EPA Nanoparticle Air Monitoring Workshop
2-3 March 2009
Session #2
Technology Needs and Gaps

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Costs identified for items may differ from actual and are only provided as a gross gauge for estimation purposes

Question # 1

- How applicable are the existing size measurement instruments? Are these sufficient?
- Answer:
  - **No one technique will likely suffice**
  - **Direct-reading instruments for nano**
    - Sometimes difficult to distinguish from background
    - “Affordable” and practical to unaffordable and impractical
    - Lack of personal sampling technologies

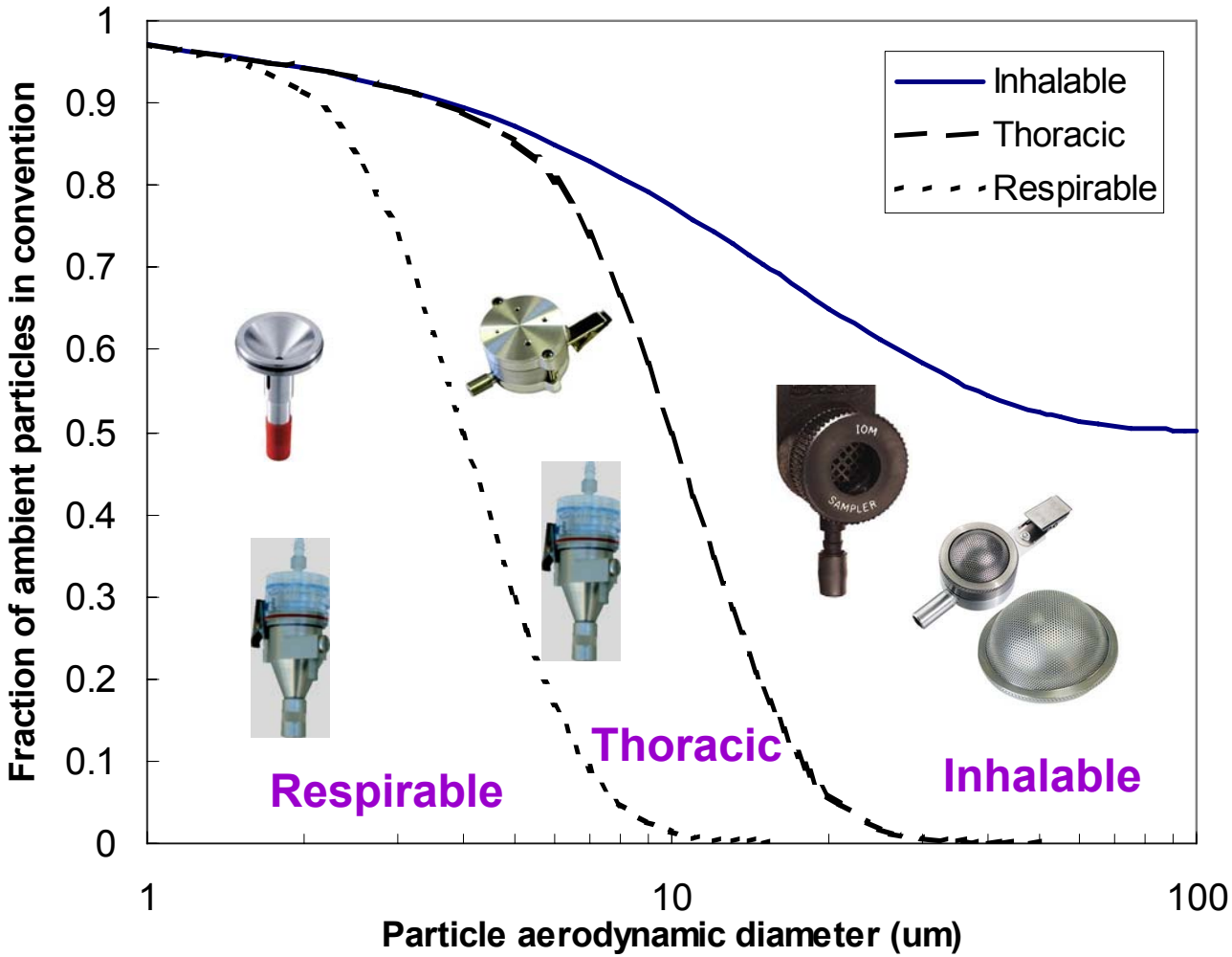
Answer # 1 Con't

- Off-line techniques (chemistry, morphology, physical dia.)
  - **No ACGIH/ISO/CEN air sampling conventions or pre-selectors for nano regime**
  - **Lack of semi-validated or validated sampling and analytical methods (e.g., CNTs, fullerenes)**
  - **Microscopy (e.g., TEM, etc.)**
    - Can be expensive
    - Lack of standard methods for counting
    - Measure diameter by dimension rather than by behavior

Answer #1 Con't

- **Limited personal sampling technologies**
- **What do the results mean?**
- **Lack of exposure limits** –
  - existing exposure limits (e.g., TLVs, PELs, WEELs, etc.) and associated pre-selectors may or may not be relevant

Penetration (Inhalable/Thoracic/Respirable)



Inhalable Fraction

"Total" Fraction

Thoracic Fraction

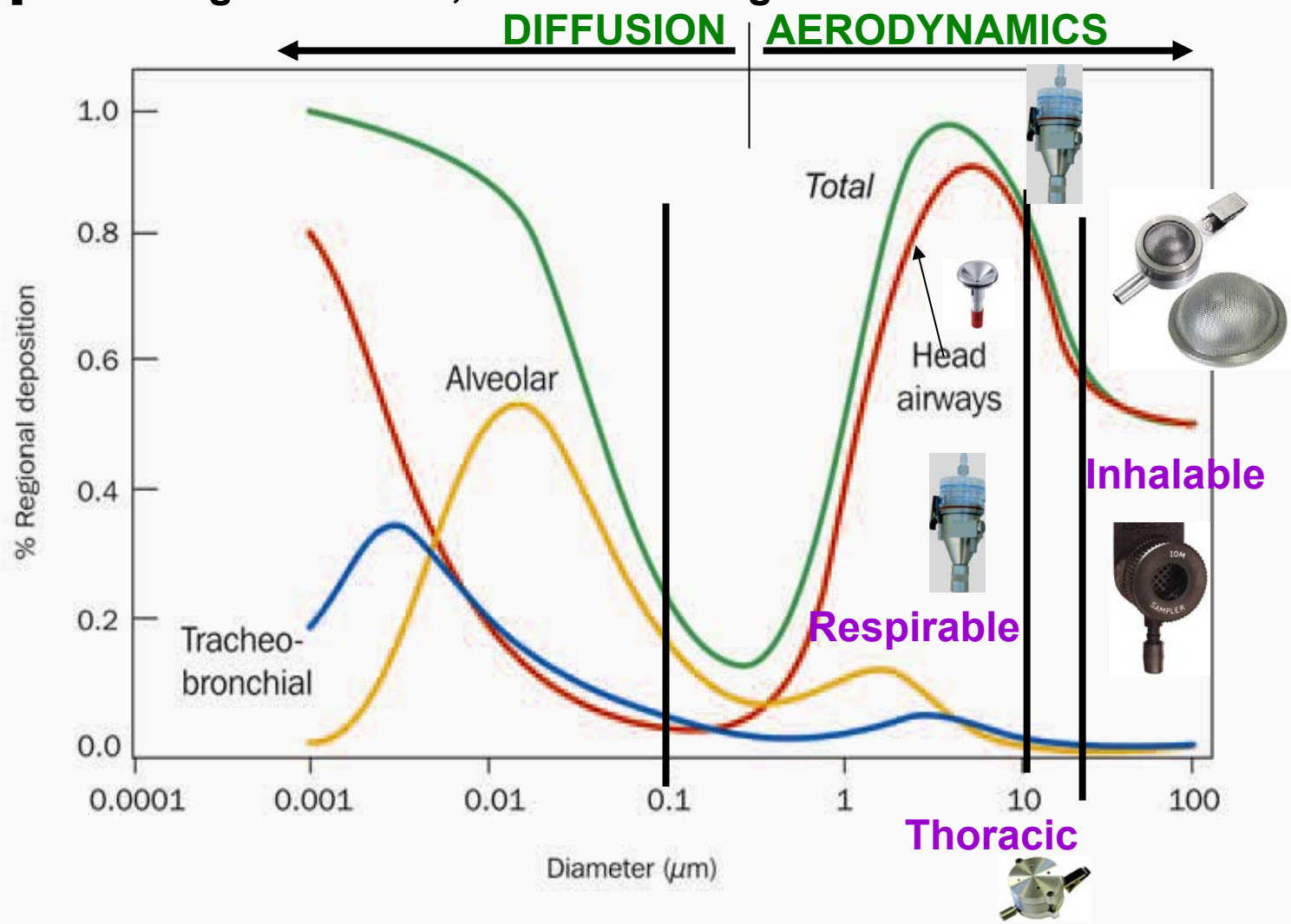
PM10

Respirable

PM2.5

Penetration (Inhalable/Thoracic/Respirable) and Deposition

Predicted deposition of inhaled particles in the human respiratory tract (ICRP [1994] model: light exercise, nose breathing



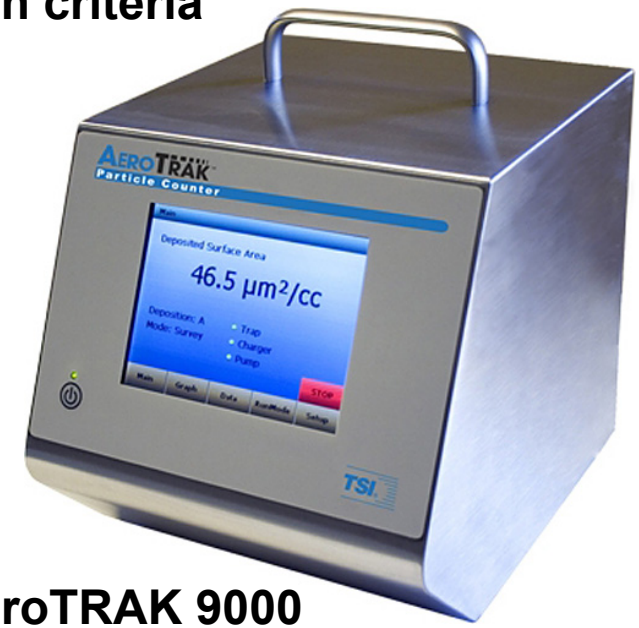
Surface Area Concentration Monitors, Diffusion Charger, Direct-Reading, Non-Specific

User selectable response modes indicate lung deposited surface area of nanoparticles deposited in the tracheobronchial (TB) and alveolar (A) regions of the lung, corresponding to the ICRP lung deposition criteria

TSI Model 3550 **Cost; $16,000**

Concentration range:
TB:1 to 2,500 μm²/cc
A: 1 to 10,000 μm²/cc

Size range: 10 to 1000 nm (with 1μm cyclone on inlet)



TSI AeroTRAK 9000
Battery-Operated

Cost: $10,000

Generally insensitive to particle porosity

Measures active DEPOSITED surface area in the TB or A regions of the lung

Measures Deposited External Surface Area

Naneum Personal Size Unit based On Remote Monitor (Particle Detector/Monitor)

- Expected to be launched/available in **late 2009**
- FIRST **direct-reading particle number concentration** sampler that can be used as a **PERSONAL sampler**
- Particle Size Range: **5/10 nm up to 300nm**

Naneum Remote Monitor Particle Detector/Monitor

- **Expected to be available end 2009**
- **Specification:**
  - Battery or mains operated
  - Continuous un-tended operation (24/7,1year)
  - Single digit read-outs
  - Wireless network, or alarm
  - **10 nm – 500nm**
  - **Total number concentration**
- **Est. Cost based on volume:**
  - 1 ea. ($8,000)
  - 10 or more ($6,000 ea.)
  - Larger orders ($5,000 to $6,000 ea.)

Portable Particle Detector/monitor

Naneum Selector and Counter (SAC) Model 3

$35,500

www.naneum.com

Specification:

- **9V (x7) battery operated**
- hand-held, 2.7 kg
- on-line measurement
- Response time: from 3 minutes, depending on conc., resolution
- **Size range covered 3 - 500 nm**
- USP output to PC (requires Naneum SAC Software)

Properties measured:

Particle concentration (10 to 10^7 p/cc)
Particle size distribution

Applications

- Particle distribution mapping
- Identify “hot spots”
- Background from engineered particles
- Continuous monitoring
- Identify “events”
- Exposure/dose

Intellectual property

- EU Application
- Patents in preparation but not yet filed

Number Concentration, Mass Concentration, Surface Concentration, Non-Specific

Real-time size-selective mobility diameter detection of number concentration

2.5 to 1000 nm and display data using up to 167 actual size channels (up to 64 channels per decade

Data may be interpreted in terms of aerosol mass concentration only if particle shape and density are known or assumed

Data may be interpreted in terms of aerosol surface area in some circumstances, e.g., mobility diameter of open agglomerates correlates well with projected surface area

$50,000 to $80,000

Scanning Mobility Particle Sizer

Particle Number Concentration, Direct-Reading Hand-Held Condensation Particle Counters (CPC), Non-Specific, < 1 µm diameter

Cost: $6,000

TSI P-Trak

20 nm to 1 µm

0 to 500,000 particles/cc

Cost: $8,000

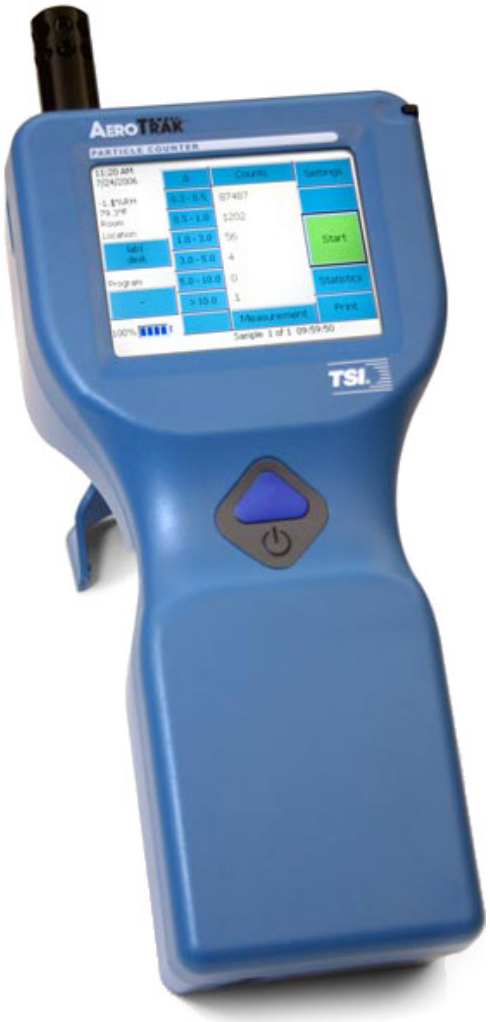
TSI Model 3007

10 nm to 1 µm

0 to 100,000 particles/cc

Without a nanoparticle pre-separator, they are not specific to the nanometer size range.
(no suitable pre-separators are currently available)

Particle Number Concentration,
TSI AeroTrak Optical Particle Counter (OPC)
> 0.3 to > 10 µm diameter



Counts in 1 to 6 user-adjustable bin sizes from 0.3 to > 10 microns

GRIMM dust Monitor Model 1.108

Particle Size: **0.30**/0.40/0.50/0.65/0.80/1.0/1.6/2.0/3.0/4.0/5.0/7.5/10/15/**20** **µm**

Count Range: 1 to 2,000,000 **counts/liter**

Mass Range: 0.1 to 100,000 **µg/m3**

Size channels: 15 channel sizes, mass in µg/m^3 and particle counts/liter

Sensitivity: 1 particle/liter

The 47-mm PTFE Filter Size can be analyzed for chemical composition and gravimetric mass correlation

NIOSH 2008 PDC

- **If p/cc > 25% during task than background**
- **Collect side-by-side 37 mm open-face filter cassette samples (nominally 7 lpm, 15-30 min.)**
  - Background – 1 for TEM, 1 for Mass (metals)
  - Task – 1 for TEM, 1 for Mass (metals)
- **Future research – Personal/BZ air samples**

Peters, T.M. et. al. (2009), JOEH, 6:2,73-73

- **Differentiate between background incidental nanoparticles and lithium titanate metal oxide nanomaterial**
- **Respirable cyclone with MCE filter**

- **SEM and TEM-EDS Analysis**
  - Lithium titanate particles: spherical aggregates > 200 nm (clusters of fused 10-80 nanoparticles)
  - Nanoparticles due to incidental sources (e.g., welding, grinding, propane-powered forklift)

Peters, T.M. et. al. (2009), JOEH, 6:2,73-73

- **Lithium titanate respirable mass concentration**
- **Respirable cyclone with filter**
  - Gravimetric (NIOSH 0600, PVC filter)
  - ICP-AES for Ti and Li

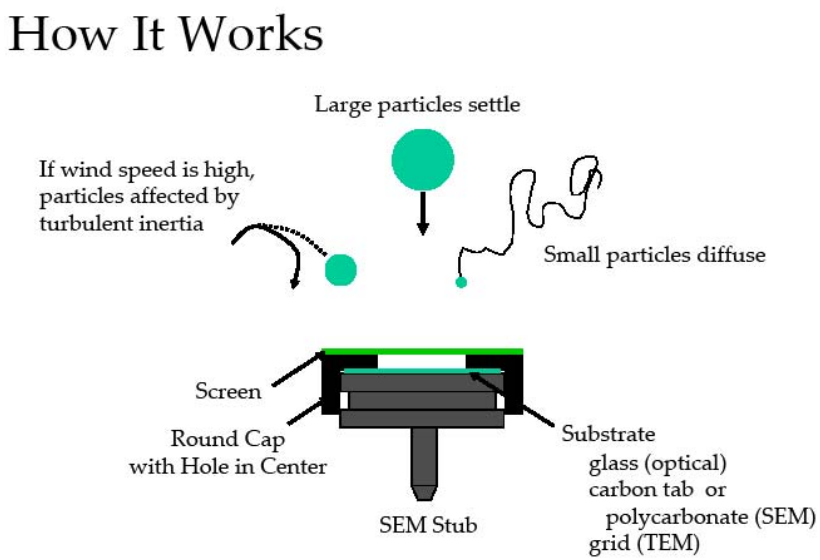
DOE Nanoscale Science Research Centers (June 2007)

- **25 mm electrically conductive cassette, open-face, 0.1 µm nucleopore filter**
- Air Sampling train: ASTM D 6059 (Ceramic Whiskers by SEM)

- **Sampling volume based on getting proper filter loading or particle density on filter:**
  - NIOSH Method 7402 (Asbestos by TEM)
  - Direct-reading CPC particle concentration
- **Air sampling cassettes sent for SEM and TEM analysis based on ASTM D 6058 and 6059**
  - Airborne concentration, morphology, chemical composition

DOE Nanoscale Science Research Centers (June 2007)

- Wagner-Leith Passive Aerosol Sampler used in addition to active filter sampling
- Sampler analyzed for particle concentration and size distribution



Where TLVs and PELs exist for an insoluble/poorly-soluble nanomaterial

- **Sample per the TLV/PEL criteria (e.g., "total," inhalable, thoracic, respirable)**
- **Sample for submicron fractions (e.g., less than 10/30/50/100/200/300 nm????)**
- **Take samples for particle number, surface area (maybe), and mass for smaller particle sizes**
- **Consider that the mass-based TLVs/PELs may possibly not be adequate**

Off-Line, Respirable Fiber Fraction Collected with BGI GK 2.69 Cyclone @ 1.6 lpm

Mean Diameter of Aerosol Particles < 1 µm

$nm = 10^6 \times [(EAD) \div (CPC)]$

$10^6 \times$

÷

0.01 to 2500 mm/cc

10 nm to 1,000 nm

TSI Model 3007
10 nm to 1 µm
0 to 100,000 particles/cc

e.g., 100 nm = 10^6 x (10 mm/cc)/(100,000 p/cc)

Size Distribution
Mass, Chemistry, Personal Sampling

50% cut-points (µm):

0.18, 0.32, 0.56
1.0, 1.8, 3.2
5.6, and 10

Aerodynamic diameter

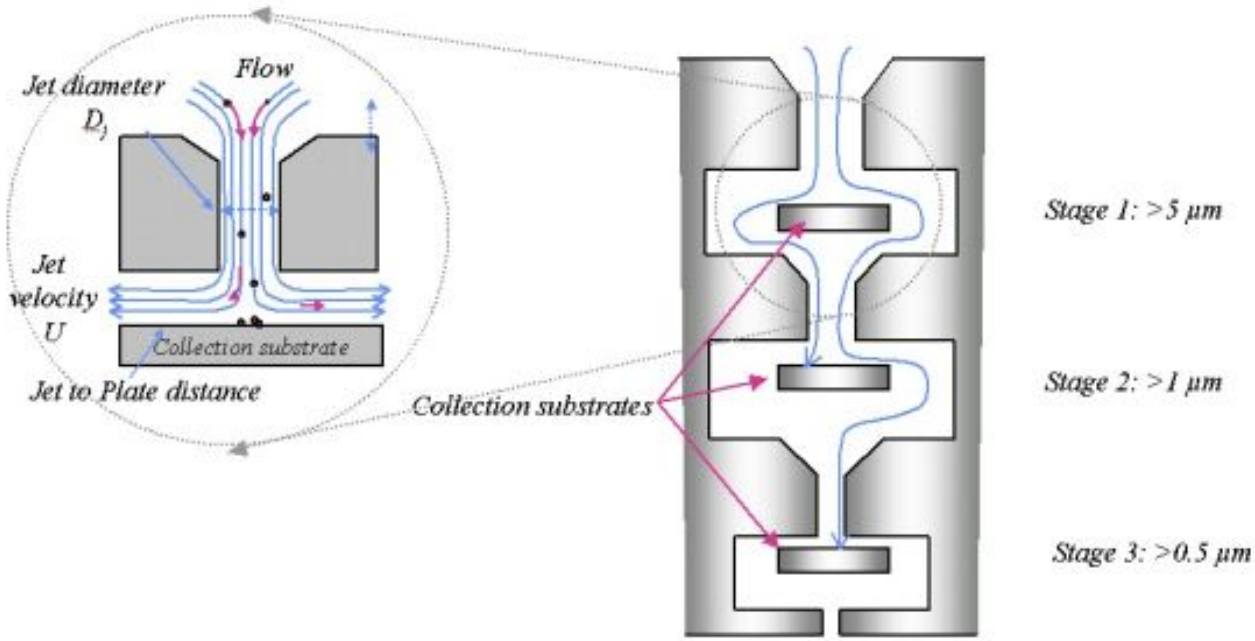
Analysis: gravimetrically, chemically, and microscopically

MSP M135-8 MiniMOUDI™ Impactor (M135-6 shown)

Size Distribution, Mass Concentration, Chemistry,

Dekati Low Pressure Impactor

$20,000



Aerodynamic diameter from 30 nm up to 10 µm. With the filter stage accessory, particles below 30 nm can be collected on a 47 mm filter.

Mass Concentration (mg/m³), Filter for Collecting Particles, Personal Sampling

< 1 µm: 1.7 lpm

< 400 nm: about 3 lpm

Theoretical:

< 200 nm: about 6 lpm

< 100 nm: about 10 lpm

SKC: Diesel Particulate Matter (DPM) Cassette

At 1.7 to 2.0 LPM, particles less than 1.0 µm aerodynamic diameter are collected on heat-treated low carbon quartz filters. Samples are analyzed for organic and elemental carbon content using a highly sensitive Evolved Gas Analysis (EGA) technique with thermal-optical analyzer as specified in NIOSH Method 5040.

Meets specs for NIOSH 5040 for analysis of elemental carbon (EC) to determine total carbon (organic and elemental) in a sample. Total carbon represents more than 80% of diesel particulate emissions.

Wagner-Leith
Passive Aerosol Sampler

Naneum Personal Sampler

- Would be based on same principles as WRAS, except:
  - **2/3 nm to 10 microns**
  - **Up to 10 size bins**
- Not available yet and currently no plans by Naneum to make:
  - Can be made by Naneum in 2009 IF there is a “clear, large attractive opportunity” given a market demand

Naneum Personal Sampler

- Cost based on volume:
  - **1 ea. ($4,000)**
  - **10 or more (about $2,000 ea.)**
  - **large orders (between about $500 and $1,000)**

Naneum Wide range Aerosol sampler (WRAS)

- **Specification:**
  - Mains operated portable sampler weighing approx 10kg
  - Continuous collection of size resolved samples on custom substrate
  - **Up to 15 size "bins" from 2/3nm-20µm**
  - Flow rates from 5lpm-1000lpm
  - Samples suitable for off-line analysis using SEM/TEM, MS, Atomic Adsorption,HPLC etc.
- **Properties measured:**
  - **Size resolved chemical composition**
  - **Size resolved morphology**
- **Technical Principles**
  - **Inertial deposition (300 nm to 20 µm) and Diffusion (2 -300 nm)**
  - Integrated to give seamless size resolution across aerosol rang
- **Intellectual property**
  - 2 granted UK patents
  - USA application
  - Patents in preparation but not yet filed

$31,000

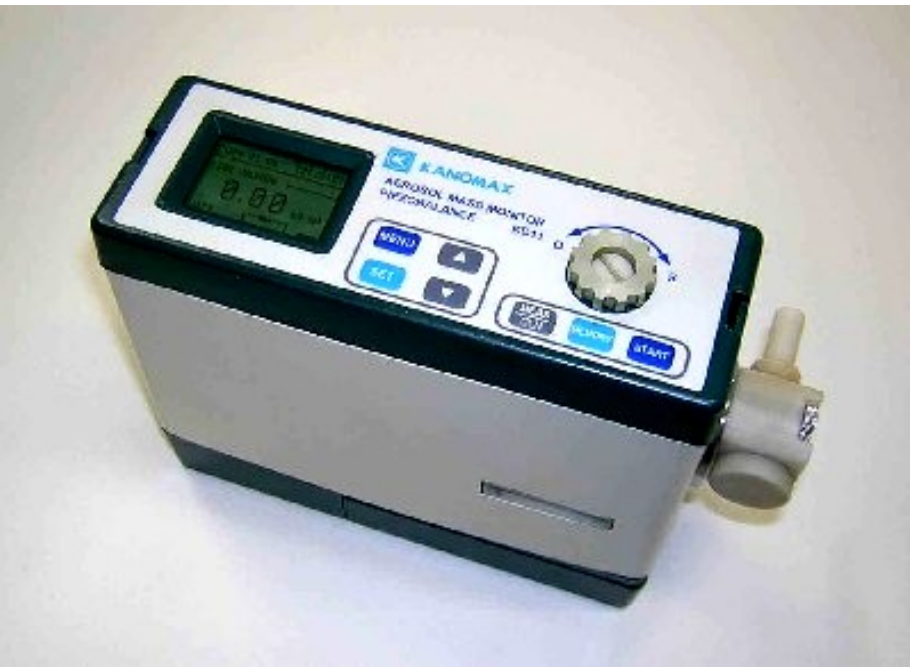
WRAS Accessory- “Near on-line” scanner/analyser

- **Accessory to WRAS**
- **Analyses sample substrates**
- **Mass –size distribution**
- **Available mid 2009**

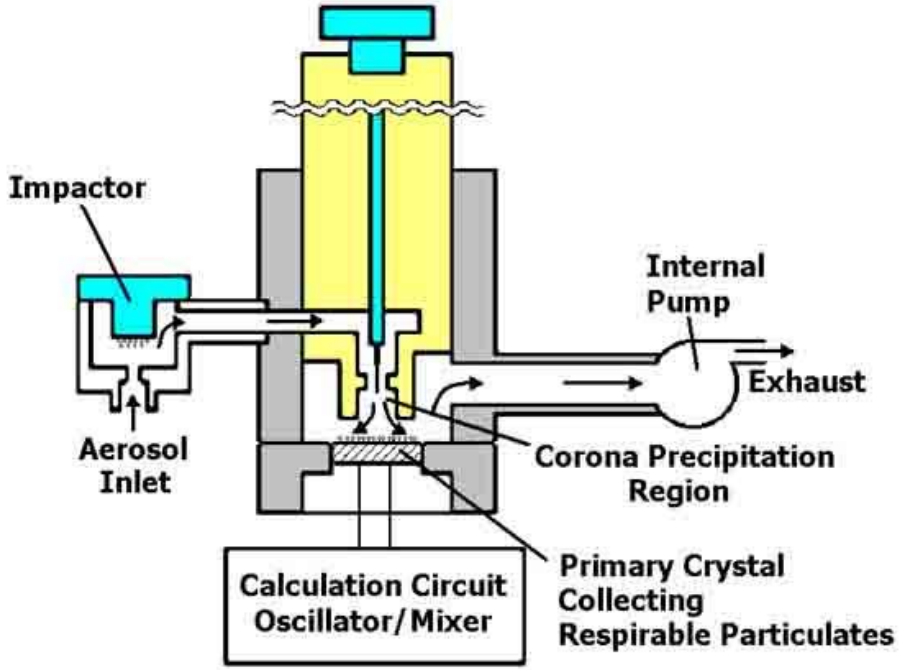
Applications

- **PM_{10},$PM_{2.5}$,$PM_{1.0}$ etc from same sample set**
- **Toxicology testing**

Mass Concentration (mg/m^3), Piezobalance Dust Monitor, Non-Specific, General Area



KANOMAX USA, INC.



Size range: < 10 microns

Concentration: 0.02-10 mg/m3

Accuracy: +/-10% of reading +/-1 digit

Mass Concentration (mg/m^3), Photometers Non-Specific but With Capability for Off-line Analysis of Filter, Personal Sampling

Particle Size Range of Maximum Response :
0.1 to 10 µm

Range: 0.001 to 400 mg/m^3

Impactor cut-point (d_{50}):
1 µm to 10 µm
depending upon flow rate of pump

After passing through the cyclone, a direct reading is provided (mg/m^3), and the filter can be sent to lab for analysis

Question # 2

- What characteristics (physical or chemical) should we focus on to identify and quantify nanoparticles?
- Answer:
  - Depends - whatever toxicology data says is correlative with toxicity for the material or like materials – or use associated metric
  - Size-selective particle monitoring and analytical methods used in tox assessment should drive or inform air monitoring methods

Bulk Sample of Material Data Supplied (e.g., Manufacturer)

- **Chemical composition (mass%):**
  - **Coating, if applicable**
  - **Intended core product(s)**
  - **Trace impurities (e.g., metal catalysts, etc.)**
- **Crystallinity (amorphous or crystalline)**
- **Crystalline form (e.g., rutile, anatase TiO_2)**

Bulk Sample of Material
Data Supplied (e.g., Manufacturer)

- **Method of synthesis and/or preparation**
- **Size and size distribution (dry & wet states)**
- **Surface area (m^2/g, "total"; dry state, BET)**
- **Porosity**
- **Microscopic images (shape; agglomeration, aggregation state, porosity)**
- **Solubility**
- **Dispersability**
- **Density (tapped/"true"? and bulk)**

Bulk Sample of Material
Data Supplied (e.g., Manufacturer? Chemist? Toxicologist?)

- **Surface reactivity (e.g., ROS)**
- **Surface Charge**

Air Monitoring

- **Particle size and distribution concentration**
  - Number
  - Mass
  - Surface area (external, maybe)
- **Microscopy (e.g., TEM, SEM) -** morphology, state of aggregation and agglomeration, physical diameters, chemistry

Question # 3

- Should the Focus be anthropogenic or naturally occurring particles?
- Answer: Both
  - **Subtracting out background for Engineered Nanomaterials**
  - **Incidental Anthropogenic Nanoparticles. What has been learned?**
    - EPA future NAAQS for PM0.2 or smaller?
    - Future ACGIH/ISO/CEN air sampling convention for ultrafine particles?
      - Future TLV PNOS for ultrafine particles?

Nanoparticles Are All Around Us

- We inhale **BILLIONS** of particles having diameters < 1,000 nm each day (P-Trak)
- Example:
  - $(10^4$ p/cc$)(10^6$ cc/m$^3)$(20 m^3/d) = **200 billion particles inhaled**

Natural

- **Forest fire combustion products**
- **Volcanic eruptions (hot lava)**
- **Viruses**
- **Sea spray (sea salt nuclei)**
- **Organic terrestrial Sources (e.g., plants, animals)??**
- **Inorganic sources. Asbestos in lungs:**
  - Amosite:
    - 30 to 1,600 nm width
    - 11,000 nm long, average
  - Chrysotile:
    - 40 to 400 nm width
    - 500 to 23,000 nm long

Anthropogenic, Incidental Outdoor Air Pollution

Circulation Research Journal of the American Heart Association

American Heart Association
Learn and Live

- Araujo, et. al., Ambient Particulate Pollutants in the Ultrafine Range Promote Early Atherosclerosis and Systemic Oxidative Stress, Cir. Res., 17 Jan. 2008
- **Exposed genetically susceptible mice in mobile animal facility close to a Los Angeles freeway**
- **Compared proatherogenic effects in mice:**
  - **Concentrated ultrafine particles < 0.18 µm AED**
  - **Concentrated $PM_{2.5}$ particles <2.5 µm AED**
  - **Filtered air**

Circulation Research
Journal of the
American Heart Association

American Heart Association
Learn and Live

- Ultrafine **($PM_{0.18}$)** particle-exposed mice had significantly larger early atherosclerotic lesions than mice exposed to **$PM_{2.5}$** or **filtered air**
- **UFPs data demonstrated that they:**
  - **are more proatherogenic**
  - **exert the strongest prooxidative effects**
  - **are associated with the largest decrease in HDL protective activity**
  - **Are of considerable significance from a regulatory perspective**

Incidental Nanoparticles – Outdoors (5,000 to 3 million p/cc)

- **3,000,000 p/cc during pollution episodes, otherwise 5,000 to 10,000 p/cc (Borm et. al., 2006)**
- **20,000 to 50,000 p/cc urban pollution (BSi, 2007)**
- **10,000 to 50,000 p/cc (Fujitani, 2008)**
- **25,000 to 40,000 p/cc (NIOSH, 2006)**
- **13,000 p/cc to 23,000 p/cc (roadside parking) (Brouwer et. al., 2003)**
- **12,000 p/cc (Wallace, L, 2006)**
- **8,000 p/cc (Carroll, 2003)**

Incidental Nanoparticles – Home (2,500 to 50,000 p/cc)

- **No active sources** – 2,500 p/cc Ave.
- **Active sources**
  - **> 20,000 p/cc**
  - **Complex cooking – 35,000 to 50,000 p/cc**
    - 3,500 p/cc no active sources; 12,000 p/cc outdoors
  - **Cooking – up to 10 to 50 ug/m^3 increase**
- **Ratio of Indoors (with active sources on) to Outdoors = 6-10 times**
- **Source: Wallace, L (2006)**

Incidental Particles, Home – Candles (3,000 to 125,000 p/cc)

- **2-3 times background (Wright et. al.)**
- **3,000 to 15,000 p/cc > background (Matson, 2005)**
- **8,000 p/cc > background during burning (Carroll, 2008)**
- **125,000 p/cc > background when candle blown out**
- **< 241,000 p/cc (Chamber study – Afshari et. al. (2005)**

Background Nanoparticles – Indoors (2,500 to 17,000 p/cc)

- **2,500 p/cc Ave., No active sources, (Wallace, L, 2006)**
- **3,800 p/cc (welding), non-production (Dasch and D'Arcy, 2008)**
- **10,000 -16,000 p/cc (fullerene factory), non-work period (Fujitani, 2008)**
- **10,000 – 15,000 p/cc (carbon nanofiber handling), background (NIOSH, 2008)**
- **8,000 – 17,000 p/cc (lab exercise), background (Carroll, 2008)**

Engineered Nano-objects

- **Fullerenes (Fujitani, 2008)**
  - 10,000 p/cc, Non-work period
  - No or marginal increase above background during bagging
- **Carbon nanofibers (NIOSH, 2006)**
  - 10,000 to 12,000, background
  - No increase above background during weighing
- **SWCNT (Maynard, 2004)**
  - No increase when material was handled
- **Particle concentrations larger than nanoscale increase - agglomerates**

Incidental Nanoparticles – Workplaces (94,000 to 700,000 p/cc)

- **Bakery - < 640,000 p/cc (BIA)**
- **Plasma cutting – < 500,000 p/cc (BIA)**
- **Soldering – < 400,000 p/cc (BIA)**
- **Welding – < 390,000, 2 ft away (Brouwer et. al., 2003)**
- **Metal grinding – < 130,000 p/cc (BIA)**
- **Fork Lifts in Warehouse – 94,000 p/cc (NIOSH, 2008)**
- **Airport field - < 700,000 p/cc (BIA)**
- **Outdoors, at heater exhaust – 500,000 p/cc (Carroll, 2003)**
- **Outdoors, 10-15 ft from heater exhaust – 165,000 (Carroll, 2003)**

Question # 4

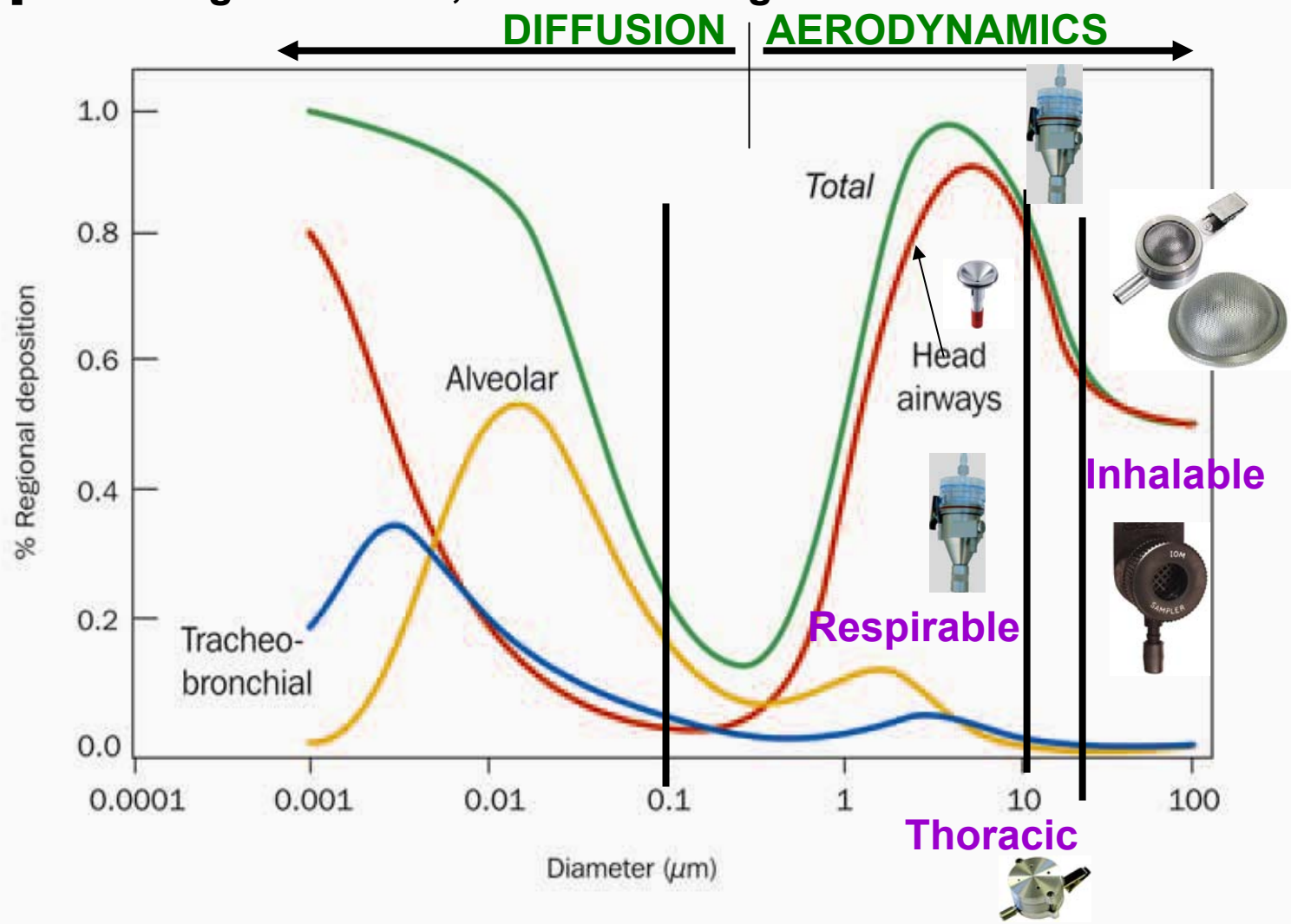
- What considerations should be made about fate and transport?

Ambient Air

- **Aerosol aging** - particle number concentration and size distribution can change with time
- **Particle agglomeration** –
  - Engineered nanoparticles can agglomerate up into the micron range (up to 100 um AED and higher)

Penetration (Inhalable/Thoracic/Respirable) and Deposition

Predicted deposition of inhaled particles in the human respiratory tract (ICRP [1994] model: light exercise, nose breathing



Particle Sizes Can Change After Entering the Body

- **If hygroscopic, inhaled particles can grow in size before they are deposited**
- **Once deposited, particle sizes can change**
  - **Dry state vs. wet state**
  - **Depends on chemistry of particle & fluid**
  - **May agglomerate or de-agglomerate**
  - **May increase in size due to opsonization of proteins on surface**

Translocation Probability After Deposited in the Body

- **Surface Chemistry (including charge)**
- **Particle Size (physical/geometric dia., hydrodynamic diameter)**
- **Solubility.** Affected by

*__temperature__ (37 deg C normal body temperature)

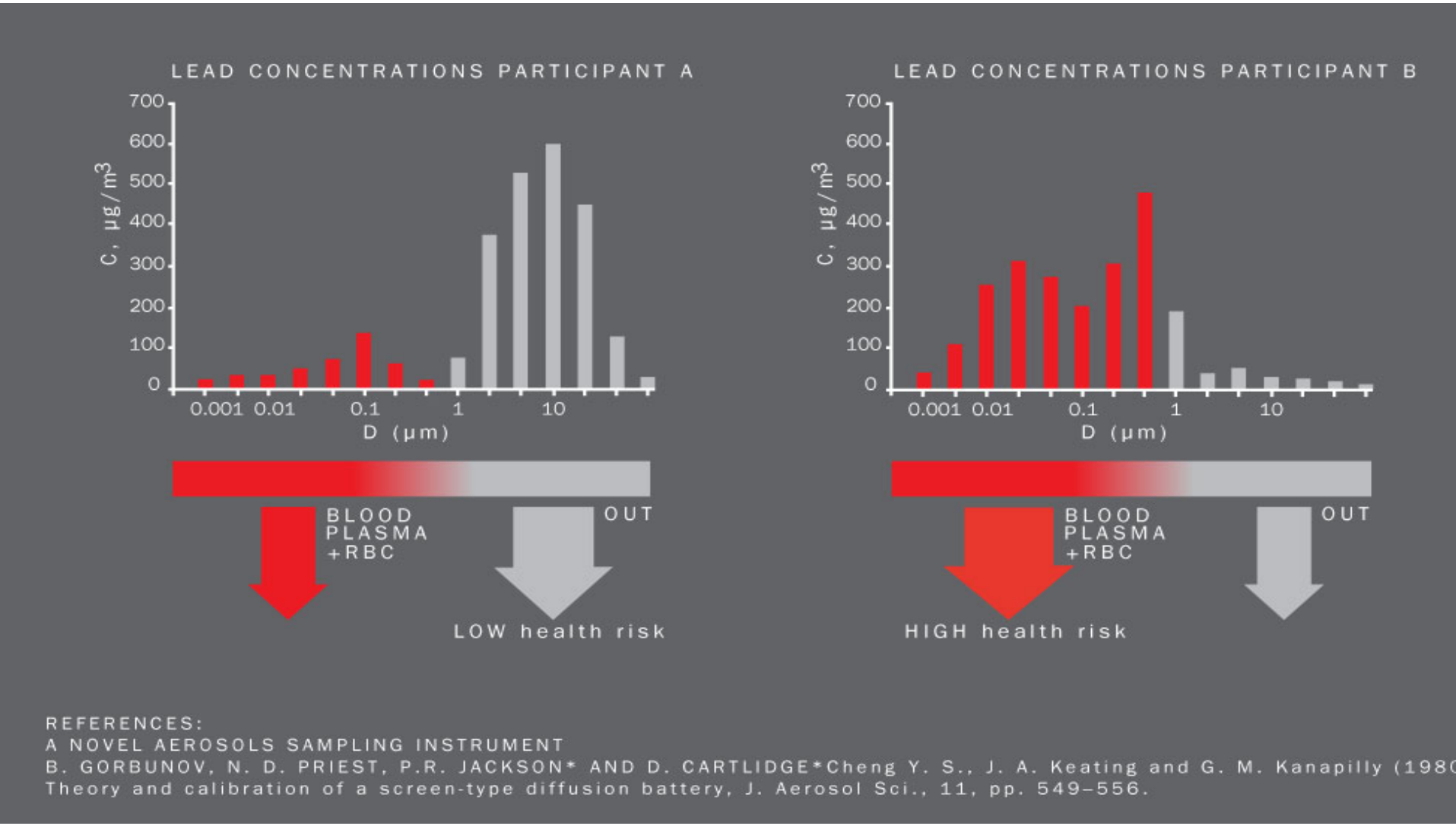
*__pH__ (saliva, lung fluids, stomach fluids, small intestine fluids, subcellular compartments such as lysosomes)

*__proteins and other solutes__ (in body fluids)

Translocation from Respiratory Tract to Other Organ Systems

- **Sensory neurons to brain (Hankin et. al., 2008)**
  - **30 nm polio virus**
  - **30 nm MnO particles**
  - **35 nm Carbon particles**
  - **50 nm colloidal gold particles**
  - **Is there a maximum particle size that can translocate??**

European Crystal Glass Industry Studies of Lead Concentration, Particle Size, and Lead in Blood



REFERENCES:
A NOVEL AEROSOLS SAMPLING INSTRUMENT
B. GORBUNOV, N. D. PRIEST, P.R. JACKSON* AND D. CARTLIDGE*Cheng Y. S., J. A. Keating and G. M. Kanapilly (1980
Theory and calibration of a screen-type diffusion battery, J. Aerosol Sci., 11, pp. 549–556.

Highly correlated (R2 = 0.95) blood lead with particles < 200 nm but not as total dust (R2 = 0.58), PM10 (R2 = 0.61), or respirable fraction (R2 = 0.59).

Translocation from Respiratory Tract to Other Organ Systems

- **Lung to blood**
  - **Worker blood lead highly correlated for Pb < 200 nm (Naneum), unpublished**
  - **240 nm lecithin-coated polystyrene translocated, but uncoated polystyrene did not (Kato, 2003)**
  - **22 nm TiO_2 rapidly enters the blood via interstitium**
- **Lung to lymphatics to pleural surface**
  - **Fibers < 500 nm physical dia.) (Witshci et. al., 2008)**

Asbestos Fiber Clearance from Respiratory Tract

- **Short dimension associations (diameter):**
  - **To reach alveoli:** ≤ 3 µm
  - **Mesothelioma:** < 200 nm (Tran et. al., 2008)
- **Long dimension associations (length)**:
  - **Lung cancer:**
    - > 10 µm (Witshci, 2008)
    - > 15-20 µm (Tran et. al, 2008)
  - **Asbestosis:** > 2 µm (Witshci, 2008)
  - **Mesothelioma:** > 5 µm (Witshci, 2008)

Cell Entry (Hankin et. al., 2008)

- **Diffusion?**
- **Facilitated Diffusion**
  - Nanoparticle entry possible if the size is less than the pore channel dia of **10-30 nm**
- **Active Transport**
  - Conducted by specific transport proteins
  - Nanoparticle entry possible if physico-chemistry resemble the transported protein

Cell Entry – Endocytosis (Hankin et. al., 2008)

- **Phagocytosis**
  - **particles > 500 nm dia.**
- **Clathrin-mediated endocytosis**
  - **particles < 200 nm dia.**
- **Caveolae-mediated endocytosis**
  - **particles 200 nm to 1μm dia.**
- **Clathrin- and caveolae-independent endocytosis**

Other Biological Barriers

- **Endothelial pores** (< 20 nm particles can transit out of blood vessels through pores)
- **Blood-Brain (Hankin et. al., 2008)**
  - **Passive diffusion**
  - **Carrier-mediated endocytosis**
- **Nuclear membrane**
- **Mitochondria**

Liver and Kidney Particle Filtration of Dendrimers

- **< 10 nm particles** cleared by kidney
- **10-80 nm particles** cleared by liver bile duct
- **80-220 nm particles** tend to recirculate in the body until they degrade. Tend to accumulate in tumor tissue.

Question # 5

- Should we try to classify these particles into some types or groups?
- Answer: Yes

Natural

- **Forest fire combustion products**
- **Volcanic eruptions (hot lava)**
- **Viruses**
- **Sea spray (sea salt nuclei)**
- **Organic terrestrial sources (e.g., plants, animals???)?**
- **Inorganic sources. Asbestos in lungs:**
  - Amosite:
    - 30 to 1,600 nm width
    - 11,000 nm long, average
  - Chrysotile:
    - 40 to 400 nm width
    - 500 to 23,000 nm long

Incidental, combustion-derived

- **Internal combustion engine exhaust**
- **Diesel exhaust**
- **Jet engines**
- **Industrial air pollution (condensed gases, etc.)**
- **Propane-powered fork lifts**
- **Natural gas appliances**
- **Fireplaces (burning of wood, coal)**
- **Candles**
- **Tobacco smoke**
- **Fires (e.g., housing, forest, etc.)**

Incidental, Hot Processes

- **Welding fumes**
- **Soldering fumes**
- **Smelting fumes**
- **Asphalt fumes**
- **Thermal cutting and spraying**
- **Plasma cutting**
- **Pyrolysis products**
- **Polymer fumes**

Incidental, Hot Processes

- **Food production**
  - Grilling
  - Frying
  - Baking
- **Liquid particles formed from SVOCs evaporating and then forming particles (Morawska et. al., 2009)**
  - **Laser printers:**
    - **SVOCs from hot toner and paper**
    - **Trace amounts of Ca (from calcium carbonate coating on paper) and Fe (from iron oxide in toner) found in SVOC liquid particles**

Incidental, Mechanically Derived

- **Machining**
  - Grinding
  - Milling
  - Drilling
  - Sanding
- **Powder dispersion into the air**
- **Suspension dispersion into the air (particles suspended in a liquid)**

Historical Products Containing a Fraction of Nanoparticles

- **Titanium dioxide (rutile pigment-grade)**
- **Carbon black**

Engineered Nano-objects for Medical Purposes

- **Dendrimers**
- **Nanosomes**
- **Nanoshells**
- **Quantum dots**

Engineered Nano-objects

- Quantum dots
- Nanoscale metal oxides
- Fullerenes
- Nanotubes
- Nanofoam
- Nanohorns
- Nanofibers

Engineered Nano-objects

- Nanosheets
- Nanowires
- Nanoplates
- Nanotrees
- Nanoflowers
- Nanosprings
- Nanobelts
- Nanorings

Nano-objects, Engineered Metal "X" (e.g. Powder, Suspension, etc.) Air Samples

- Open-face filter cassette (e.g., 25 mm, 37 mm)
- Inhalable (100 µm AED 50% cut-point)
- "Total" (37 mm closed-face cassette, 30-40 µm AED cut-point)
- Thoracic (10 µm AED 50% cut-point)
- Respirable (4 µm AED 50% cut-point)
- < 1,000 nm AED cut-point

Nano-objects, Engineered
Metal “X” (e.g. Powder, Suspension, etc.)
Air Samples

- < 20 µm
- < 10 µm
- < 5 µm
- < 4 µm
- < 3 µm
- < 1 µm
- < 500 nm
- < 300 nm
- < 200 nm

Nano-objects, Engineered
Metal "X" (e.g. Powder, Suspension, etc.)
Air Samples

- < 100 nm
- < 80 nm
- < 50 nm
- < 40 nm
- < 30 nm
- < 20 nm
- < 10 nm
- < 5 nm

Source, Process

- **Handling of a powder containing nano-objects (e.g., recovery from reactor)**
- **Leakage from reactor used to synthesize engineered nanoparticles from the gas phase**
- **Propane fork lift**
- **Candles**
- **Diesel engine**
- **Natural gas appliances**
- **Welding**
- **Etc.**

Sampling and Analytical Method(s) Used (e.g.)

- Direct-reading (on-line) or Indirect (off-line)
- Cascade impactor and ICP
- Filter and microscopy (e.g., TEM, SEM)
- CPC, direct-reading
- OPC, direct-reading
- Diffusion charger, direct-reading
- Scanning mobility particle sizer, direct-reading

Size and size distribution

- Dimension (e.g., microscopy, etc.)
  - Width
  - Length
- Equivalent diameter
  - Thermodynamic
  - Aerodynamic
  - Hydrodynamic
  - Mobility
  - Projected
  - Optical
  - Volume

By Dimension

- **Nano-objects (at least one dimension in the nanoscale)**
  - **Nanoparticle (all three dimensions in the nanoscale)**
    - **< 100 nm?**
    - **< 80 nm?**
    - **< 50 nm**
    - **< 40 nm?**
    - **< 30 nm?**
    - **< 20 nm?**
    - **< 10 nm?**

By Dimension

- **Objects larger than nanoscale:**
  - **< 500 nm?**
  - **< 300 nm?**
  - **< 200 nm?**
  - **Fibers:**
    - **< 200 nm diameter?**
    - **< 3,000 nm diameter?**
    - **> 5,000 nm length?**
    - **> 10,000 nm length?**
    - **> 15,000 nm length?**
    - **> 20,000 nm length?**

By Equivalent Diameter

- **Percent deposition in the respiratory tract:**
  - **1 nm to 300 nm: thermodynamic diameter**
  - **300 nm to 100 µm: aerodynamic diameter**
  - **Total (HA, TB, and ALV)**
  - **Head airway region**
  - **Tracheobronchial region**
  - **Alveolar region**
- **Hydrodynamic**
- **Projected**

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- **Four nanoparticle hazard types** in the Selection of Controls

- **FIBROUS nanomaterial:** a high aspect ratio insoluble nanomaterial

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- **CMAR nanomaterial:** any nanomaterial which is already classified in its larger particle form as carcinogenetic (C), mutagenic (M), asthmagenic (A) or a reproductive toxin (R):
  - Due to potential for increased solubility in nanoparticle form

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- **INSOLUBLE nanomaterial:** Insoluble or poorly soluble nanomaterials not in the fibrous or CMAR category

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- **SOLUBLE nanomaterial:** Soluble nanomaterials not in fibrous or CMAR category
  - For materials that are highly soluble in any case, nanoparticle forms are unlikely to lead to greater bioavailability
  - Types of effects associated with insoluble particles are NOT likely to occur

Other Possible Groupings

- **Toxicity:**
  - **Cytotoxicity**
  - **Inhalation toxicity**
  - **Relative toxicity to known materials with known toxicity or exposure limits**
- **Surface reactivity (e.g., ROS) per gram**
- **Surface charge**
- **Agglomerates vs. aggregates**
- **Clearance rate/probability from the body**
- **Respiratory tract translocation probability**
- **Cell entry probability**

Bulk Sample of Material Data Supplied (e.g., Manufacturer)

- **Chemical composition (mass%):**
  - **Coating, if applicable**
  - **Intended core product(s)**
  - **Trace impurities (e.g., metal catalysts, etc.)**
- **Crystallinity (amorphous or crystalline)**
- **Crystalline form (e.g., rutile, anatase TiO_2)**

Bulk Sample of Material
Data Supplied (e.g., Manufacturer)

- **Method of synthesis and/or preparation**
- **Size and size distribution (dry & wet states)**
- **Surface area (m^2/g, "total"; dry state, BET)**
- **Porosity**
- **Microscopic images (shape; agglomeration, aggregation state, porosity)**
- **Solubility**
- **Dispersability**
- **Density (tapped/"true"? and bulk)**

Bulk Sample of Material
Data Supplied (e.g., Manufacturer? Chemist? Toxicologist?)

- **Surface reactivity (e.g., ROS)**
- **Surface Charge**

Question # 6

- **Do we need real-time measurement techniques?**
- Answer: yes.
  - **See question #1**
  - **Aids in identification of relative emissions of various processes**
  - **Gauges relative effectiveness of work practices and controls**
  - **Helps identify if and when other methods (e.g., off-line chemical analysis) are necessary**

Other

- **Measurement if one-dimension is less than 100 nm (or some other diameter).** Nothing available for direct-reading instruments.
  - That is, other than equivalent diameter (e.g., mobility, aerodynamic, optical, etc.)
- **Explosion proof (UL Listed).**
  - Are any direct-reading instruments explosion proof?

Mass Concentration: Tapered Element Oscillating Microbalance (TEOM)

- **Widely used to continuously monitor ambient outdoor air for PM10 and PM2.5**
- **Detection limit of 0.01 ug**
- **Precision of +/- 5 µg/m^3 for 10-min ave., +/- 1.5 µg/m^3 for 1 hour ave.)**
- **Why is there not a pre-selector for the ultrafine fraction??**
- **Should the government be monitoring PM0.2 in ambient air as for PM2.5 and PM10?**
- **Are personal samplers feasible?**

Personal Sampling

- **Mass distribution down into nanoscale**
  - **Nothing available**
  - **Can be made:**
    - **Naneum Personal sampler (based on WRAS),**
    - **followed by "near on-line" mass distribution analysis by WRAS accessory, and**
    - **if chemical or microscopic analysis is needed, substrates can be sent for further analysis**

Hand-Held Monitors

- **Mass concentration**
  - **Piezobalance, < 10 µm AED cut-point available. Nothing available exclusive for**
    - < 10 nm
    - < 30 nm
    - < 50 nm
    - < 100 nm
    - < 200 nm
    - < 300 nm, < 500 nm, < 1,000 nm, < 4000 nm
  - **Photometers – have cut-points of 1 to 10 µm AED, detecting particles down to 100 nm.**

Personal Sampling

- **Particle number distribution down into nanoscale.** Nothing available.
- **Total particle concentration 5/10 nm to 300 nm**. Coming in late 2009 - Naneum Personal Size unit based on remote monitor
- **Surface area.** Nothing available.
  - External (e.g., diffusion charger)
  - Total (e.g., BET)

Hand-Held CPC Monitors

- **Particle number concentration distribution in the nanoscale**
  - Only “total” available
  - Nothing available for distribution (in nm)
    - < 10
    - < 30
    - < 50
    - < 100
    - < 200
    - <300

Hand-Held OPC Monitors

- **Detection down to 300 nm**
- **None available, but laser with wavelength of 560 nm could detect down to 100 nm**