

The Detection and Characterization of Nanoparticles in the Environment

An Overview on Nanotechnology Detection and Analysis Methods

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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.

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What Are You Looking For ?

- **Manufacturer's Characterization Information:**

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

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What Are You Looking For ? (cont.)

- **Environmental Transformation:**

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

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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

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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





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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

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Environmental Analysis Process

- Sample Collection 
- Extraction 
- Fractionation/Concentration/Cleanup 
- Analysis 

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Environmental Analysis Method Types

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



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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)



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Aerosols: Isolation of Nanoparticle Fractions- Aerodynamic Mobility

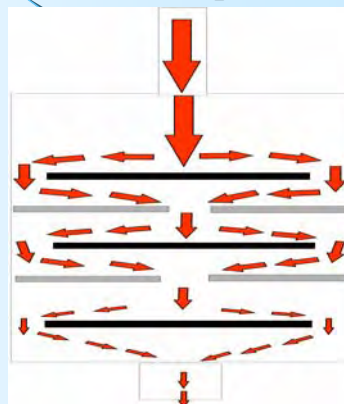
- **Inertia Impactors**

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

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

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

Cascade Impactor



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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**

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Aerosols: Isolation of Nanoparticle Fractions-Electrical Mobility

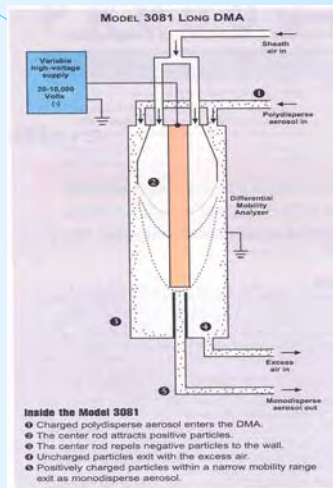
- **Differential Mobility Analyzer (DMA)**

- 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

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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

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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 wire-mesh screen grids. Smallest particles exit first where they are counted using CPC/CNC.
 - Sensitivity down to about 3 nanometers

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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

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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

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Aerosol Analysis: Single Particle Analyses, Size and Chemical Composition

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

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Non-Aerosol Bulk Samples

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



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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)



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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

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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



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

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

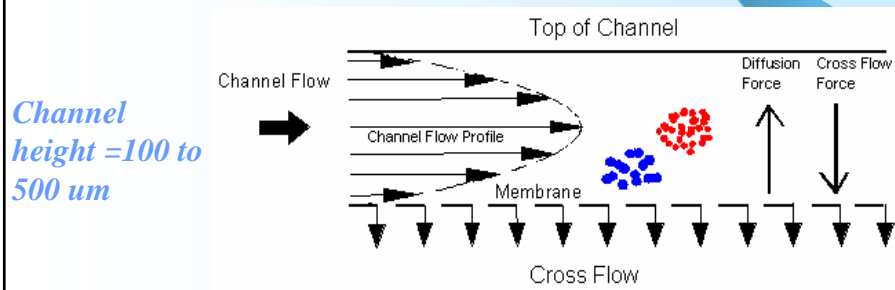


Diagram Courtesy of Postnova Analytics at www.postnova.com

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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 eluent per minute**

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Sample Fractionation & Analysis: Chromatography



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

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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)**

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Collected Fraction Off-Line Single Particle Analysis: Electron Microscopy

- Analysis on a particle by particle basis

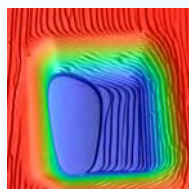
Scanning Electron Microscopy (SEM)

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

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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

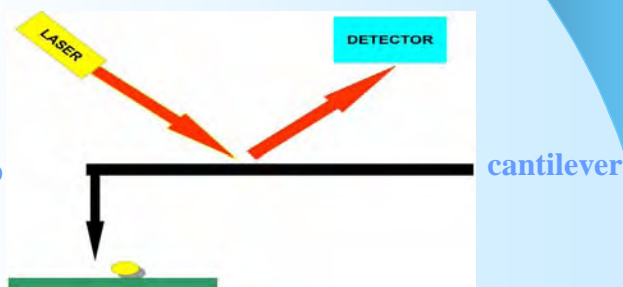
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Off-Line Single Particle Analysis: Atomic Force Microscopy (AFM)



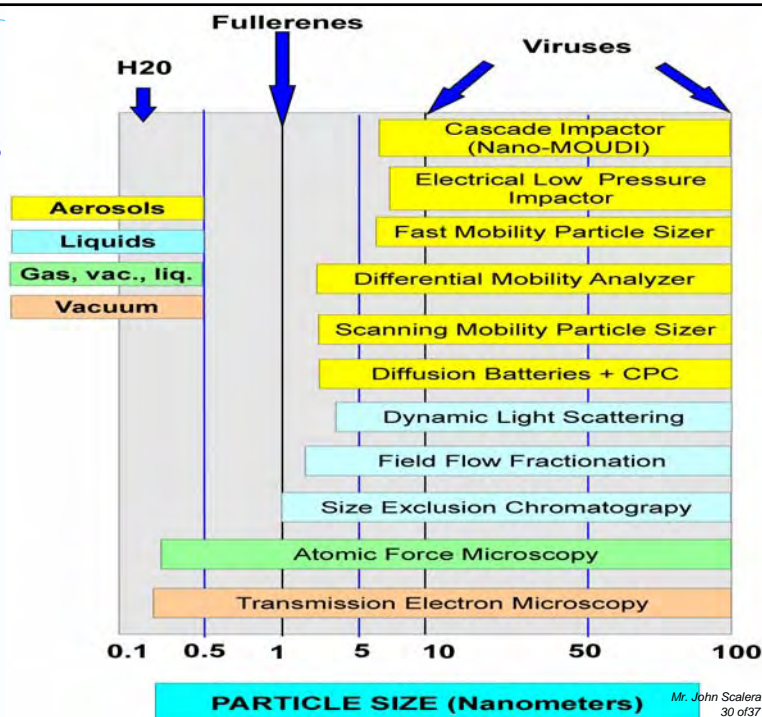
- Applied in air or liquid mediums
- Uses the interaction of van der Waals forces between the microscopic tip of the AFM and the particle.
- Provides information down to the molecular level
 - **particle size, morphology**

3 micron tall
pyramidal tip
with a 30 nm
end radius



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Particle Sizing Methods



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

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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)

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Standards Development: ASTM

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

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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.)

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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.)

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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.**

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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)

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