OSC 10
Ohio Safety Congress & Expo

Development of an ultrafine /nanoparticle occupational exposure detection sensor

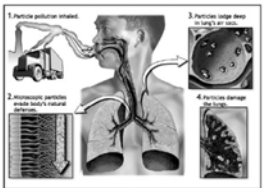
313

Sang Young Son

Tuesday, March 30, 2010 10:45 to 11:45 a.m.

Heath Effects of Particle Pollution

- Many scientific studies have linked breathing particle pollution to a series of significant health problems, including:
  - Exposure to particulate matter (PM) has been significantly associated with wheezing and **asthma**[1-3]
  - Increases in **respiratory symptoms** like coughing and difficult or painful breathing
  - Ultrafine particulates have a higher association with respiratory symptoms than coarse particles[4]
  - Chronic bronchitis
  - Decreased lung function
  - Premature death in people with **heart and lung disease**



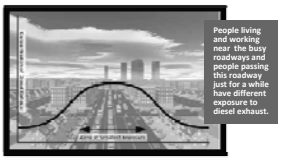
American Lung Association, http://www.lungusa.org/

1. Noris et al., An association between fine particles and asthma emergency department visits for children in Seatle. EHP 1999, 107(6), 489-493.
2. Jalaludin BB et al., Acute effects of urban ambient air pollution on respiratory symptoms, asthma medication use, and doctor visits for asthma in a cohort of Australian children. Environ Med. 1999, 56(12), 802-812.
3. Pino P et al. Fine particulate mater and wheezing illnesses in the first year of life. Epidemiology, 2004, 15(6), 702-708.
4. Schwartz J, Neas L.M. Fine particles are more strongly associated than coarse particles with acute respiratory health effects in schoolchildren. Epidemiology 2000, 11(1), 6-10.

Actual Human Exposure to PM

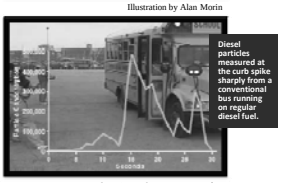
- Exposure level to many pollutants is highly variable over short distances and dependent upon personal activity patterns
  - Children are more active than adults and therefore breathe more rapidly
  - Children are exposed to elevated levels of diesel as a result of the buildup of diesel exhaust inside school buses
  - Ambient diesel levels are highest near highways, busy roadways, bus depots, construction sites, etc.

→ Personal monitors capable of measuring micro environmental PM exposure with time and location data logging is needed.



People living and working near the busy roadways and people passing this roadway just for a while have different exposure to diesel exhaust.

Illustration by Alan Morin

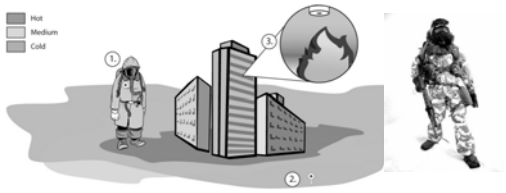


Diesel particles measured at the curb spike sharply from a conventional bus running on regular diesel fuel.

From Clean Air Task Force, www.catf.us

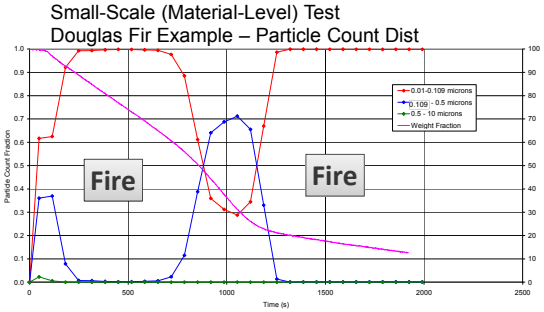
Ultrafine Particle as an Indicator of Emergency

The change of Ultra-fine particle number density is a key indicator of environmental hazard level associated with critical human respiratory health.



Ultrafine Particle as an Indicator of Emergency

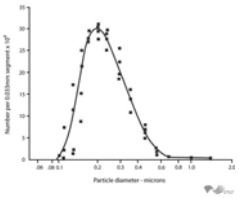
Small-Scale (Material-Level) Test
Douglas Fir Example – Particle Count Dist



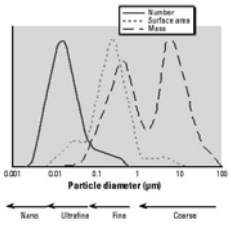
US DHS Assistance to Firefighters Grant

Env. Particle Size Distribution

Dominant Particle Size: less than 100 nm

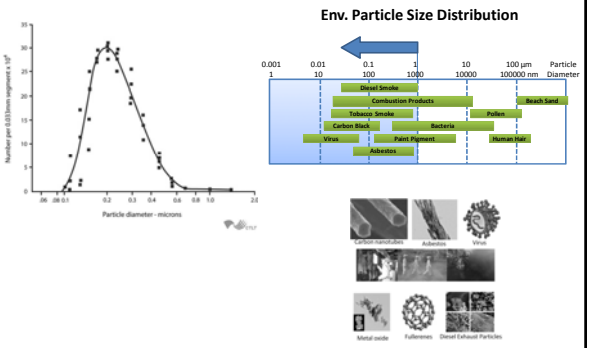


Copyright © Johns Hopkins Bloomberg School of Public Health



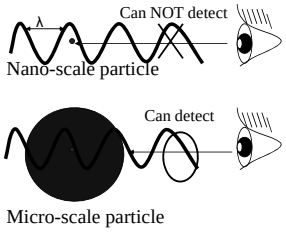
Ultrafine Particles in the Urban Air: To the Respiratory Tract--And Beyond?
Günter Oberdörster and Mark J. Utell
Environmental Health Perspectives Volume 110, Number 8, August 2002

Environmental Particles



Condensate Particulate Counter

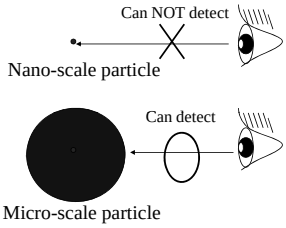
MIE Scattering: Detection



Even though high-intensity light energy is exposed to nanoparticle surface, we can not detect the particles due to the scattering is Rayleigh mode.

Scattered light from micro-scale size particles is MIE scattering. We can easily detect the particles with proper exposing light intensity.

MIE Scattering: Detection



How can we increase the particle size for detection purpose?

→ CONDENSATION

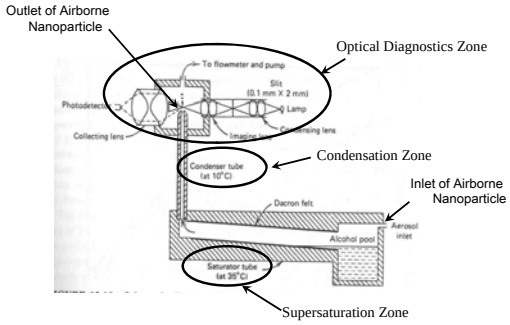
Condensation: Ultrafine Particle Detection

Methodology of Particle Condensation

By Cooling ***By Heating***

Supersaturation Condition

Conventional Condensate Particle Counter



Conventional Condensate Particle Counter

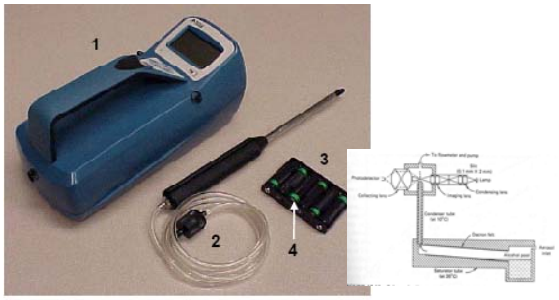


Figure 1-1: Model 8525 P-TRAK Ultrafine Particle Counter With Inlet Probe Assembly, Battery Pack, and Batteries

Requirements of Personal Sensor

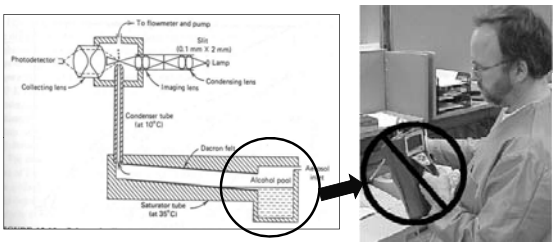
Requirements of Personal Sensor

1. ***Small*** Sensor Volume & Mass
2. Sensor should be ***independent*** from gravity effect.

1-g

Not 1-g

Limitation of Conventional Sensor

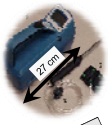


Micro Thermofluidics Technology

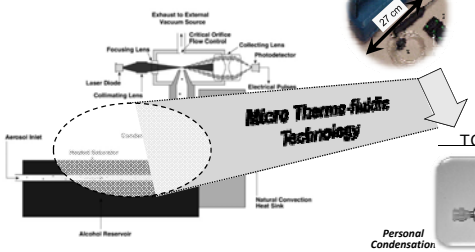
CPC (Condensation Particle Counter)

is the most traditional, but still the most powerful tool for detecting ultrafine particles.

AS IS



Handheld CPC



TO BE

Personal Condensation Device

From TSI Inc.

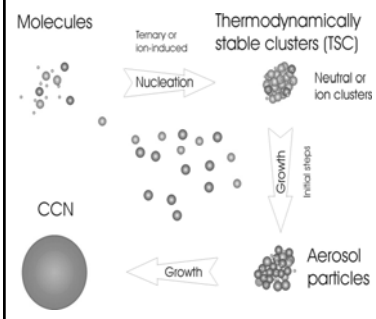
Principles

Ultrafine Particle Characteristics

- **High fraction of atoms at or near the surface.**
- **Surface Tension: liquids surfaces behave as though they are an elastic film.**
- **Kelvin Effect: higher vapor pressure over smaller droplets**
- **Ostwald Ripening: large particles grow at the expense of smaller particles**
- **Adsorption: *impurities* tend to stick to surfaces**
- **Surface charge: adsorption of ions can leave the nanoparticle electrically charged**

OU NanoLab/NSF NUE/Bumm & Johnson

Condensate Particle Formation in Nature

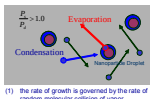


- **Nucleation**
  - **Ternary/Kinetic Nucleation**
- **Initial steps of the growth**
  - **Heterogeneous Nucleation**
- **Growth**
  - **vapours**
- **Aerosol dynamics**
  - **competition between processes**

Kulmala: Science 302, 1000-1001, 2003

Droplet Growth Rate by Heterogeneous Condensation

for $D_p < \lambda$



(1) the rate of growth is governed by the rate of random molecular collision of vapor molecules. The rate of collisions is given by the kinetic theory of gases.
(2) Using distribution of molecular velocities which is described by the Maxwell-Boltzmann distribution, mean molecular velocity can be derived.

$$z = \frac{n\bar{v}}{4} = \frac{P}{\sqrt{2\pi mkT}}$$: from kinetic theory of gases

$n = \frac{P}{kT}$: Ideal gas law

$\bar{v} = \int_0^\infty v f(v) dv = \sqrt{\frac{8RT}{\pi M}}$:Maxwell-Boltzman distribution

$(z_{in} - z_{out}) A_{surface}$: the net rate of arrival of molecules to the entire droplet surface

$$(z_{in} - z_{out}) A_{surface} = \frac{\pi d_p^2 (P - P_d)}{\sqrt{2\pi mkT}}$$: the rate of loss is given with P_d from Kelvin or Thomson-Gibbs equation

$$\frac{dV_p}{dt} = \{(z_{in} - z_{out}) A_{surface}\} V_{molecule}$$: the rate of change of droplet volume, where Vmolecule is the vapor molecular volume; $V_{molecule} = \frac{M}{\rho_p N_a}$

$$\frac{d(\pi d_p^3)}{dt} = \frac{6 \cdot \pi d_p^2 (P - P_d)}{\sqrt{2\pi mkT}}$$

$$\frac{dD_p}{dt} = \frac{2M(P - P_d)}{\rho_p N_a \sqrt{2\pi mkT}}$$

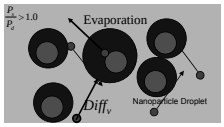
where,
M : molecular weight of liquid , $Diff_v$: diffusion coefficient
m: mass of a vapor molecule, λ: gas mean free path, ρ : density of liquid
P : partial pressure of vapor in the gas surrounding the droplet
P_d: *partial pressure of vapor at the droplet surface given by the Kelvin equation*
P_s : *saturation vapor pressure*, N_a: Avogardro Number (6.7×10^{23})
z: the number of molecular collisions per unit area of a stationary surface per second

Droplet Growth Rate by Heterogeneous Condensation

for $D_p > \lambda$

$$z_{net} = 2\pi D_p Diff_v N$$: With Diffusion Coefficient or Fick's Law

$$z_{net} = \frac{2\pi D_p Diff_v (P - P_s)}{kT}$$



For particles larger than the gas mean free path, growth does not depend on the rate of random molecular collisions but on the rate of diffusion of molecules to the droplet surface. This is completely analogous to the coagulation of aerosol particles. The rate of collisions of vapor molecules with a droplet of diameter Dp can be derived for particles of equal size and diffusion coefficient diffusing to each other with assumption of negligible diameter of molecule to a droplet.

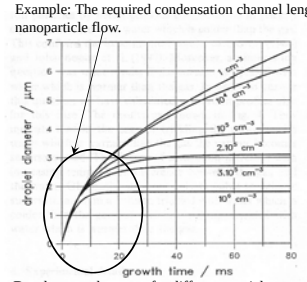
$$\frac{dD_p}{dt} = \frac{4 Diff_v M (P - P_s)}{\rho_p d_p RT}$$

for $D_p > \lambda$

where,
N: net concentration of vapor molecules
M : molecular weight of liquid
m: mass of a vapor molecule
λ: gas mean free path
ρ_p : density of liquid
P : partial pressure of vapor in the gas surrounding the droplet
P_d: *partial pressure of vapor at the droplet surface given by the Kelvin equation*
P_s : *saturation vapor pressure*
N_a: Avogardro Number (6.7×10^{23})
$Diff_v$: diffusion coefficient
z: the number of molecular collisions per unit area of a stationary surface per second

Droplet Growth Rate by Heterogeneous Condensation

Example: The required condensation channel length is only 5 cm for the 0.1 m/s nanoparticle flow.



Droplet growth curves for different particle number concentration, Supersaturation ratio = 1.5 and $T_{initial}$ = 35°C (Heidenreigh et al., 2000)

$$\frac{dD_p}{dt} = \frac{2M(P - P_d)}{\rho_p N_a \sqrt{2\pi mkT}}$$ for $D_p < \lambda$

$$\frac{dD_p}{dt} = \frac{4 Diff_v M (P - P_s)}{\rho_p d_p RT}$$ for $D_p > \lambda$

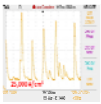
Kinetic theory estimates that less than 20 ms is required to increase particle size from nano-scale to micro-scale through heterogeneous condensation.

UC-NIEHS Personal Ultrafine Particle Sensor Development

Condensation Chamber Design

Schematic of condensation chamber design

Pictures of CC



Sample pictures of the prototypes

Pictures of CC

Sensor Volume & Mass Reduction

Sensor Picture

Sensor Picture

(a) First prototype developed
(b) Second prototype developed in this work
(c) Saturator wick used in conventional handheld CPC
(d) Alcohol cartridge for conventional handheld CPC

Sensor Volume & Mass Reduction

Mass Transfer Equation by Evaporation

$$\dot{m}_{evp} = h_{mass} \cdot A_{evp} \cdot \left(\frac{p_{sat}}{p_{tot}} - \frac{p_{sat,\infty}}{p_{tot,\infty}} \right)$$

Sensor Volume & Mass Reduction

Mass Transfer Equation by Evaporation

$$\dot{m}_{evp} = h_{mass} \cdot A_{evp} \cdot \left(\frac{p_{sat}}{p_{tot}} - \frac{p_{sat,\infty}}{p_{tot,\infty}} \right)$$

Body of Condensation Chambers Schematic

$$A_{evp,partial} > A_{evp,fully}$$

Sensor Mobility: Gravity Independence

Conventional

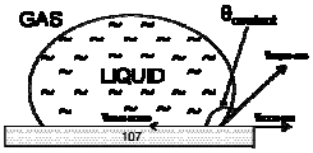
Vs.

UC Sensor

Sensor Mobility:

Young-Laplace Equation of Capillary Force

$$0 = \sigma_{solid-liquid} - \sigma_{solid-gas} - \sigma_{liquid-gas} \cdot \theta_{static-contact}$$



Sensor Mobility: Gravity Independence

Young-Laplace Equation of Capillary Force

$$p_{capillary} = p_{workingliquid} - p_{gas} = \frac{2 \cdot \sigma_{liquid-gas} \cdot \cos\left(\theta_{dynamic-contact}\right)}{r}$$

Body of Condensation Chambers Schematic

UC-NIEHS Ultrafine Particle Sensor

Packaged Ultrafine PM Sensing Part

Condensation Chamber

Control Daughter Board

PM1.0 Cyclone

Optical Detection Module

Sensor Picture

Gravity-independent Liquid chamber

Miniature Phase-separator

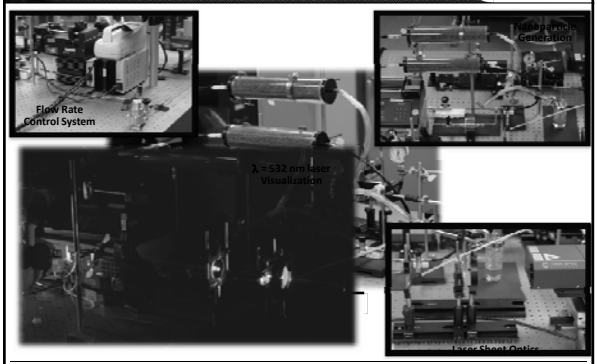
Air-pump

UC-NIEHS Personal Ultrafine Particle Sensor Performance

Experimental Setup - Schematic

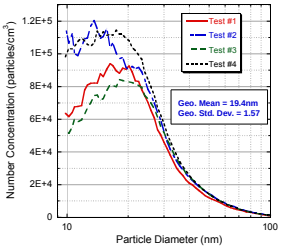
Test Setup

Experimental Setup - Picture



Testing Ultrafine Particle

Size Distribution of Nanoparticles used for Test: Generated by Atomizing Distilled Water



Distilled water source for particle
- Class I DI water
- 18.2 MΩ - cm

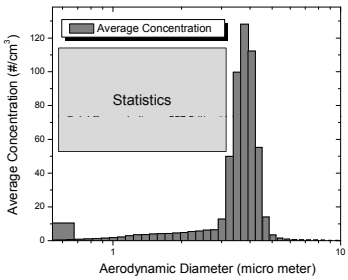
$$D_{mean,\ UFPM} = 20\ nm$$

Airborne Ultrafine Particulate Matter

Sample Image Analysis Results

Reference Temp.	41.9 °C	49.3 °C	57.7 °C	62.7 °C
Conden-sation Image				
Particle Count	53	96	101	97
Average Pixel Size	29.151	34.656	51.941	66.825
Particle Size	< 1 micron	1 micron	2 micron	3 micron

Droplet Size Verification: APS Results



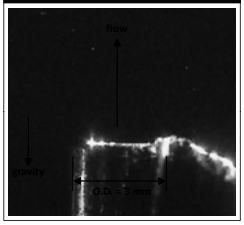
- Size Distribution of Condensed Droplets Measured by the Aerosol Instrument , APS 3321 (TSI Inc.)

Inlet particles: potassium chloride particles of 20 nm generated by a collision-type nebulizer and a differential mobility analyzer (DMA, TSI Model 3081) .

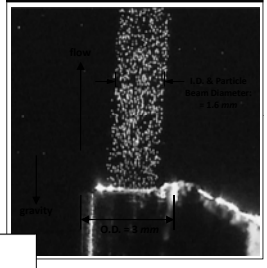
Output droplets: the mean diameter – 3.60 µm, more than 95% of the droplets are in the size range from 2 to 5 µm, the counting efficiency is about 90% .

Visualization of Particle Condensation

Without Condensation

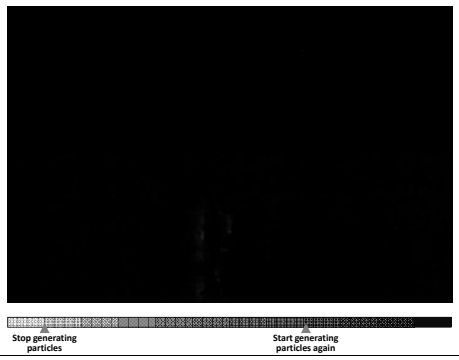


With Condensation



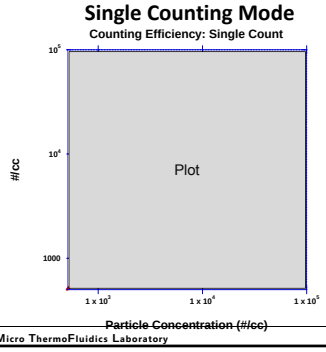
Air flow rate = 0.21 lpm
Counting Efficiency: more than 80%
Condensation Chamber Volume: about 0.5 cm³
Inlet particle concentration = 60,000 – 70,000 #/cm³

Visualization of Condensation – Movie



Counting Efficiency

Sensor performance in evaluating Single Counting Mode



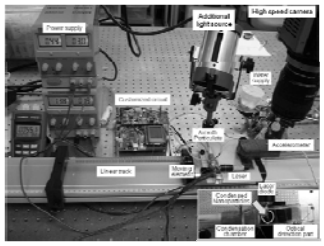
2010 January:
Single Counting Mode
10,000 #/cc

2010 March:
Single Counting Mode
***30,000* #/cc**

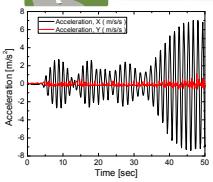
Mobility : Mechanical Shock test

Mobility concern

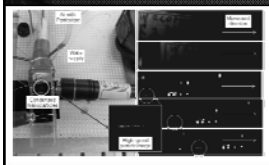
- Project target : stable sensor operation under ±5 g
- Acceleration test setup is prepared.

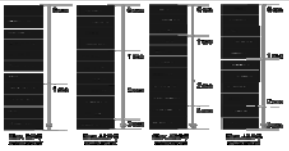


Mechanical shock system setup



Mobility : Mechanical Shock test

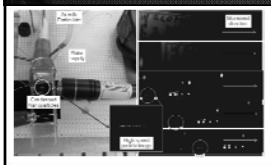


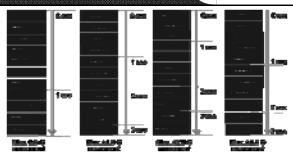


1g

Mobility in Action

Mobility : Acceleration test





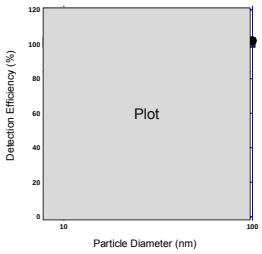
1g

1g

Mobility in Action **Particle View**

Detection Efficiency: Single counting

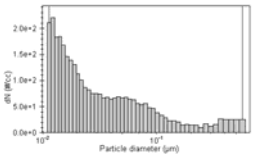
Sensor performance in evaluating
Single Counting and Stationary mode



Field Test

Environmental Particle Concentration

By Time of Day, University of Cincinnati, Cincinnati

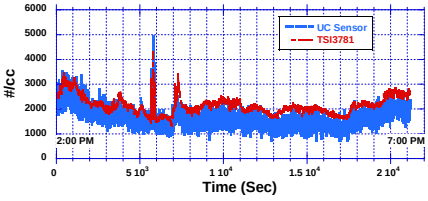


Range: 10 nm < Dp < 600 nm
Mean: 51 nm
Total Concentration: 3,266 /cc, 1:30 PM

Test & Calibration: Single counting

Environmental Particle Concentration

By Time of Day, University of Cincinnati, Cincinnati



TSI 3781: Averaged
UC Sensor: Real Time

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Thank you

Question and Comment