting—CPC, CNC

- Condensation Particle Counters (CPC), or Condensation Nuclei Counters (CNC)
  - Detection of particles down to approximately 3 nm
  - Supersaturated vapor (water, isopropyl or butyl alcohol)
  - Particle grows 100 to 1000 times larger in size.
  - Optical detection

Mr. John Scalera
14 of37

## Aerosols: Nanoparticle Size Characterization—Diffusion Technology

- Diffusion Batteries
  - Particles demonstrating increasing diffusion character with smaller particle sizes.
    - Aerosol flows through a diffusion battery consisting of a series of fine capillaries or wi mesh screen grids. Smallest particles exit first where they are counted using CPC/CNC.
    - Sensitivity down to about 3 nanometers

Mr. J
15 of37

## Mass Analysis

- Mass of nanoparticle $10^{-18}$ gram
- Weighing of collection filters possible
  - concentration factor
  - significant collection time period
  - controlled env. (e.g, humidity control)
- Piezoelectric crystal balance
  - Quartz Crystal—alteration in resonance frequency as particles attach
  - Sensitivity limits is approximately 1 nanogram
- Beta Meter
  - Measures the change in detected beta radiation through a filter as particles deposit on the filter.
  - Particle mass is proportional to the degree of signal attenuation
  - sensitivity is approximately 25 ug per cm2

Mr. John Scalera
16 of37

## Mass Analysis(cont)

- Calculating an approximate mass of a particle fraction:
  - particle count for a size fraction
  - assume shape; get a particle volume
  - use a known or an approximate particle density

Mr. John Scalera
17 of37

## Aerosol Analysis: Single Particle Analyses, Size and Chemical Composition

- **Aerosol Time-of-Flight Mass Spectrometry (ATOFMS)**
  - **Real-time Analysis**
  - **Range = 30nm to 3 um.**

Mr. John Scalera
18 of37

## Non-Aerosol Bulk Samples

- Grab Samples: water/soils/sediments
  - **Agglomeration/Coagulation Issues**
    - **Sonication**
    - **Dispersing Agent**

*Mr. John Scalera*
*19 of37*

## Bulk Samples Analysis: Sample Preparation/Extraction

- Solid or Liquid Matrix: sieves—40 micron limit
- In a liquid matrix: filtration, centrifugation
- Liquid/Liquid Extraction: organic vs water soluble fractions; separatory flask
- Soxhlet Extraction: extraction of organic soluble fraction from sediments or soil.
- Solid Phase Extraction: extraction of analytes from liquid fraction
  - Ion Exchange Columns
- Supercritical Fluid Extraction (SFE)

*Mr. John Scalera*
*20 of37*

## Bulk Samples Analysis: Sample Preparation/Extraction/Fractionation

**Filtration/Ultrafiltration Techniques (samples in liquid medium)**

– Variable Cut-off size membranes
– Stirred filtration cells
– Continuous loops for maximized extraction and concentration /diafiltration techniques

**Centrifugation/Ultracentrifugation**

– Based upon particle density
– Centrifugal filters or membranes

*Mr. John Scalera*
*21 of37*

## Isolation of Nano Sample Fractions from Collected Samples (cont)

- **Field Flow Fractionation (FFF)**
  – Based upon particle diffusion; the diffusion coefficient is inversely proportional to particle size
  – Approximately 1nm to a few micrometers
    - **Asymmetric Flow Field Flow Fractionation (AF4)**
    - **Gravitational**
    - **Thermal**
    - **Magnetic**
    - **Electrical**

*Mr. John Scalera*
*22 of37*

## Isolation of Nano Sample Fractions from Collected Samples (cont.)

- **Asymmetric Flow Field Flow Fractionation ( AF4)**

*Channel height =100 to 500 um*

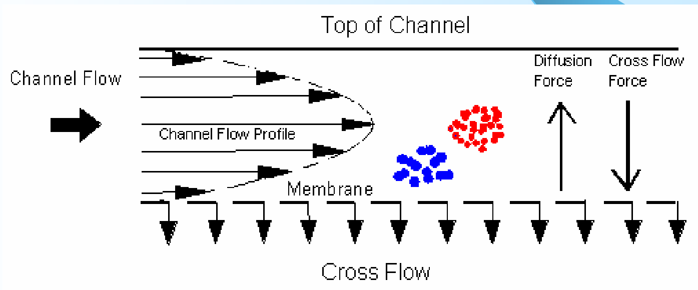



Diagram Courtesy of Postnova Analytics at www.postnova.com

*Mr. John Scalera*
*23 of37*

## Isolation of Nano Sample Fractions from Collected Samples (cont)

- **Field Flow Fractionation (FFF)**
  - **Greater the particle density, the lower the fractionation particle size limit**
  - **0.2000 mg mass in 20 to 100 uls injected**
  - **One hour analysis time at 1 to 2 mls of elutent per minute**

*Mr. John Scalera*
*24 of37*

## Sample Fractionation & Analysis: Chromatography

- Chromatographic Technologies
  - High Pressure Liquid Chromatogra phy (HPLC)
    - Size exclusion chromatography-separati sed on particle size, physical impedance
    - Ion Chromatography-separation based upon i properties of the particle
  - Supercritical Fluid Chromatography
    - Separation based on solvency in supercritical fluid

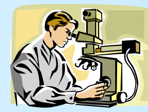
Mr. J

## Analytical Techniques: Particle Size Distribution

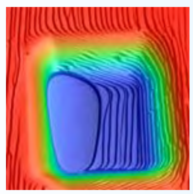
- Dynamic Light Scattering (DLS) or Photon Correlation Spectroscopy (PCS)
  - **Particle size analysis in liquids**
  - **Range less than 5 nm to over 1 micron**
  - **Can be used on-line in tandem with fractionation methods (e.g., HPLC-DLS)**

Mr. John Scalera
26 of37

# Collected Fraction Off-Line Single Particle Analysis: Electron Microscopy



- Analysis on a particle by particle basis
  - Scanning Electron Microscopy (SEM)
  - Transmission Electron Microscopy(TEM)
    - Energy dispersive X-ray analysis (EDX)
    - Electron energy loss spectroscopy (EELS)
- Particle size, morphology, chemical composition



Silicon wafer structure
Image courtesy of the National Institute of Standards and Technology

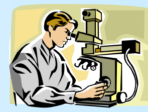
Mr. John Scalera
27 of37

# Off-Line Single Particle Analysis: Electron Microscopy (cont.)

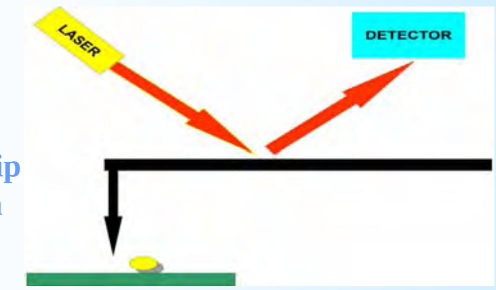
- Collection and preparation challenges:
  - Loss due to volatilization
  - Electrostatic forces
  - Resuspension and uniform deposit of onto analysis substrate.
- Cost
- Time
- Highly Skilled Analyst
- Statistical Accuracy requires large analyzed population of particles

Mr. John Scalera
28 of37

## Off-Line Single Particle Analysis: Atomic Force Microscopy (AFM)

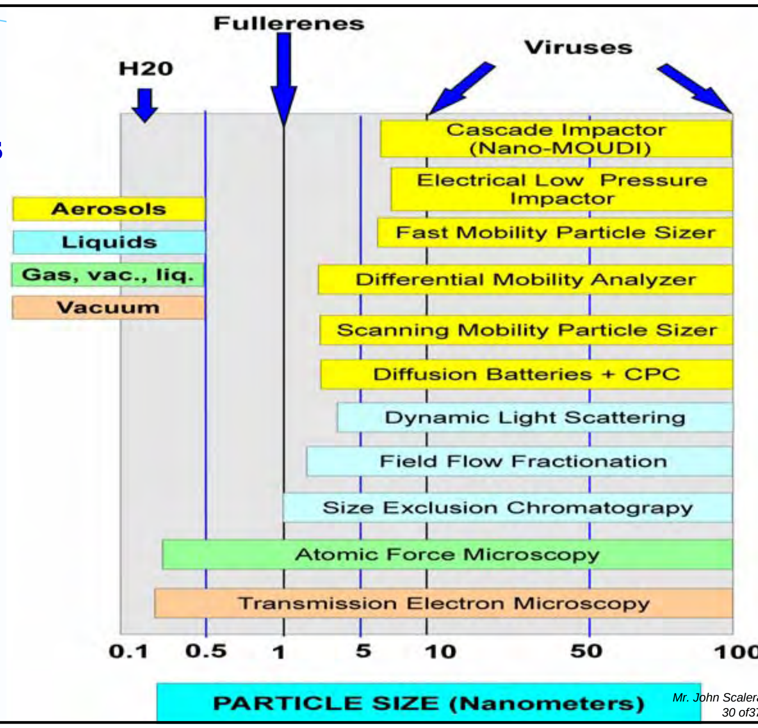


- Applied in air or liquid mediums
- Uses the interaction of van der Waals forces between the microscopic tip of the AFM and the particle.
- Provides information down to the molecular level
  - **particle size, morphology**




Mr. John Scalera
29 of37

## Particle Sizing Methods




Mr. John Scalera
30 of37

## Surface Area Analysis

- Surface Area
- Epiphaniometer
  - Particles exposed to radiation ($^{211}$Pb),then passed through capillaries and collected onto filters for radiation level analysis (radiation level measure is proportional to particle surface area).
- BET-Method (Brunauer, Emmet, and Teller) *[Burtscher]*
  - Measures the amount of gas absorbed onto surface areas.
- TSI Model 3050 “Nanoparticle Surface Area Monitor”

www.TSI.com

*Mr. John Scalera*
*31 of37*

## Analytical Techniques: Chemical Composition

- X-ray Fluorescence (XRF)
- Mass Spectrometry (MS)
- Proton-Induced X-ray Emission (PIXE)
- Inductively Couple Plasma-Atomic Emission Spectroscopy (ICP-AES)
- ICP-Mass Spectroscopy (ICP-MS)

*Mr. John Scalera*
*32 of37*

## Standards Development: ASTM

- Committee E56 on Nanotechnology
  - E56.02 Characterization: Physica Chemical, and Toxicological Properties
    - WK8705: Measurement of Particle Size Distri Nanomaterials using Photon Correlation Spectros
    - WK9952: Standard Practice for Measuring Length ar Thickness of Carbon Nanotubes Using AFM Methods
    - WK10417: Standard Practice for the Preparation of Nanomaterials Samples for Characterization

*Mr.*
*33 of37*

## Standards Development: International Organization for Standardization (ISO)

- ISO TC 229 Nanotechnologies
  - Nov. 2005 inaugural meeting
    - WG 1 Terminology and Nomenclature (Canada)
    - WG 2 Measurement and Characterization (Japan)
    - WG 3 Health, Safety and Environment (U.S.)

*Mr. John Scalera*
*34 of37*

## Standards Development: American National Standards Institute (ANSI) & U.S. TAG to ISO TC 229

- ANSI Nanotechnology Standards Panel
  - ANSI-NSP formed in August 2004
  - U.S. Tech. Advisory Group (TAG) to ISO TC 229
    - ANSI accredited
    - July 2005 inaugural meeting
    - Workgroups: Terminology and Nomenclature, Measurement and Characterization, Health, Safety and Environment (U.S.)

*Mr. John Scalera*
*35 of37*

## Standards Development: Institute of Electrical and Electronics Eng. (IEEE)

- **Standard Methods for the Characterization of Carbon Nanotubes Used as Additives in Bulk Materials (P1690TM) (In Progress)**
  - **This project will develop standard methods for the characterization of carbon nanotubes used as additives in bulk materials.**

*Mr. John Scalera*
*36 of37*

## Additional Information Sources: Analysis Overviews

- "Overview of Methods for Analysis Single Ultrafine Particles," Andrew Maynard. Phil Trans. R. Soc. Lond. A(2000)358, pp 2593-2610.
- "Nanoparticles and the Environment," Pratim Biswas, Chang-Yu Wu. J. of Air & Waste Management Assoc., Vol. 55, June 2005.
- "A Review of Atmospheric Aerosol Measurements," Peter McMurry. Atmospheric Environment, Vol 34, Issues 12-14, 2000, pp 1959-1999.
- "Emerging Issues in Aerosol Nanoparticle Science and Technology" NSF Workshop Report. Workshop held at U.of CA, Los Angeles, June 27-28, 2003.
- "Chapter One: Exposure Measurements." Chow J., Johann P., et. al. Chemosphere, Vol. 49, Issue 9, Dec. 2002, pp 873-901
- "Research Strategies for Safety Evaluation of Nanomaterials. Part VI. Characterization of Nanoscale Particles for Toxicological Evaluation," Kevin Powers, Scott Brown, et al. Tox. Sciences 90(2), 296-3003 (2006)

*Mr. John Scalera*
*37 of37*