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

DISCLAIMER: 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), 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

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

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
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

Environmental Analysis Process

- Sample Collection
- Extraction
- Fractionation/Concentration/Cleanup
- Analysis
Environmental Analysis Method Types

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

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

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)
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

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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**
Aerosols: Isolation of Nanoparticle Fractions-Electrical Mobility

- **Differential Mobility Analyzer (DMA)**
  - Particle size = “electrical mobility equivalent diameter”
  - 2 nm to 1 micron
  - 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

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
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.

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 µg per cm²
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

Aerosol Analysis: Single Particle Analyses, Size and Chemical Composition

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

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

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

- Asymmetric Flow Field Flow Fractionation (AF4)

Channel height = 100 to 500 µm

Diagram Courtesy of Postnova Analytics at www.postnova.com

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
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

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)
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

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
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

Particle Sizing Methods

- Aerosols
- Liquids
- Gas, vac., liq.
- Vacuum
- Cascade Impactor (Nano-MOUDI)
- Electrical Low Pressure Impactor
- Fast Mobility Particle Sizer
- Differential Mobility Analyzer
- Scanning Mobility Particle Sizer
- Diffusion Batteries + CPC
- Dynamic Light Scattering
- Field Flow Fractionation
- Size Exclusion Chromatography
- Atomic Force Microscopy
- Transmission Electron Microscopy

PARTICLE SIZE (Nanometers)
Surface Area Analysis

- Surface Area
- Epiphanometer
  - 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-M 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

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)
Standards Development: ASTM

- Committee E56 on Nanotechnology
  - E56.02 Characterization: Physical, Chemical, and Toxicological Properties
    - WK 8705: Measurement of Particle Size Distribution of Nanomaterials using Photon Correlation Spectroscopy
    - WK 9952: Standard Practice for Measuring Length and Thickness of Carbon Nanotubes Using AFM Methods
    - WK 10417: Standard Practice for the Preparation of Nanomaterials Samples for Characterization

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.)
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.)

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.
Additional Information Sources: Analysis Overviews


