

**University of Maryland Baltimore County - UMBC  
Phys650 - Special Topics in Experimental Atmospheric Physics  
(Spring 2009)**

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**CLASS1 – 1/28/2009**

**PM10 and PM2.5 Local Aerosol Characterization:**

**Introduction on Atmospheric Aerosols, Samplers and  
Measuring Devices**

# **Aerosol research and sub-areas**

*Effects on health and on the environment*

## **Climate change**

NASA – National Air and Space Administration,  
NOAA – National Oceanic and Atmospheric Administration...  
DOE – Department of Energy

## **Air quality**

US-EPA – Environmental Protection Agency...

## **Occupational safety**

NIOSH - National Institute for Occupational Safety and Health...

## **Terrorism**

Homeland Security

## **Nanotechnology**

# Aerosol properties: Size distribution

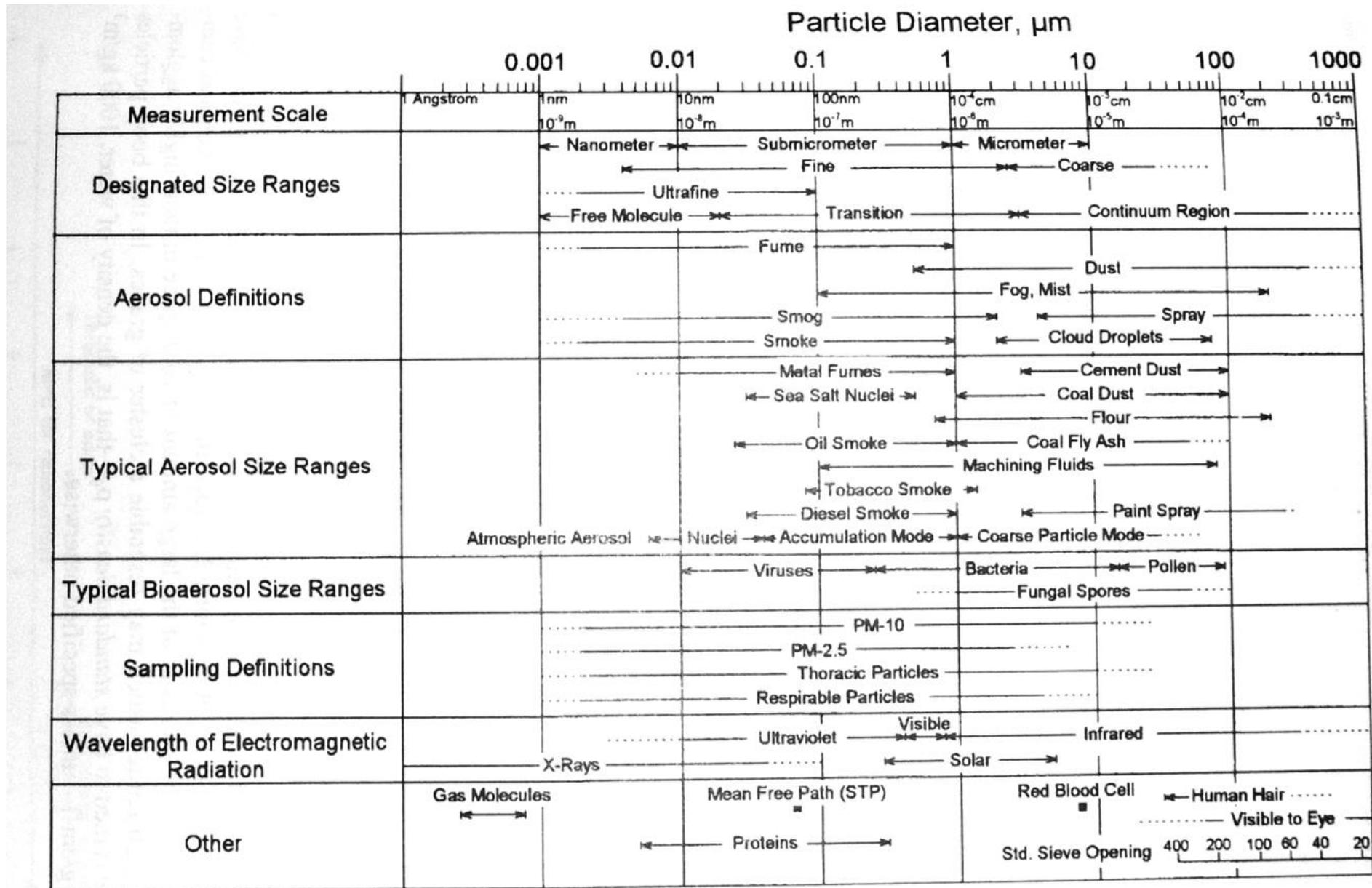


FIGURE 1.6 Particle size ranges and definitions for aerosols.

## Measuring (sampling) Aerosols

Aerosol sampling  
(where):

- Source sampling
- Workplace sampling
- Indoor air sampling
- Ambient air sampling
- Remote sensing

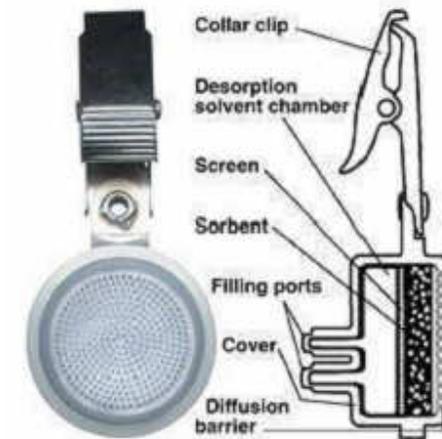
Aerosol sampling  
(how):

- mass effects
- charge effects
- chemical effects
- elemental analysis
- EM interactions

## Measuring (sampling) Aerosols: Passive or active, off-line or online sampling.

The difference between passive and active sampling lies in whether or not a pump is used

**Passive sampling** is based on diffusion, sedimentation, adsorption, or absorption (mostly for gases). Passive samplers are simple, portable, and don't need ancillary equipment. Collect an **integrated sample** over an **extended period of time**.



**Active sampling:** online or off-line analysis.

**Off-line** analysis usually collects a **time integrated sample** over an **extended period of time**. **Online** analysis can generate **instantaneous results**.

**Remote sensing:**

Based on optical properties. Usually analyses an **area integrated sample** over a **short period of time**.

## Measuring (sampling) Aerosols (some examples)

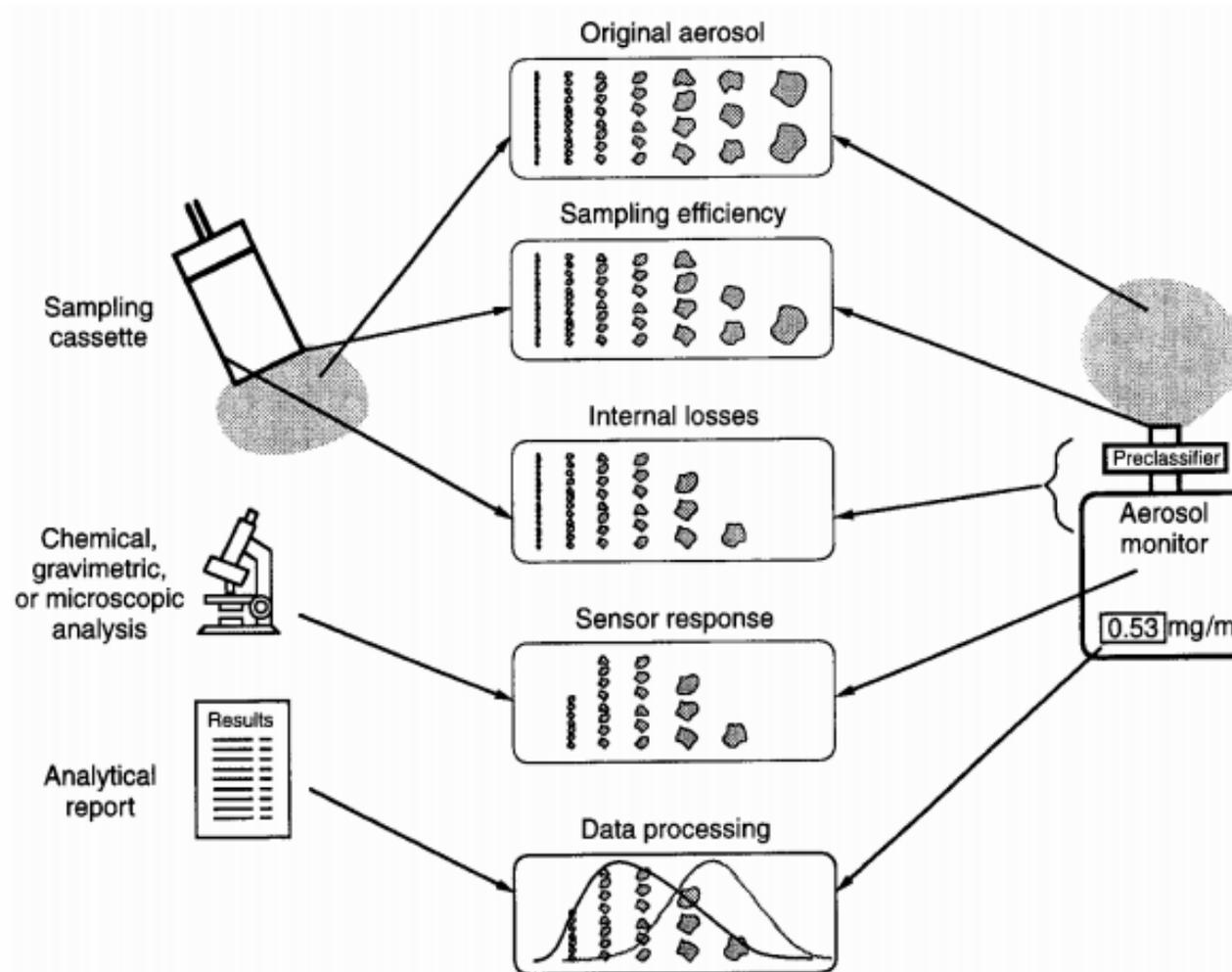
### Air Sampling and Analysis of Particulate Matter

- Direct mass measurements (filters, cascade impactors, cyclones)
  - Off-line mass measurements
  - Online mass measurements
- Tapered Element Oscillating Microbalance (TEOM ®)
- Piezoelectric Microbalance
- Beta Attenuation Monitor
- Pressure Drop Tape Sampler (CAMMS)
- Condensation Nucleus Counters

### Speciation and Major constituents

- Inorganic ions (water extraction followed by IC analysis)
- Elements and trace elements (PIXE, XRF, ICP..)
- EC and OC
- Organic compounds (Solvent extraction and instrumental analysis)

# Measuring (sampling) Aerosols



**Fig. 7-3.** Schematic representation of some important biases in aerosol monitoring. (Adapted from Willeke and Baron, 1990.)

## Factors affecting aerosol sampling:

Decide size fraction to be analyzed: PM<sub>2.5</sub>, PM<sub>10</sub>, total, etc..

*Inlet efficiency* varies as a function of particle aerodynamic diameter, inlet velocity, inlet shape and dimensions, dimensions of the body it is attached to, external wind velocity, and external wind direction. (Respirable aerosol samplers have less problems with inlet effects because the particles being sampled have low inertia and settling velocity.)

*Sizer accuracy*: Theory of classifier separation is based on standard particles ( $d_a$ ,  $\rho = 1$ , spherical). Real world is made of non-ideal particles.

*Air leaks*: Sampling cassettes and fittings should be air-tight and have no leaks.

*Electrostatic losses*: Electric charges in either the sampler (triboelectrically charged) or the particles (Boltzmann equilibrium in air ~1 hr) can create particle acceleration greater than that caused by gravity, inertia, diffusion or other mechanisms. Conductive (~10M $\Omega$ ) samplers have shown little losses.

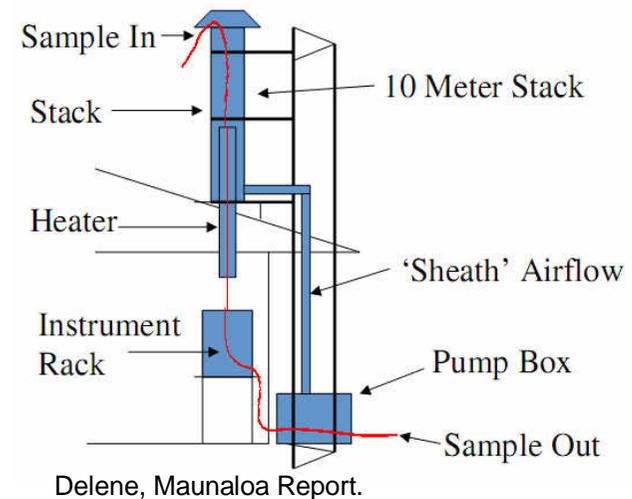
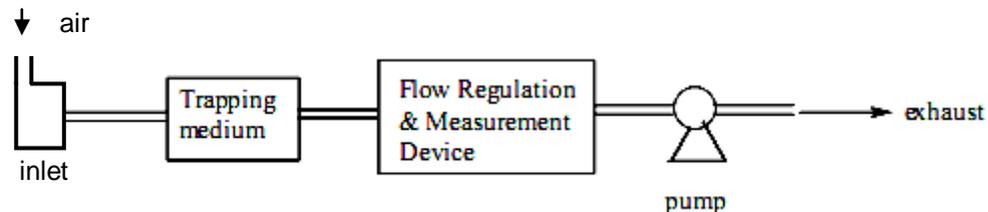
*Sample uniformity* and compatibility with the analytical method.

*Wall losses* (electrostatic, inertial, gravitational and diffusion).

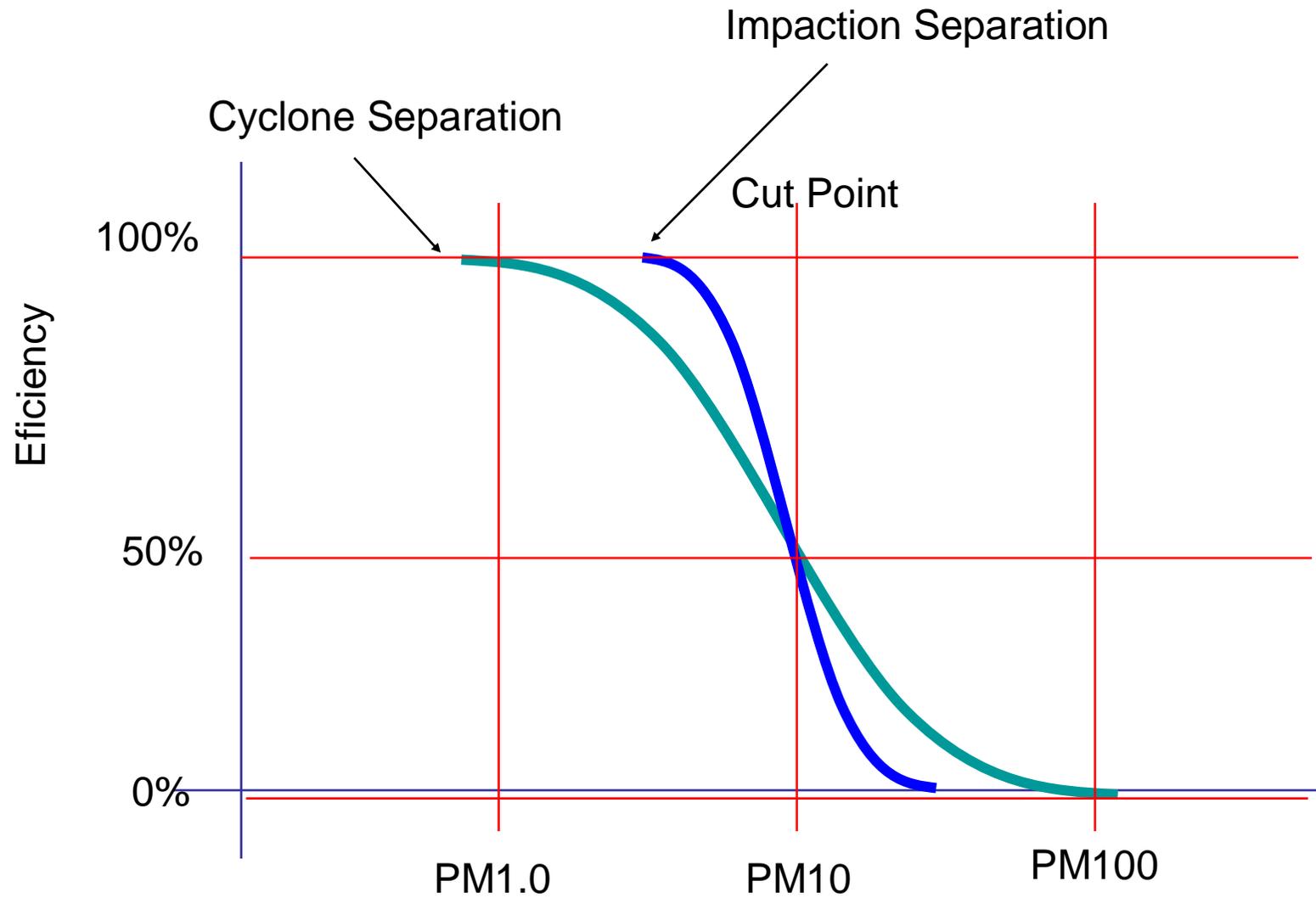
# Measuring (sampling) Aerosols

## Aerosol Sampling

- An aerosol sampler comprises a **suction** sub-system, an **inlet** sub-system, a **filter** (trap) assembly and the associated instrumentation and **control** sub-system.
- The *suction sub-system* acts as the prime mover of the air to be sampled.
- The sampled air made is sucked through a *filter*, which retains the particles (partially or totally). An *impactor* (virtual or real) or *electrostatic sampler* can also be used to trap aerosol particles.
- The flow rate and the period of sampling are controlled by the *suction system* and allied instrumentation.
- In order to prevent unwanted (higher sized) particles from entering the sampling system and interfering with the sampling, the air is passed through an *inlet system*, which diverts the unwanted dust away from the path to the filter.

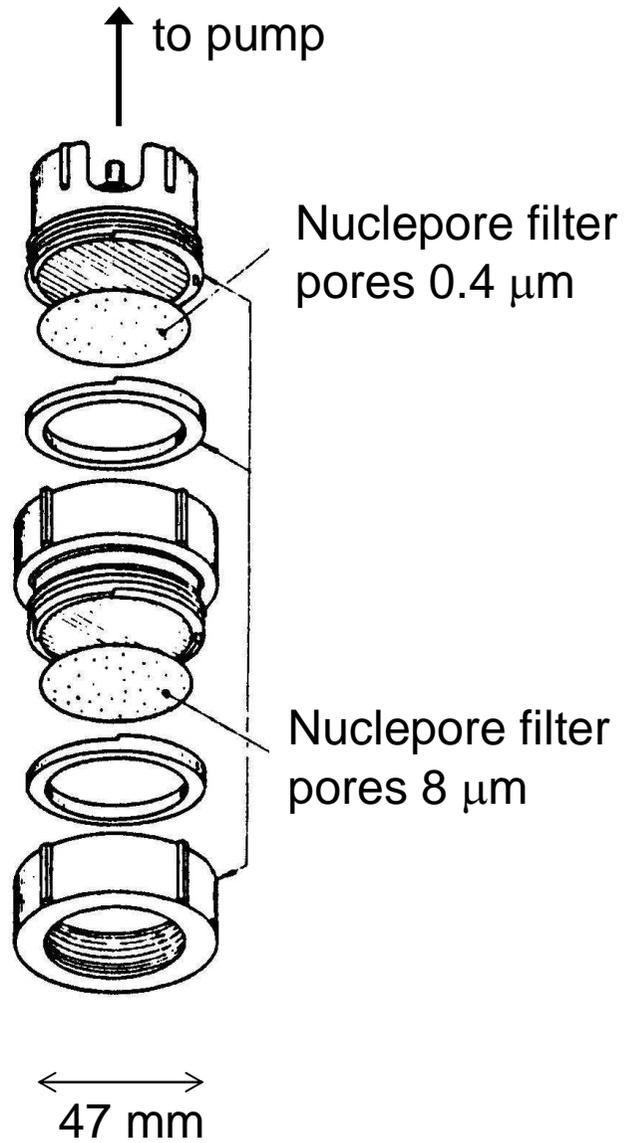


# Inlet (or sampling) efficiency curve



instrumentation

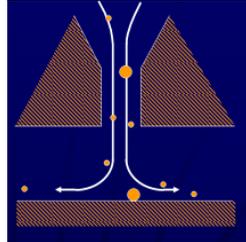
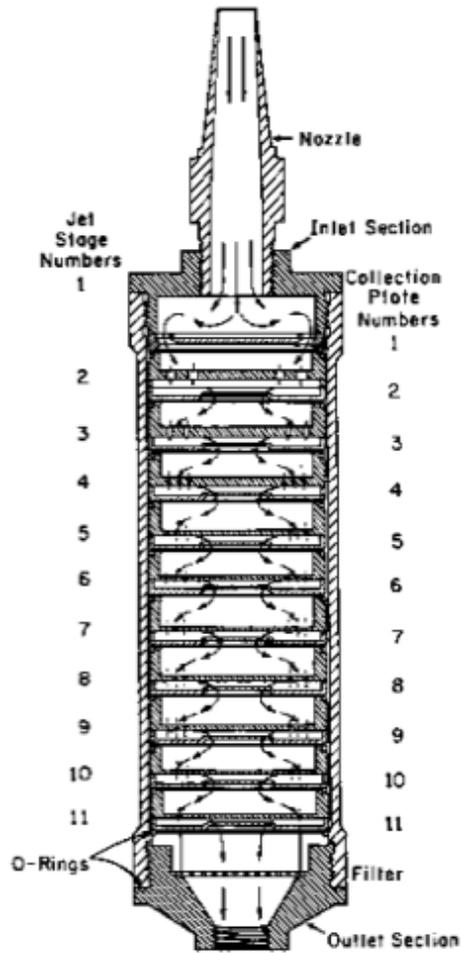
## Stacked Filter Unit



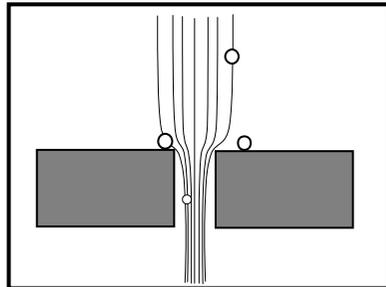
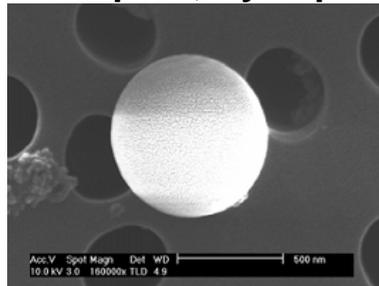
Very low cost  
PM10  
Trace element analysis  
SEM analysis  
Mass (microbalance)  
Reflectometry

# Inertial sampling

## Cascade impactor



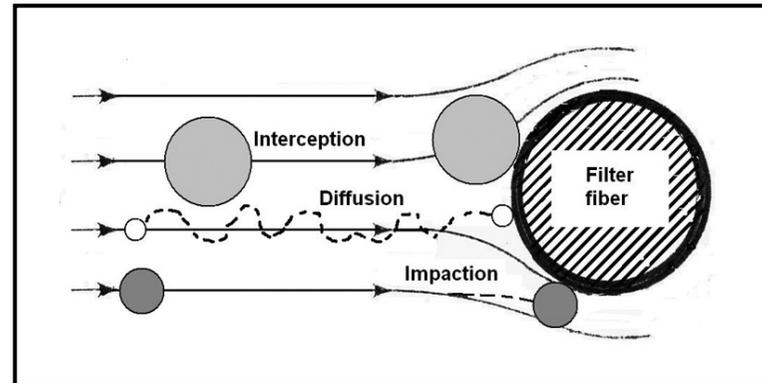
## Ion track filter Nuclepore, Cyclopore



## High-Vol sampler Uses glass-fiber filter



## fiber filter

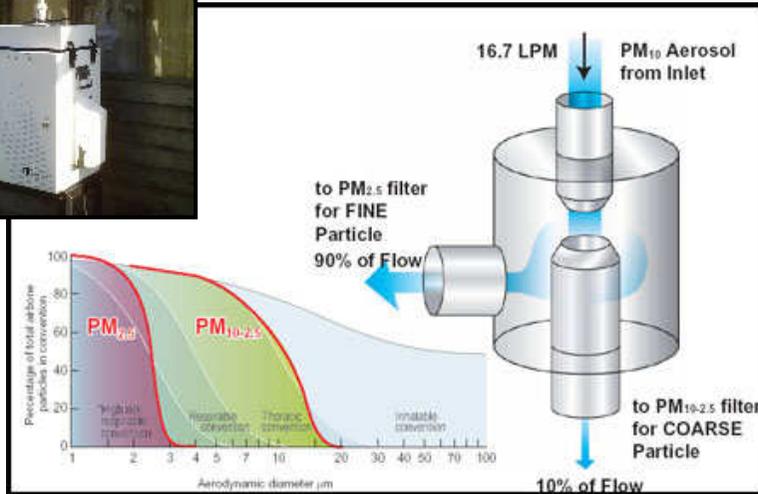


[www.asbestosguru-oberta.com/hepa.htm](http://www.asbestosguru-oberta.com/hepa.htm)

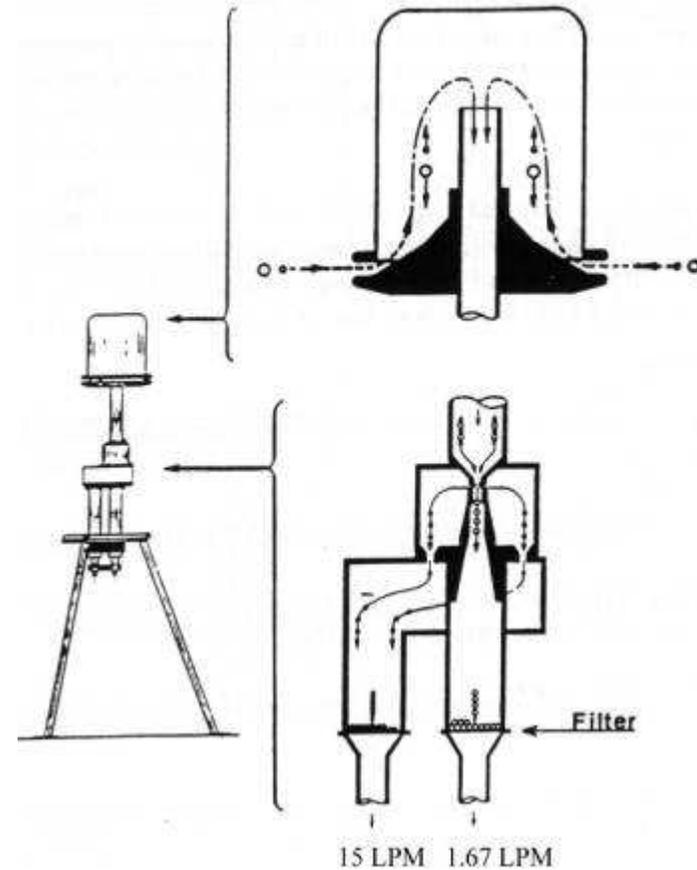
# Inertial sampling



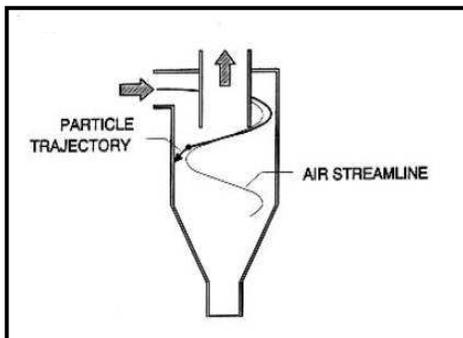
Virtual impactor  
Dichotomous sampler



DICHOTOMOUS SAMPLER  
(VIRTUAL IMPACTOR)  
PRINCIPLE OF OPERATION



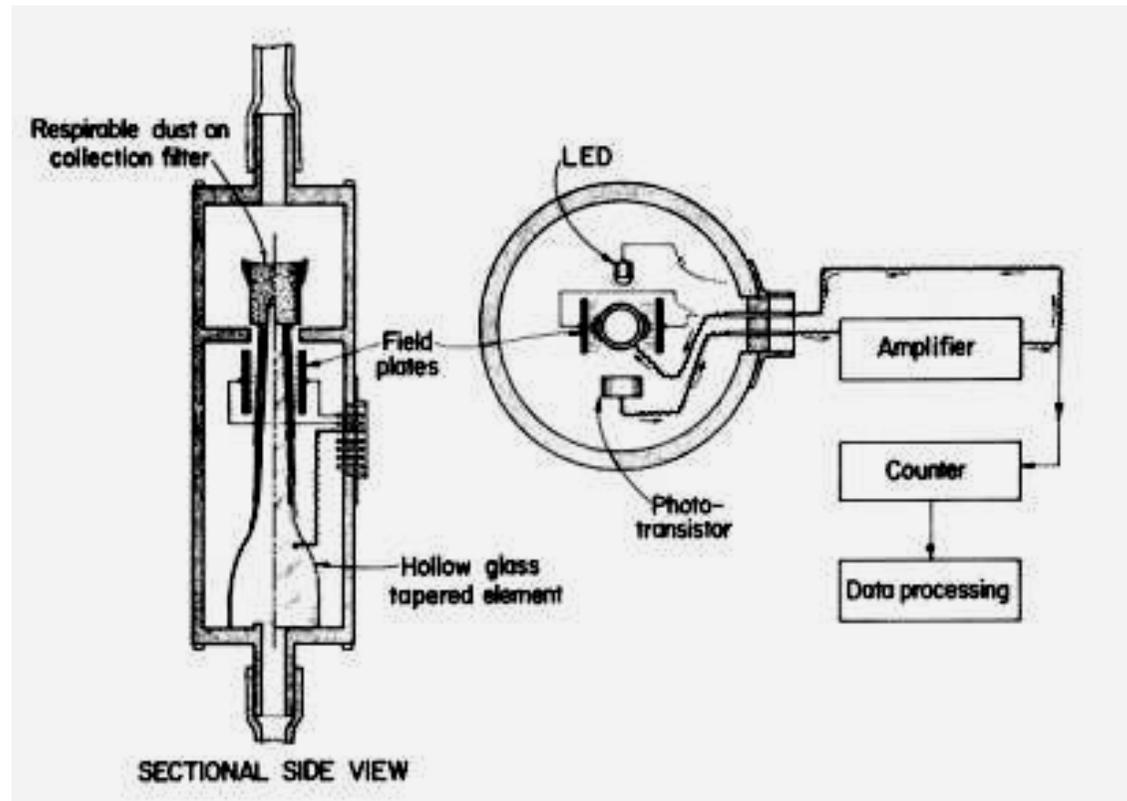
## Cyclone



# Measuring (sampling) Aerosols: TEOM



TEOM-Filter



TEOM (Tapered Element Oscillating Microbalance): The particle mass is determined by continuous weighing of particles deposited onto a filter. The filter is attached to a vibrating hollow tapered glass element. The frequency of mechanical oscillation of this element is a function of its mass.

$$m = K \left( \frac{1}{f^2} - \frac{1}{f_0^2} \right)$$

# IMPROVE Monitoring Program

The Interagency Monitoring of Protected Visual Environments

- Established in 1985 to aid the creation of Federal and State implementation plans for the protection of visibility in Class I areas - 1977 CAA amendments

## IMPROVE Monitoring

- Monitoring Began in March 1988
- **Aerosol** – particle sampling/analysis for six major species & trace constituents to aid in source attribution (24 hour samples twice weekly; every 3<sup>rd</sup> day starting in 2000)
- **Optical** – extinction by **transmissometer** &/or scattering by **nephelometer** (hourly) plus absorption on particle filters (24-hour)
- **Scene** – color **photography** to document scenic appearance (typically 3 photos/day)
  - photographic spectrums of a range of visibility conditions are generated from 5 years of photos

# IMPROVE Aerosol Samplers

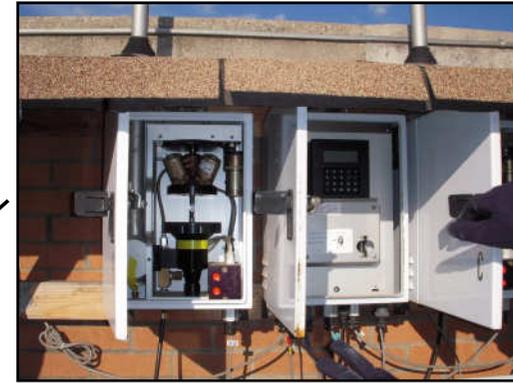
- Four independent sampling modules
- Prior to 2000, two 24 hour samples were collected twice a week, after 2000, samples collected every three days.

Module	Filter	Size	Variable	Analysis
A	Teflon	PM2.5	mass	gravimetric
			Na-Mn	Proton Induced X-Ray Emission (PIXE)
			Fe-Pb	X-ray Fluorescence (XRF)
			total H	Proton Elastic Scattering
			optical absorption	Hybrid Integrating Plate/Sphere (HIPS)
B	Nylon	PM2.5	sulfate, nitrate	Ion Chromatography
C	Quartz	PM2.5	OC, EC in 8 fractions	Thermal Optical Reflectance
D	Teflon	PM10	mass	gravimetric

# IMPROVE - UMBC



IMPROVE – UMBC on top of the Physics building.



IMPROVE filter holder and control unit



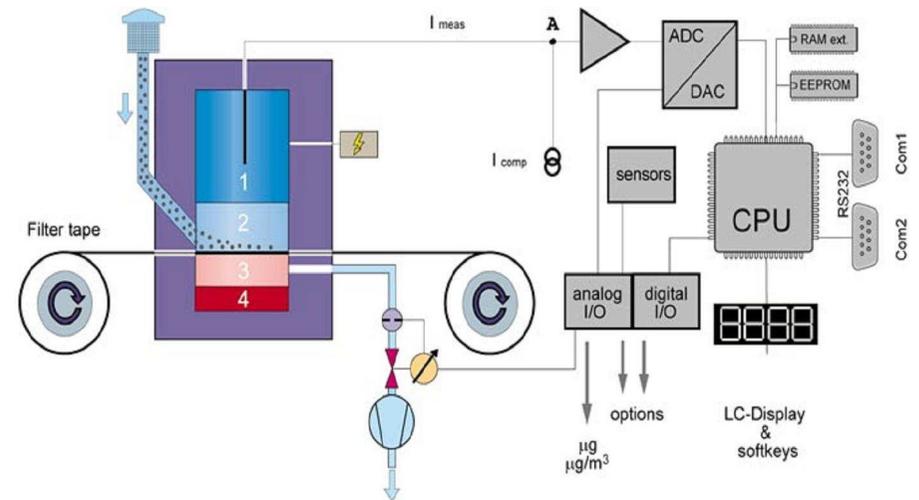
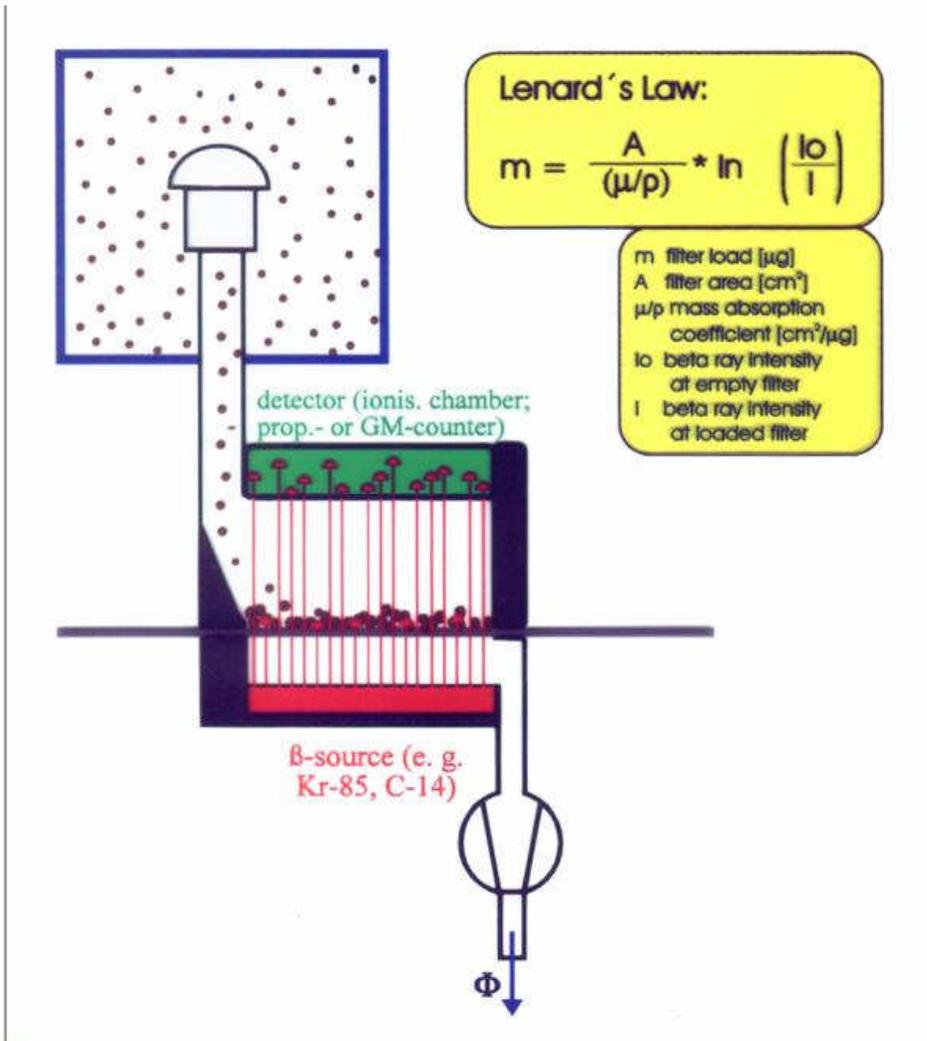
IMPROVE Pumping Unit



- Began with 20 sites in 1988, today 163 monitoring sites are in operation
- 116 monitoring sites collected some data in 2000

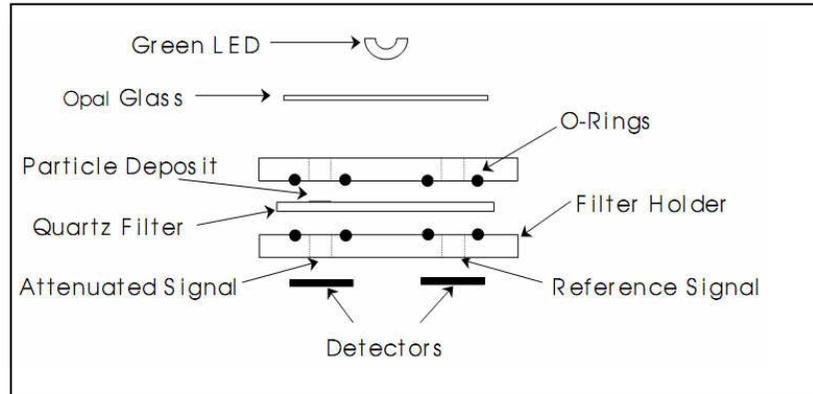
Improve aerosol database: [http://vista.cira.colostate.edu/improve/Data/DataQuery/IMP\\_Aer\\_Data\\_Acc](http://vista.cira.colostate.edu/improve/Data/DataQuery/IMP_Aer_Data_Acc)  
 Improve aerosol ASCII files: [http://vista.cira.colostate.edu/improve/Data/IMPROVE/IMPLocTable\\_Data.asp](http://vista.cira.colostate.edu/improve/Data/IMPROVE/IMPLocTable_Data.asp)

# Indirect Mass Measurement – $\beta$ attenuation

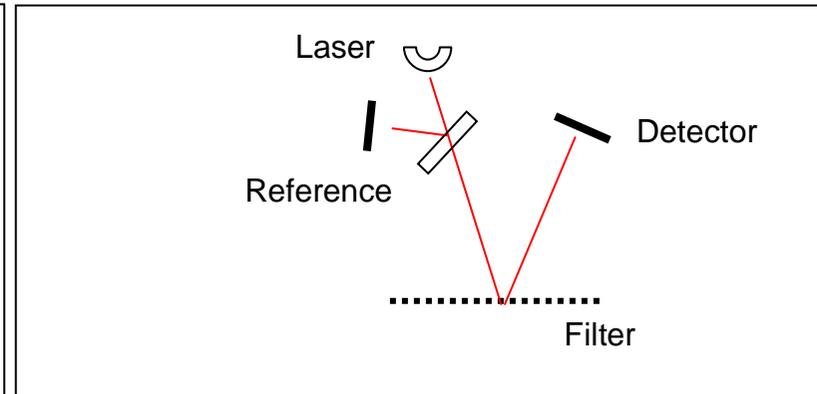


# Measuring (sampling) Aerosols: Optical methods

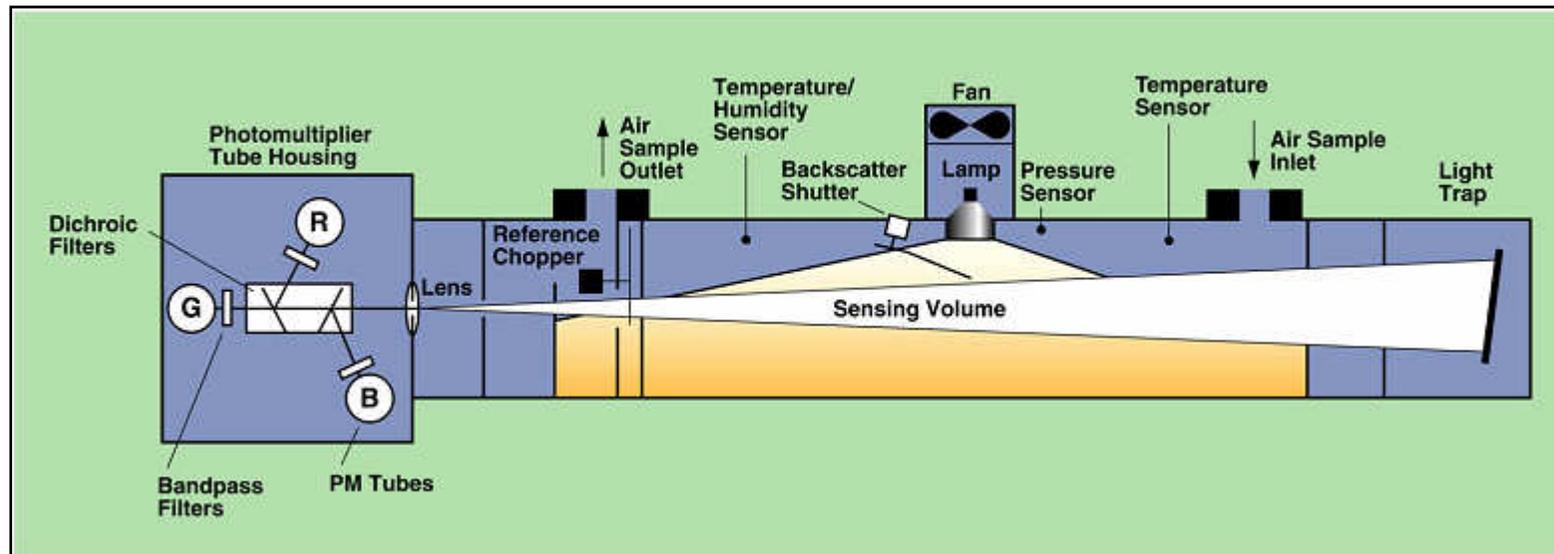
## Particle Soot Absorption Photometer



## Optical Reflectometer

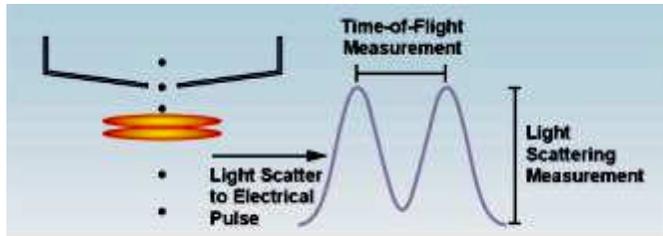


## Integrating Nephelometer

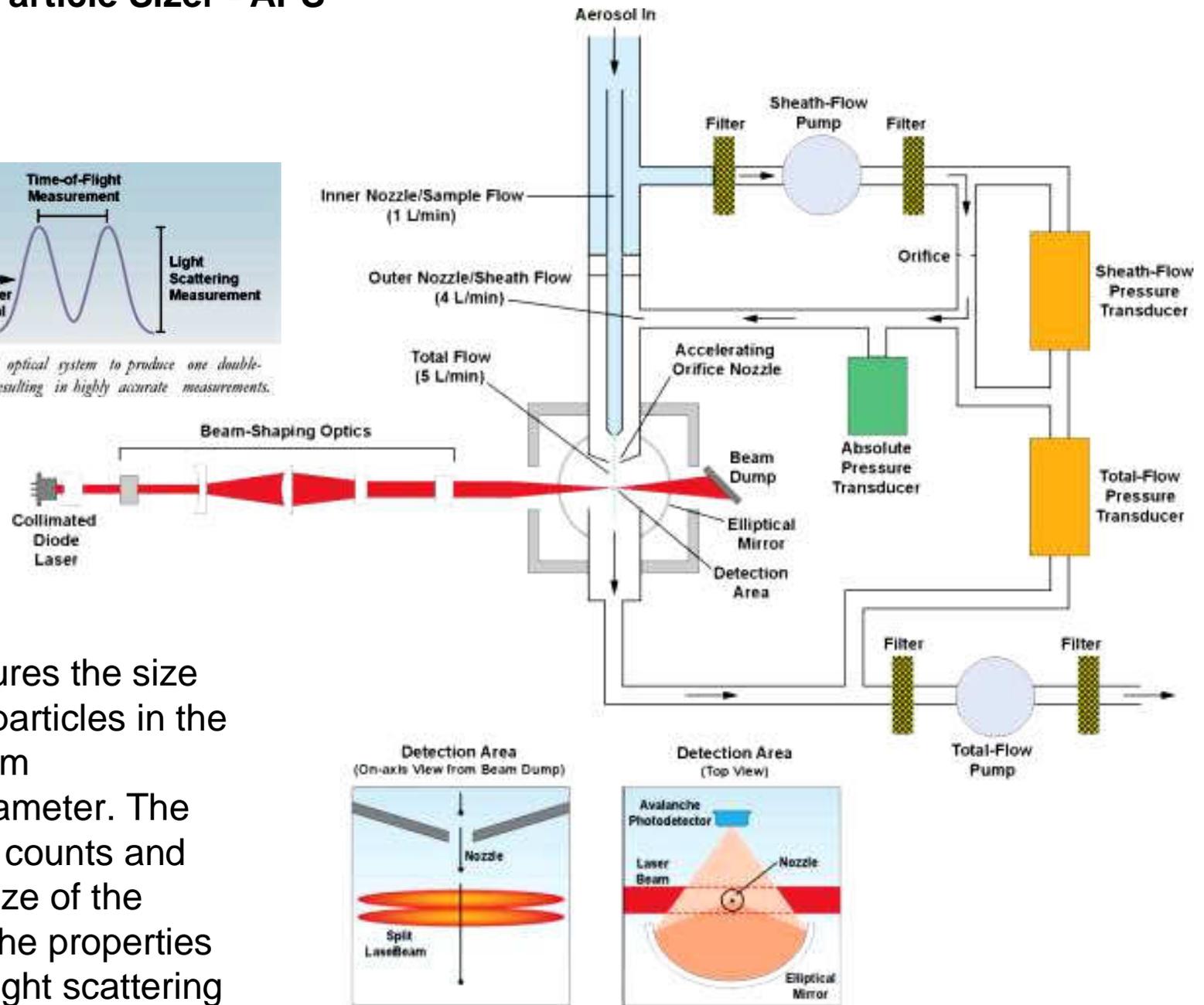


TSI 3563 Nephelometer schematic

# Aerodynamic Particle Sizer - APS



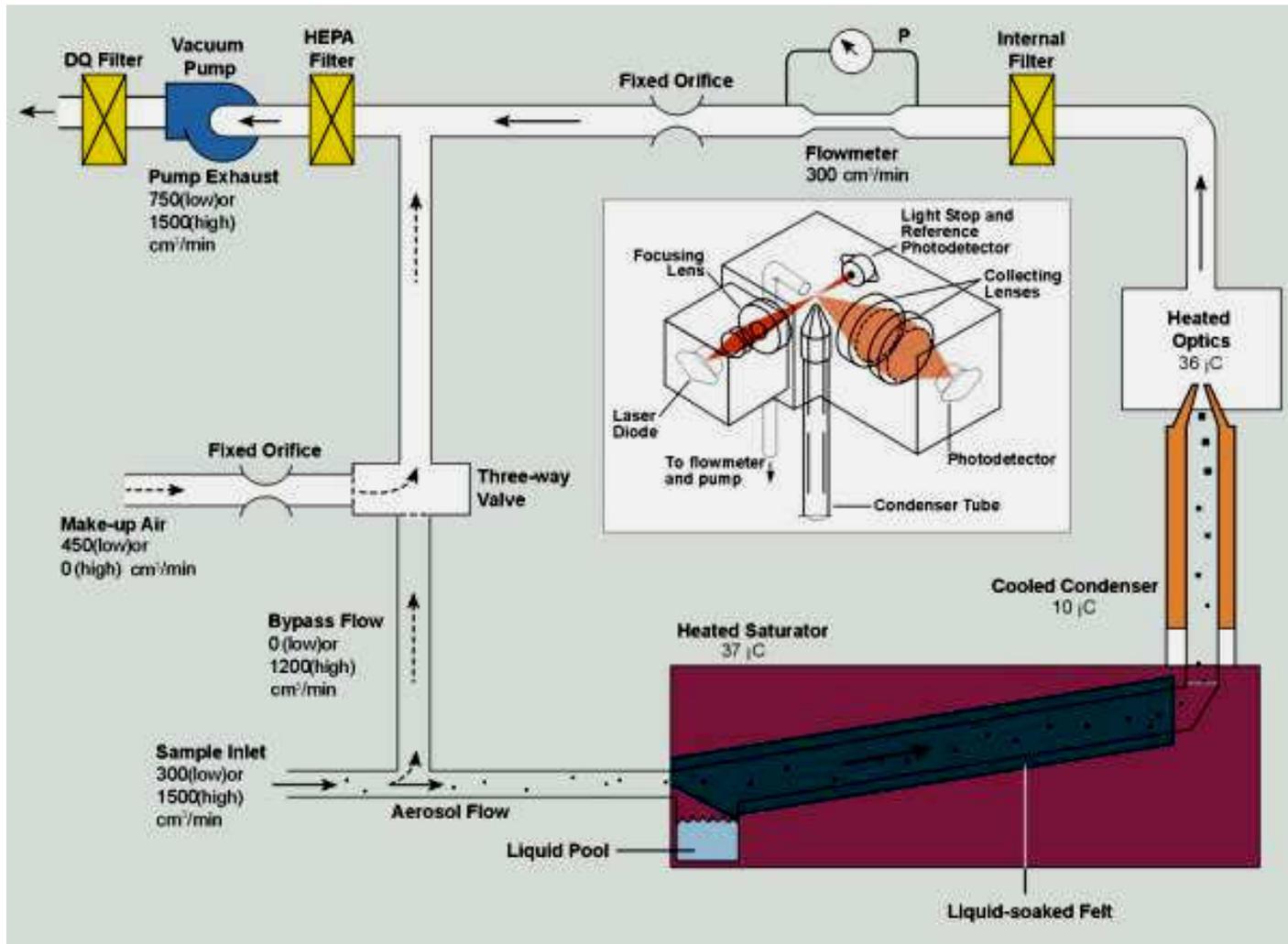
*The Model 3320 uses a patented optical system to produce one double-crested signal for each particle, resulting in highly accurate measurements.*



The APS measures the size distributions of particles in the range 0.5–20  $\mu\text{m}$  aerodynamic diameter. The instrument both counts and measures the size of the particles using the properties of the particle (light scattering and settling velocity).

# Condensation Nucleus Counter

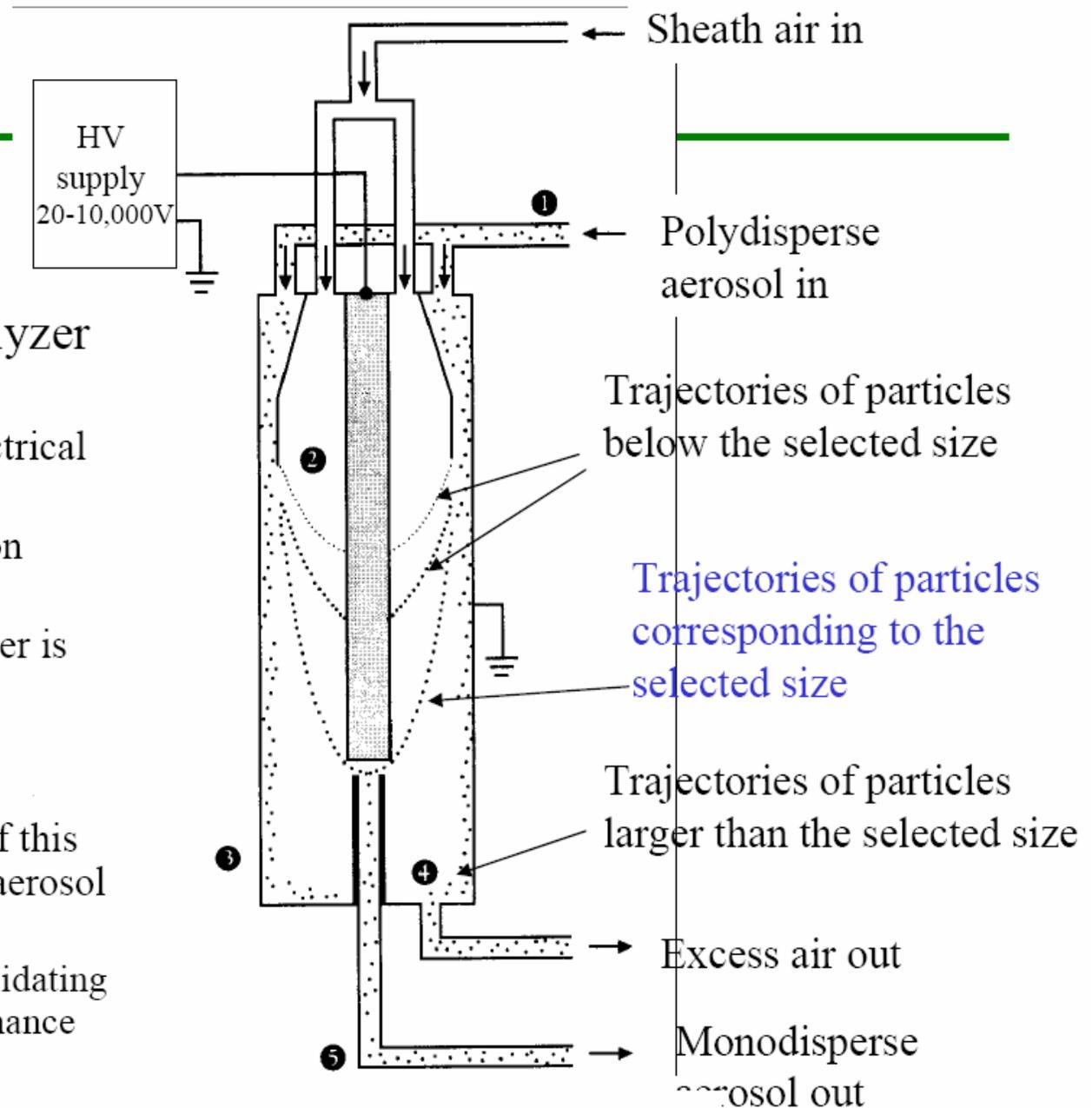
The CPC counts particles with a diameter of a few nanometres up to about one micrometer. In the CPC, the particles pass through a “cloud” of evaporated alcohol which condensates on the particle and makes them much larger and easy to detect/count. This uncontrolled increase makes it possible to count the particles but impossible to size classify them.



# DMA

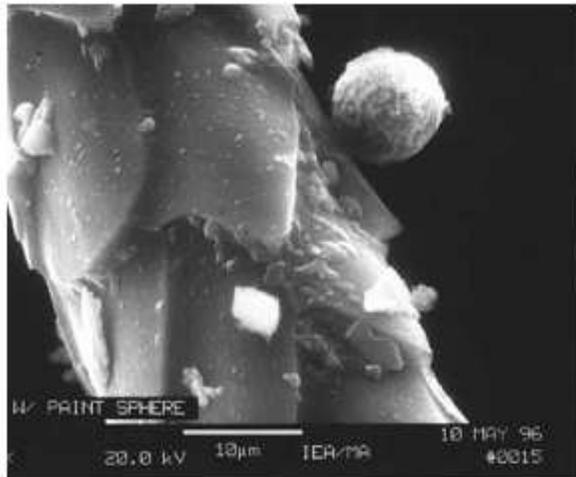
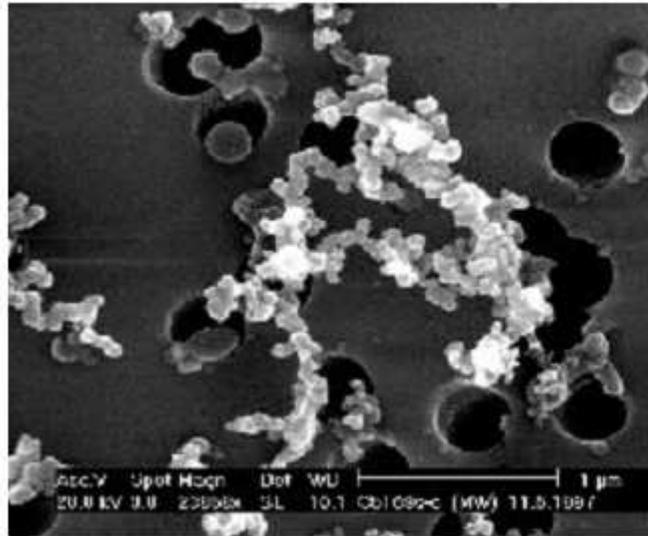
## Differential Mobility analyzer (DMA)

- Sizes particles by their electrical mobility
- Usually very high resolution measurements are possible
- Downstream particle counter is required for particle size distribution measurements
  - Usually a CNC
- Due to the high accuracy of this instrument it is a standard aerosol instrument
  - Used for testing and validating new instrument performance



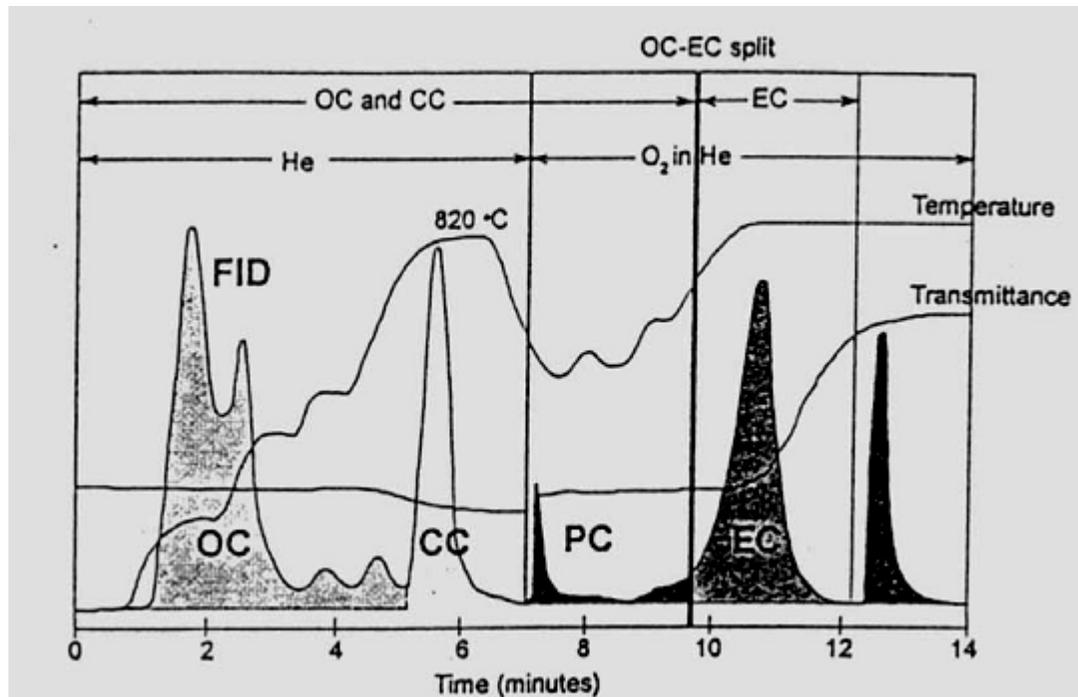
TSI 3080 DMA

# Scanning Electron Microscopy



## Analyzing Aerosols: CARBON

- Organic Carbon (OC): comprises of hundreds of individual organic compounds.
- Elemental Carbon (EC) also called black carbon, soot, graphitic carbon
- Carbonate Carbon (i.e.,  $K_2CO_3$ ,  $Na_2CO_3$ ,  $MgCO_3$ ,  $CaCO_3$ )



Determination of EC and OC by Thermal Optical Transmission (TOT). The analysis proceeds in two stages:

- 1) A filter is submitted to volatilization at temperatures ranging from ambient to  $\sim 850^{\circ}\text{C}$  in a pure helium atmosphere.
- 2) An Oxygen (5%)-Helium mix is introduced after the oven temperature is reduced, followed by increasing the oven temperature to  $860^{\circ}\text{C}$ .

Evolved carbon is catalytically oxidized to  $\text{CO}_2$  in a bed of granular  $\text{MnO}_2$  (held at about  $900^{\circ}\text{C}$ ), reduced to  $\text{CH}_4$  in an Ni/firebrick methanator (at  $450^{\circ}\text{C}$ ), and quantified as  $\text{CH}_4$  by an FID.



## Measuring (sampling) Aerosols: Filter Media

Filter Type	Physical Characteristics	Filter Type	Physical Characteristics
Ringed Teflon Membrane	Thin membrane stretched between polymethylpentane ring	Nylon membrane	Thin membrane of pure nylon
Pure quartz fiber	Mat of pure quartz fibers	Polycarbonate capillary pore membrane	Smooth, thin, polycarbonate surface with straight through capillary holes
Mixed Quartz fiber	Quartz fibers with ~5% borosilicate content	Teflon coated glass fiber	Thick mat of borosilicate glass fiber with a layer of Teflon on the surface
Backed Teflon membrane	Thin membrane mounted on thick polypropylene backing	Glass fiber	Borosilicate glass fiber
Cellulose fiber	Thick mat of cellulose fibers, often called "paper" filter		

# Measuring (sampling) Aerosols

## Offline direct mass measurements of filters

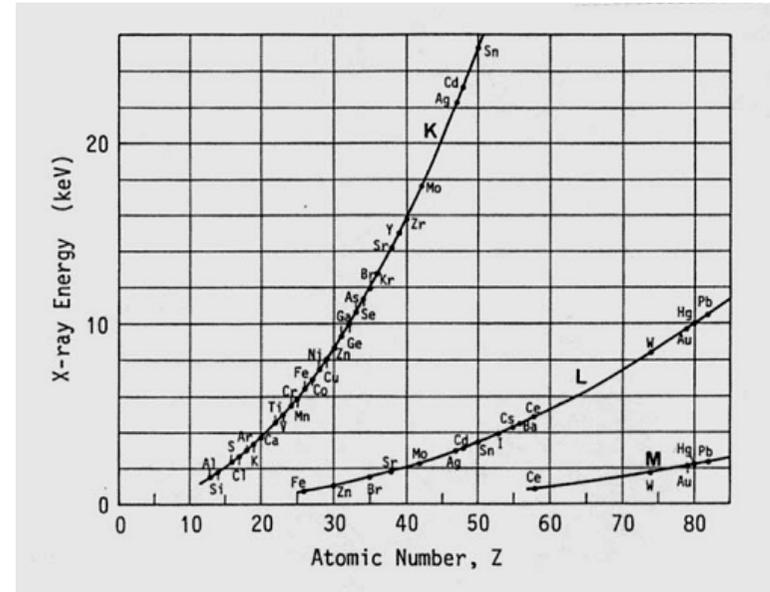
- Filters are weighed using a microbalance in a temperature and relative humidity controlled environment before and after collection of particles.
- Filters need to be equilibrated for 24 hours at a constant (within  $\pm 5\%$ ) relative humidity between 20% and 40% RH, and at a constant temperature (within  $\pm 3^\circ\text{C}$ ) between  $15^\circ\text{C}$  and  $20^\circ\text{C}$ . These values are best to conserve the particle deposits, to minimize the liquid water absorbed by soluble compounds, and the loss of volatile species.
- The main interference in gravimetric analysis of filters results from electrostatic charges, which induce forces between the filter and the balance. The charge can be removed using a low-level radioactive source or a corona source prior to and during weighing.
- Filters for mass analysis are chosen to have low dielectric constants, high filter integrity, and inertness with respect to absorbing water vapor and other gases.

# Trace Element Analysis

## Elemental Analysis

- Nondestructive techniques
  - Instrumental Neutron Activation Analysis (INAA)
  - Particle-Induced X-ray Emission
  - Photon-Induced X-ray Fluorescence (XRF)
- Destructive techniques
  - Atomic Absorption Spectrometry (AAS)
  - Inductively Coupled Plasma with Atomic Emission or Mass Spectrometry –ICP-AES/MS

## PIXE - XRF



## PIXE and XRF

Very thick filters scatter much of the excitation energy, thereby lowering the signal-to-noise ratio for XRF and PIXE. This requires

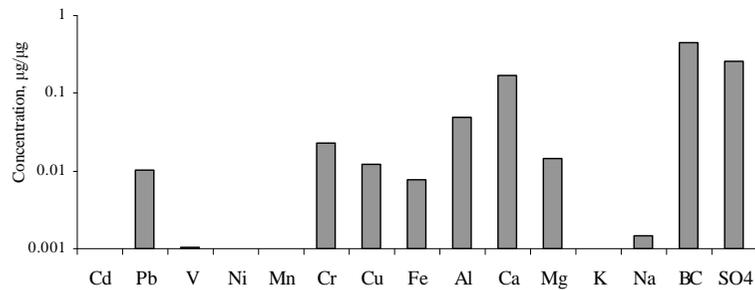
- thin membrane filters
- deposits in the range of 10 to 50  $\mu\text{g}/\text{cm}^2$

Quartz fiber filters are not suitable for PIXE and XRF analysis

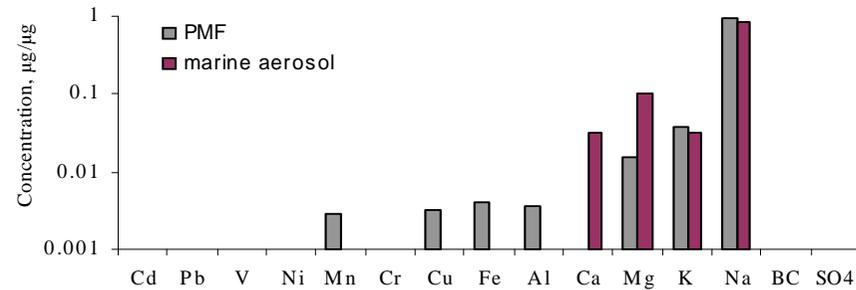
- large amount of Na, Al, and Si present in quartz filters
- the higher thickness that raises the background in XRF and PIXE analysis

# Trace Element Analysis of Aerosol

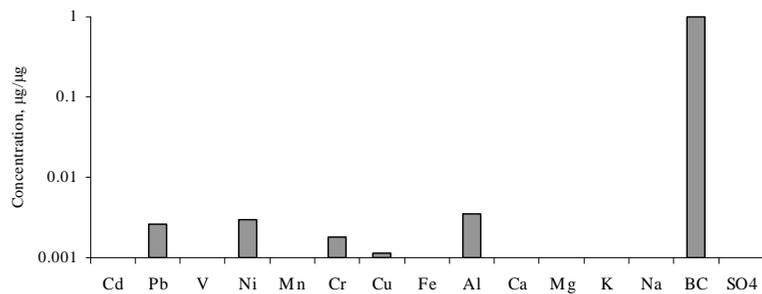
Road dust: BC, SO<sub>4</sub><sup>2-</sup>, crustal metals



Marine aerosol



Vehicles: diesel and gasoline exhaust emissions



# Receptor Modelling

A mass balance equation to account for all **m chemical species** in the **n samples** as contributions from **p independent sources**

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj}$$

Where

$i = 1, \dots, n$  samples,  
 $j = 1, \dots, m$  species and  
 $k = 1, \dots, p$  sources

**Sources Known: Chemical Mass Balance (Watson et al., 1990)**

**Sources Unknown: Principal Component Analysis (Thurston and Spengler, 1985); Unmix (Henry, 2000); Positive Matrix Factorization (Paatero and Tapper, 1993; Paatero, 1997)**