Atmospheric Chemistry Measurements

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ATM 505 – Lecture 5

April 6, 2022

References and Acknowledgements

- Books:
  - Aerosol Measurement: Principles, Techniques, and Applications. Baron and Willeke, Wiley Interscience (2001)
  - Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles, 2nd Edition, Hinds (1999)
- Paper:
  - A review of atmospheric aerosol measurements, McMurry, Atmospheric Environment (2000)
- Lectures:
  - Steven Massie and Jim Smith
  - Berko Sierau (for Joel Thorton)

Kinds of Measurements: Research vs Monitoring

- Research Measurements
  - Address scientific question or problem
  - University scientists, private foundations, national labs
  - Limited duration (a few weeks to a few months, typically)
  - Goal is to write and publish peer-reviewed papers
  - Often use state-of-the-art or research methods and measure species that are challenging to capture
- Monitoring
  - Done to establish compliance with air pollution regulations
  - Mainly states, localities, and indigenous nations
  - Long Term – often many decades
  - Well established methods and commercial instruments
  - Limited number of species measured

Measurements of Gas Phase Species

- Gaseous Criteria Pollutants (things that are specifically regulated by the Clean Air Act) - monitoring
- Greenhouse Gases
- Volatile Organic Carbon species (VOCs)
- Reactive and short lived species (research measurements)

Satellite vs in situ

- Satellite measurements play an increasingly important role
  - Measure column density (molecules cm^{-2}) and not concentration (molecules cm^{-3})
  - Only have good data for a limited number of species (~10)
- In situ measurements
  - Collect samples and measure true concentrations (mostly)
  - Hundreds (thousands?) of sites
  - Hundreds of species measured

Methods - Spectroscopy and Chromatography

- **Spectroscopy** – takes advantage of the interaction of light and matter. Chemical substances (atoms and molecules) interact with specific wavelengths of light in ways that allow them to be "fingerprinted"
  – Absorption: used for O_3, CO, CO_2, and more
  – Fluorescence: used for SO_2, NO_2, Cl, OH, and more
  – Chemiluminescence: mainly used for NO (and NO_2)

Chromatography

- **Gas Chromatography** – relies on the slight differences in structure and reactivity of a class of similar species to **separate** the species in a long, very narrow column coated on the inside with a mildly reactive coating material.
- **Separated compounds** exit the column in "time order" and are detected by one of numerous methods
- **Detection methods** include mass spectrometry, flame ionization, photoionization, electron capture, and numerous others

Matching Species with Methods

- Criteria Pollutants: in situ O_3 and CO (Absorption); SO_2 (pulsed fluorescence), and NO/NO_2 (chemiluminescence)
- VOCs: Gas chromatography on whole air samples collected in canisters and transported to analysis labs
- GHGs: in situ infrared absorption and sample collection with GC; increasingly sensitive laser based IR absorption
- Reactive species: often research, one of a kind, and state-of-the-art instruments, laser based, mass spec based


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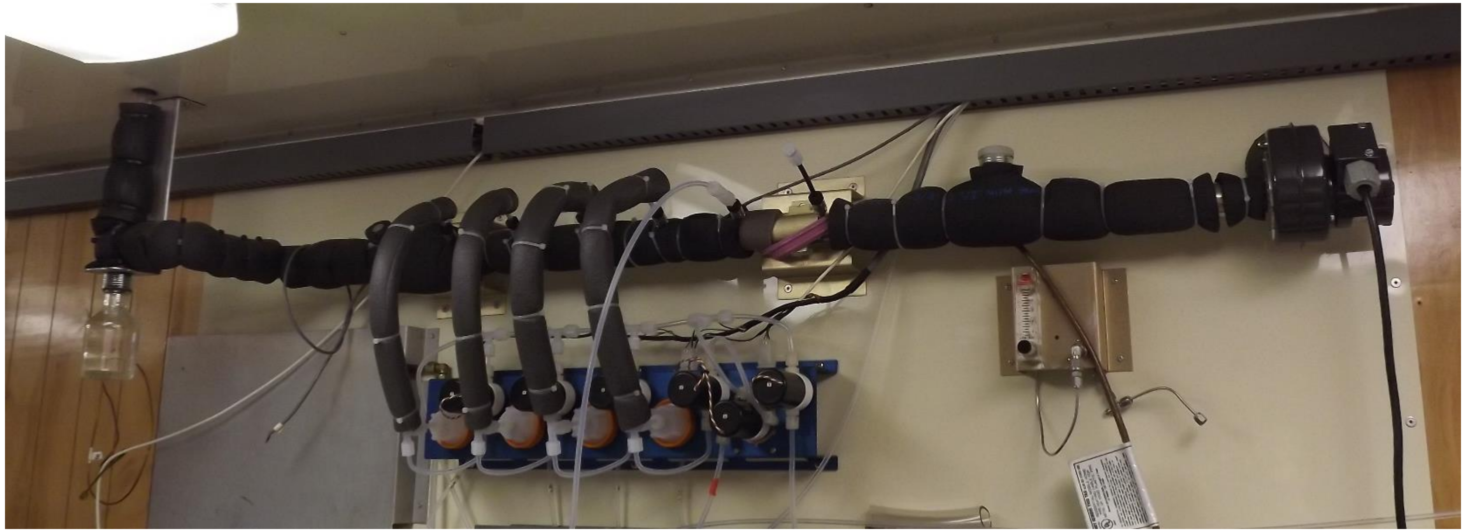

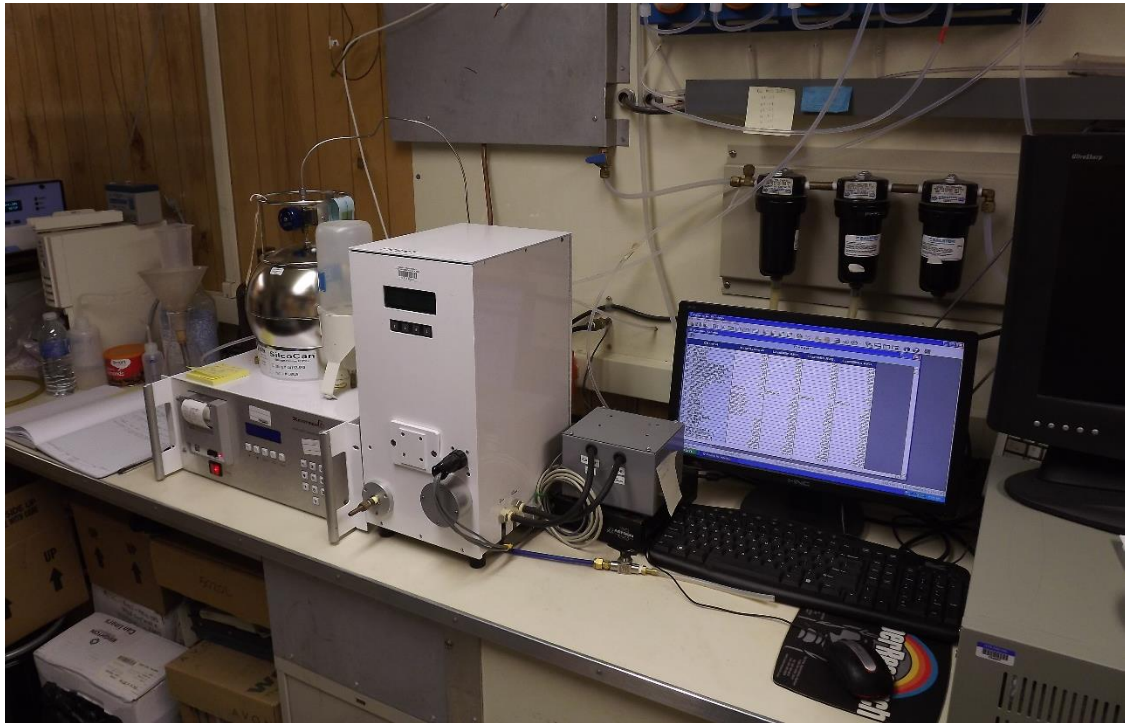
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Types of Aerosol Measurements

- Aerosol Mass Concentration (regulated quantity – NAAQS)
  - Filters (gravimetric)
  - Continuous (various)
- Physical Properties
  - Number Concentration
  - Size Distribution
  - Shape
  - Optical properties –scattering and absorption (index of refraction)
- Chemical Composition
  - Filters (various)
  - Continuous (various)

Mass Concentration

- Units are micrograms per cubic meter - $\mu g/m^3$.
- The current US National Ambient Air Quality Standard (NAAQS) regulates $PM_{2.5}$ measured on a teflon filter.
- Previous NAAQS regulated first Total Suspended Particles (TSP), then PM_{10}
- The gravimetric method (a Federal Reference Method or FRM) is described in great detail, but the result cannot be considered a “true scientific measurement”! (This is due to the complexity of the challenge, and not incompetence.)
- Probably the single largest complication is due to aerosol **volatility**.
- In spite of this measurement shortcoming, this data is consistent, reliable, and “actionable” in a regulatory sense.

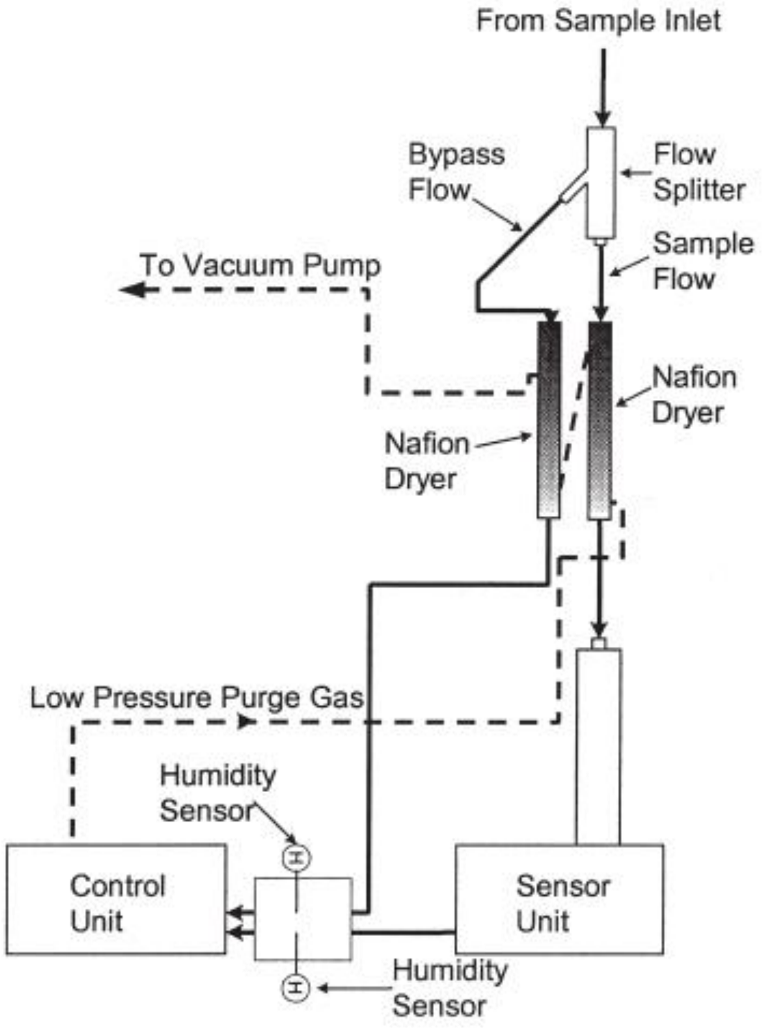
The FRM – in brief

- Filters are specified, inspected and individually stamped with a number.
- Filters are conditioned and pre-weighed, put into cassettes – then sent to sampling locations.
- Filter cassettes are loaded into samplers that have carefully audited size cutpoint and flow characteristics. They are sampled for 24 hours at the specified flow rate.
- After removal from the sampler, filters are kept cool before and during shipment back to the analysis lab (and upon arrival).
- At the lab, filters are conditioned as before and weighed.
- Mass comes from the difference between the two weighings: flow, temperature and pressure determine the sample volume. Recall - $\mu g/m^3$.

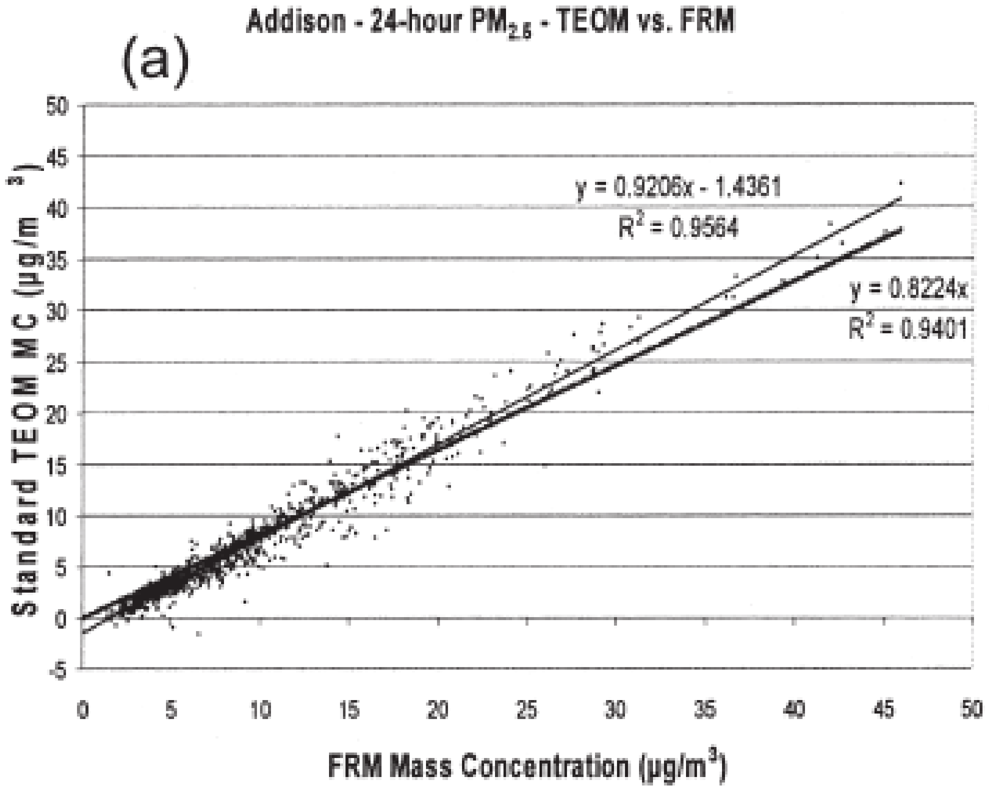
Continuous Mass Measurements

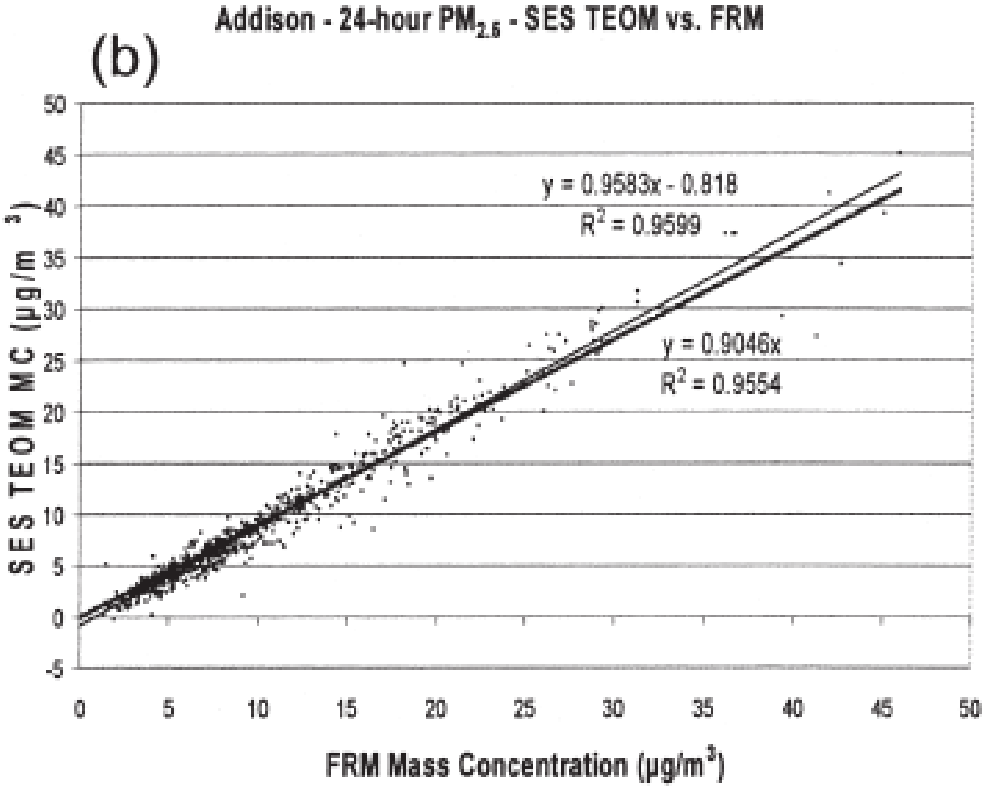
- TEOM – Tapered Element Oscillating Microbalance. Uses the relationship between oscillation frequency and mass to "directly" measure mass changes.
- β-attenuation (where β is an electron) – uses measurement of the reduction in intensity of β particles passing through a particle laden filter tape. The relationship between attenuation and particle concentration is "reasonably independent " of the chemical composition of the atmosphere.
- Optical methods – use the physical properties of scattering or extinction (more later).

Schematic of TEOM



Continuous vs. 24-hour Filter Samples





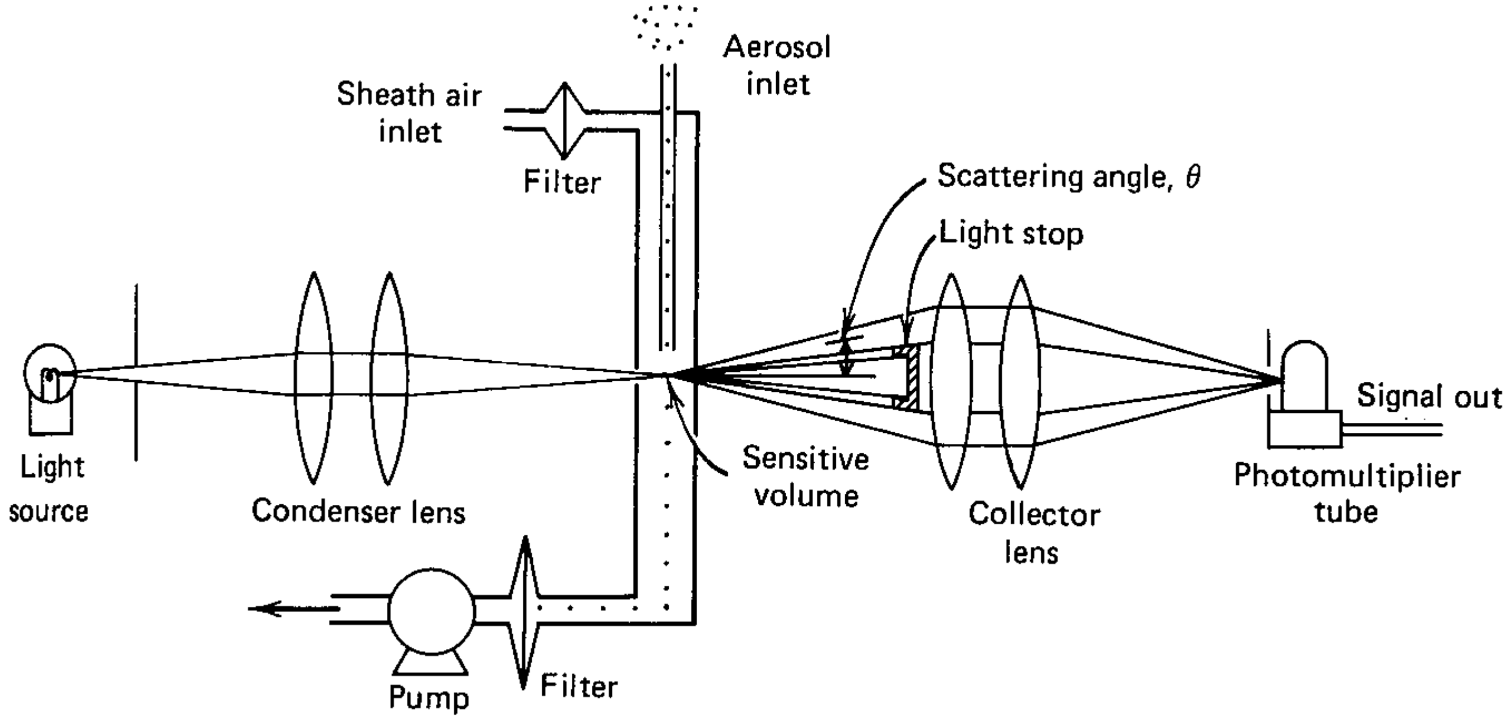
Measurements of Physical Properties

- Particle number concentration
- Particle Size Distribution (PSD)
- Particle Shape (not covered here – not routinely or easily measured)
- Optical Properties (A subject unto itself – we will only scratch the surface)

Particle Number Concentration

- Aerosol Electrometer – aerosols in the atmosphere have a steady-state charge distribution, that is a mixture of positive, negative, and (mostly) neutral charges. If this distribution is known and can be described – and it often is and can be – then a sensitive electrometer can measure total aerosol concentration.
- Condensation Particle Counter (CPC) – easiest and most reliable method.

Optical Particle Counter (OPC): ~ 100 nm to 5 μm



Size limits defined by Mie scattering, and Mie scattering theory is used to interpret integrated scattered intensity.

Advantages:

- Can detect small particles (but not the smallest)
- Non-intrusive
- Instantaneous and continuous information

Disadvantages:

- too sensitive to small changes in
  - refractive index
  - scattering angle
  - particle size
  - particle shape

Signal vs Particle Diameter

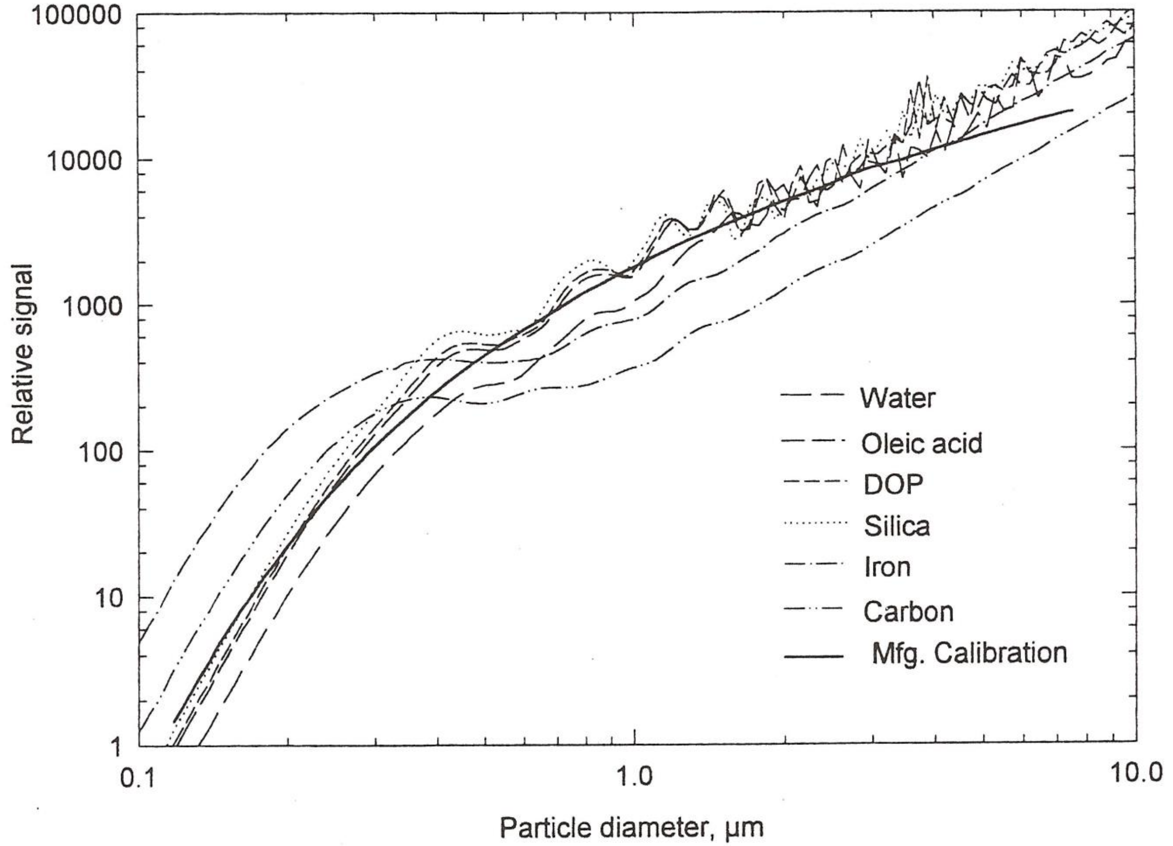


FIGURE 16.16 Calculated response curves for six materials and manufacturer's calibration curve for model LAS-X® (PMS, Inc., Boulder, CO) optical particle counter.

Hinds

Condensation Particle Counter

Saturate an aerosol with water or alcohol vapor

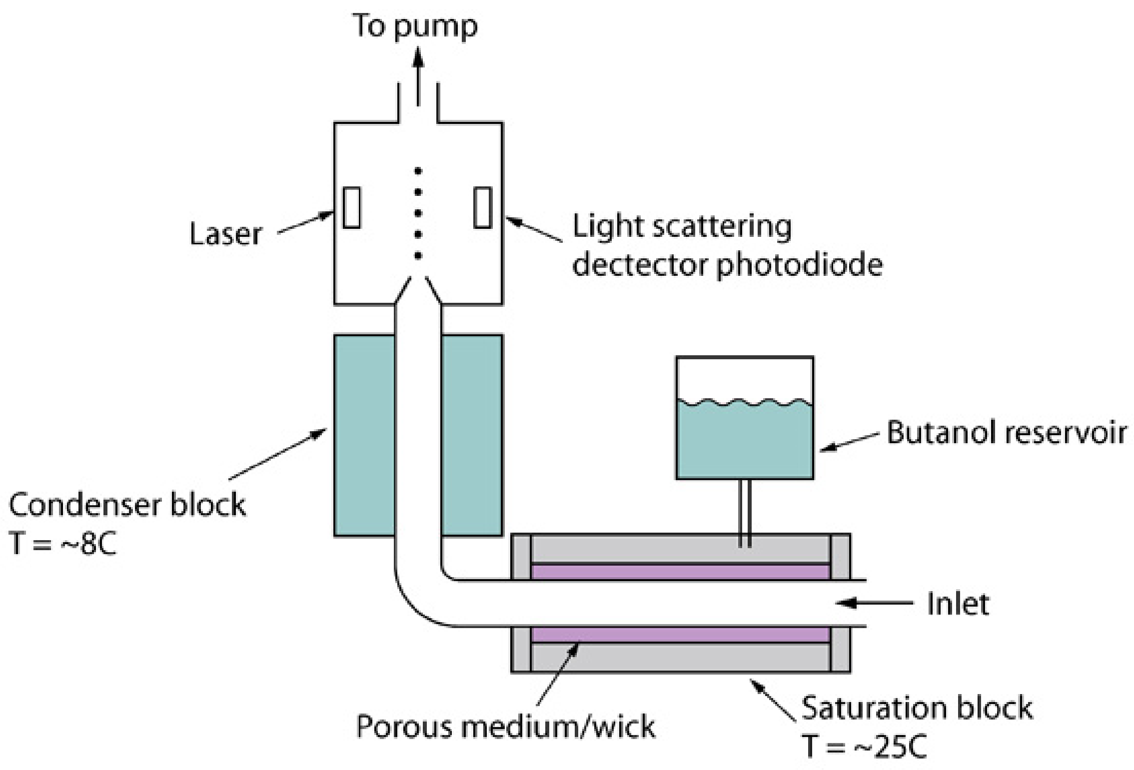
Cool by adiabatic expansion or flow through a cold tube
(can also heat in some cases, the temperature gradient is the key)

Nuclei will grow to ~ 10 μm (particles this size will scatter visible light with good efficiency)

Every condensable nuclei grows to a (small 10-12 μm) droplet

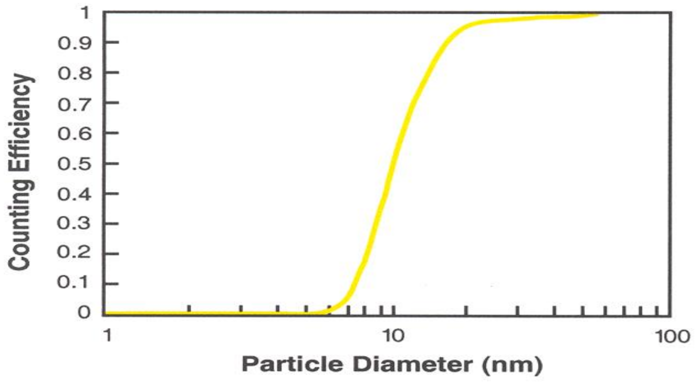
Measure the number of droplets with an e.g. single particle optical counter

Condensation Particle Counter (CPC): ~1.5 nm to 0.5 μm ambient aerosol size range

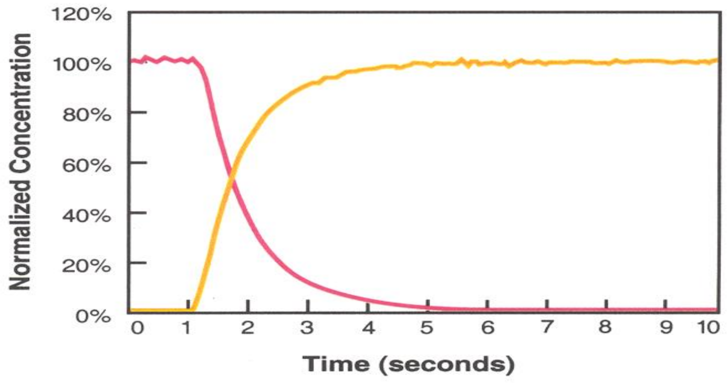


Condensation Particle Counters (CPCs) detects particles by exposing them to a region that is supersaturated with vapor (usually butanol), thus allowing particles to grow to a size that can be optically detected.

Counting efficiency curve: TSI model 3010

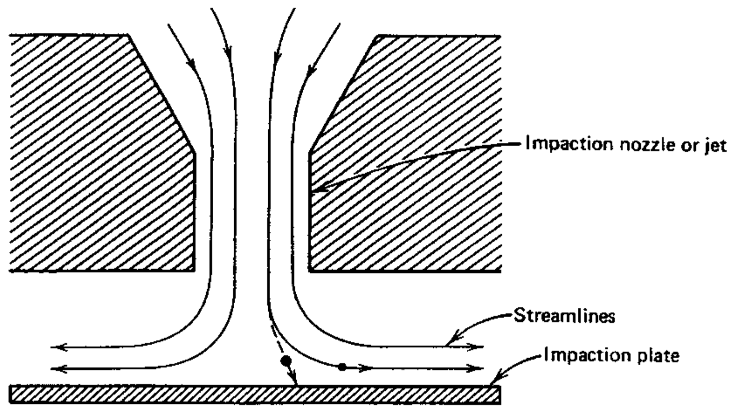


Response time: TSI model 3010

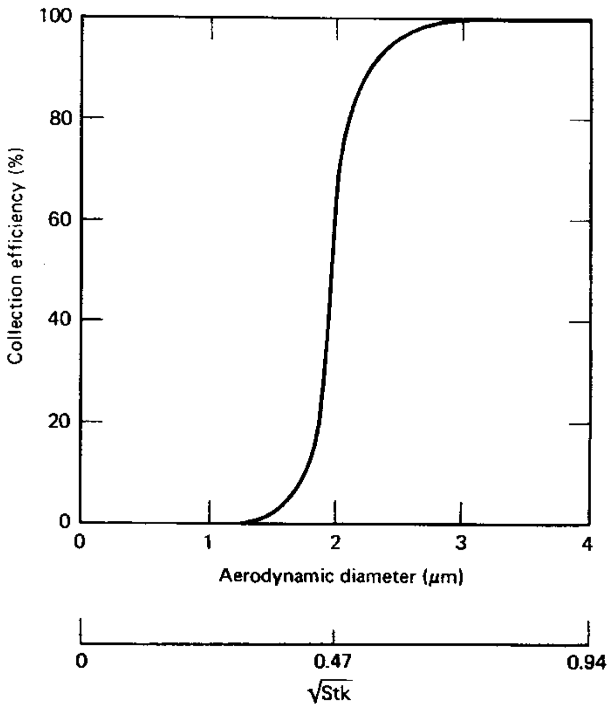


Particle Size Distribution

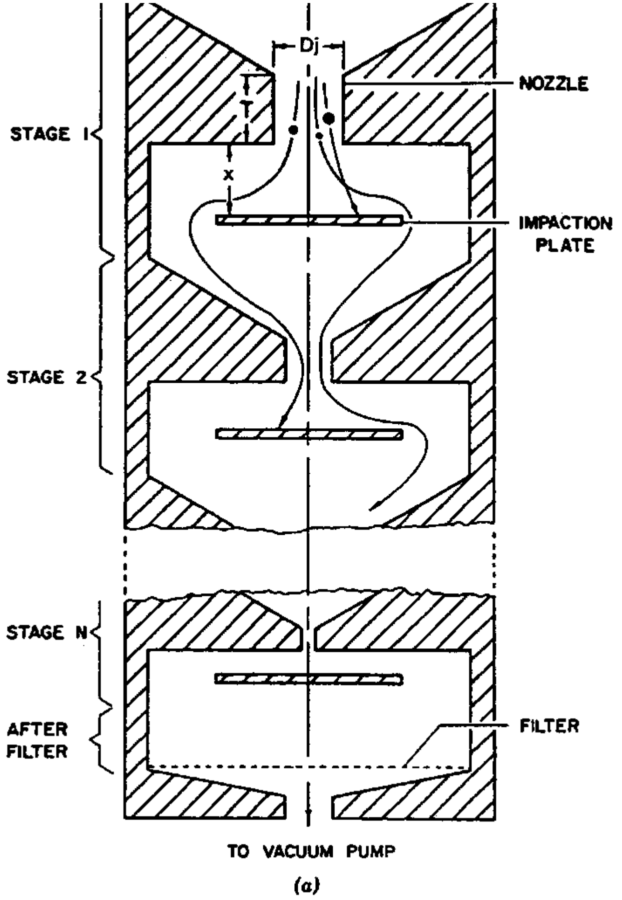
- Impactor – relies on inertial characteristics of particles (i.e., larger, more massive particles have greater inertia)
- Differential Mobility Analyzer – creates steady-state charge distribution and balance mass and charge as aerosols flow through an electric field



Cross-sectional view of an impactor.



Typical impactor efficiency curve.



Cascade impactor. Schematic diagram. Reprinted with permission from *Aerosol Measurement*, by Dale Lundgren et al. Copyright 1979 by the Board of Regents of the State of Florida.

Two things are changing with each stage:

- Diameter of nozzle
- Distance from nozzle to impactor plate

To decrease the cut-off diameter from stage to stage is achieved by

a) decreasing the nozzle diameters (increase in particle/air velocity)

b) and/or decreasing the number of nozzles

c) and/or decreasing the pressure (increase in slip correction).

DMA - Differential Mobility Analyzer

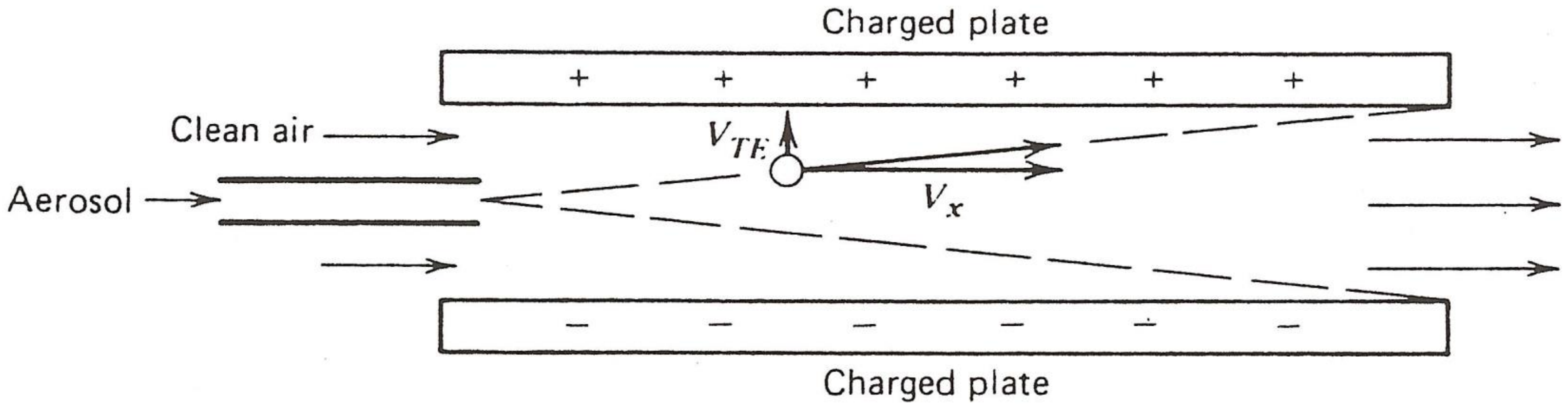
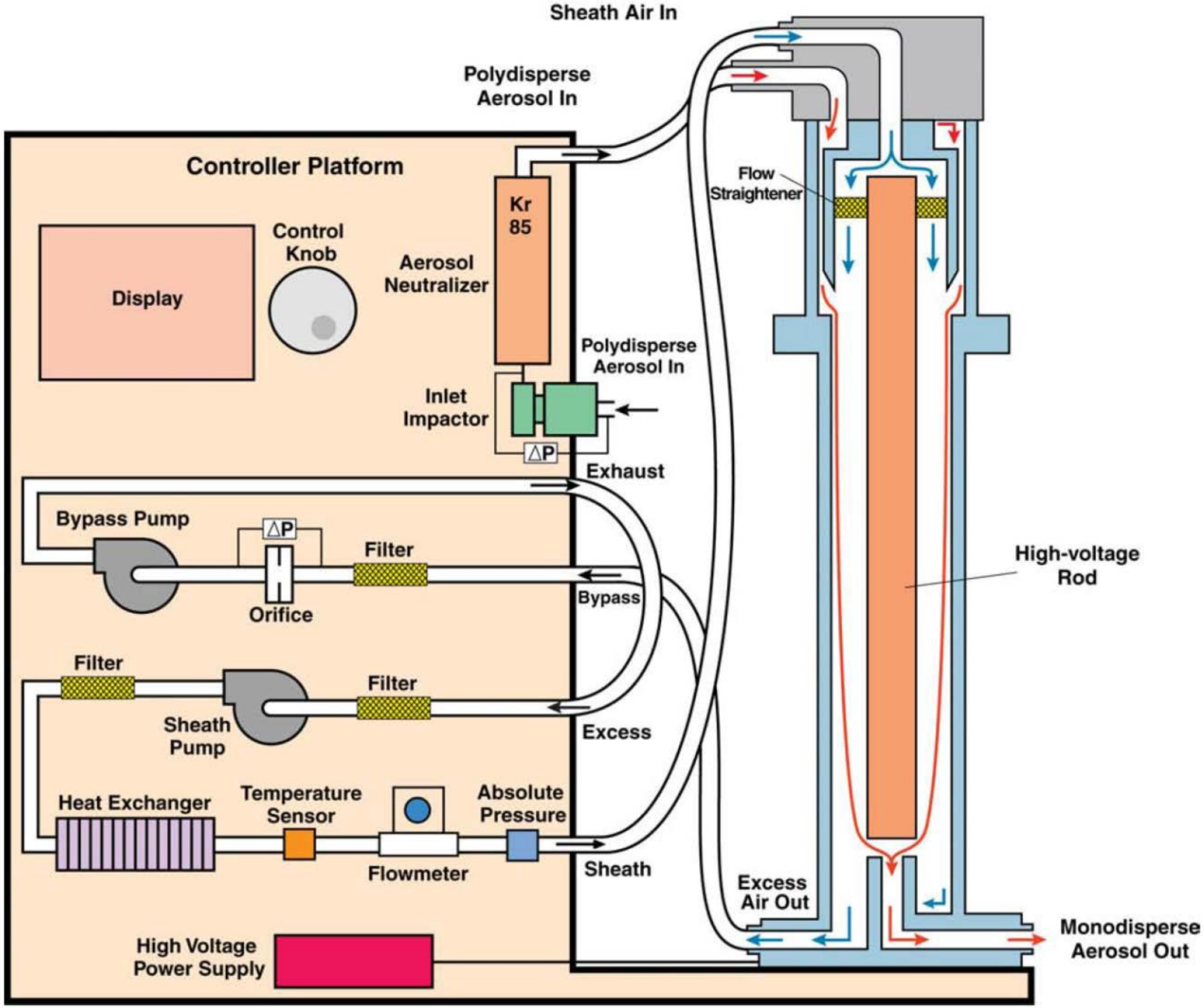


FIGURE 15.10 Diagram of a simple electrical mobility analyzer.

A charged particle will be pushed in the direction of V_{TE} by the electric field E between the two plates.

Hinds



Sheath Air In
Polydisperse Aerosol In
Controller Platform
Display
Control Knob
Kr 85
Aerosol Neutralizer
Polydisperse Aerosol In
Inlet Impactor
ΔP
Exhaust
Bypass Pump
ΔP
Filter
Orifice
Bypass
Filter
Filter
Sheath Pump
Excess
Heat Exchanger
Temperature Sensor
Absolute Pressure
Flowmeter
Sheath
High Voltage Power Supply
Flow Straightener
High-voltage Rod
Excess Air Out
Monodisperse Aerosol Out

Aerosol Optical Properties

Extinction, Scattering and Absorption

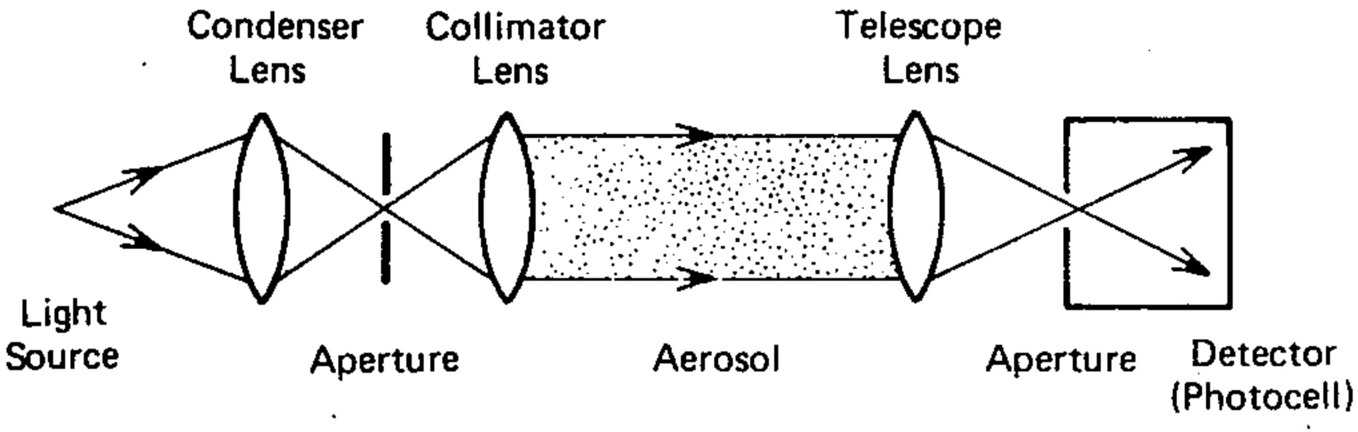
- Extinction – Attenuation of light along the axis of propagation
- Extinction = Absorption and Scattering
- Absorption – EM energy converted to thermal energy (vibrational, rotational, and ultimately translational) $\Rightarrow$ less light in the system
- Scattering – EM energy along axis of propagation re-radiated in other (all) directions, including backscatter which is used in ground based LIDARs

Index of Refraction

- “Absolute” – **$N = n' + ik'$** (where vacuum has an index of exactly 1)
- Typically the index is normalized to the index of the surrounding medium (N_0) -

  $m = N/N_0$
- N_0 most commonly refers to air, where $N_0 = 1.00029 + 0i$ at 589 nm
- Note that N (= N_0 = 1.00029) and m (= 1.0) are nearly identical for air, but for generality m is used for derivations.

Measurement of optical properties: Extinction



Beer's Law

$$\frac{I}{I_0} = \exp(-\sigma_e L)$$

Extinction Coefficient

$$\sigma_e = N A_p Q_e = \frac{\pi N d_p^2 Q_e}{4}$$

(monodisperse aerosols)

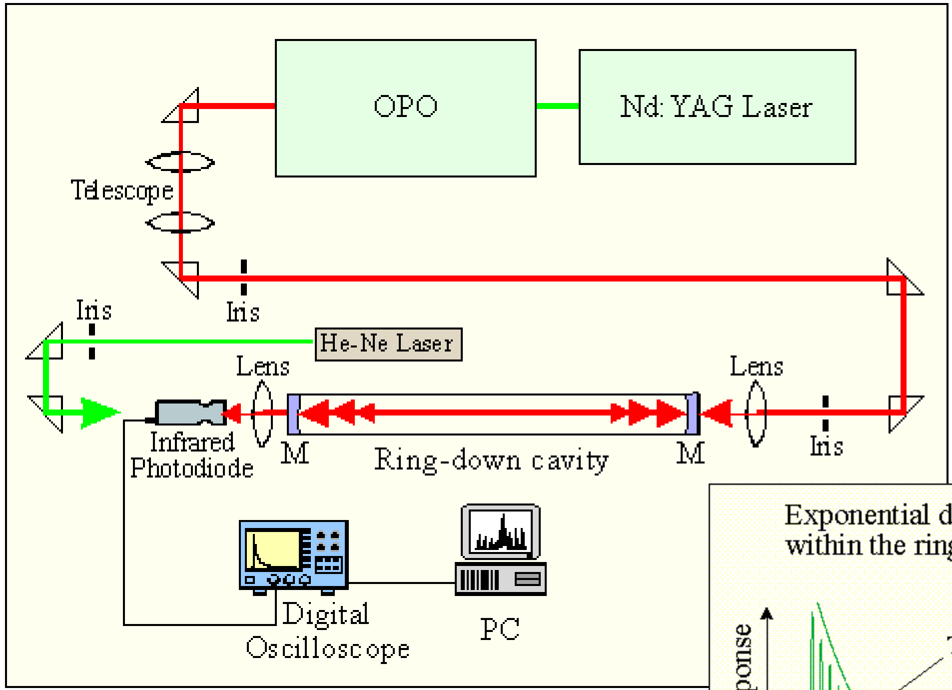
Extinction Efficiency

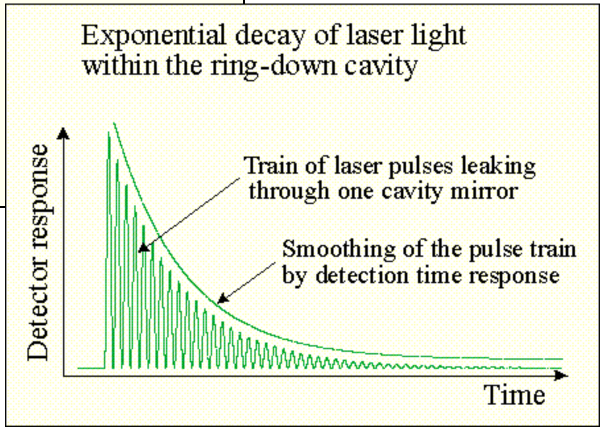
$$Q_e = \frac{\text{radiant power scattered and absorbed by a particle}}{\text{radiant power geometrically incident on the particle}}$$

L = path length, N = number of particles per volume

Extinction-based aerosol instruments

transmissometer
(used at airports)

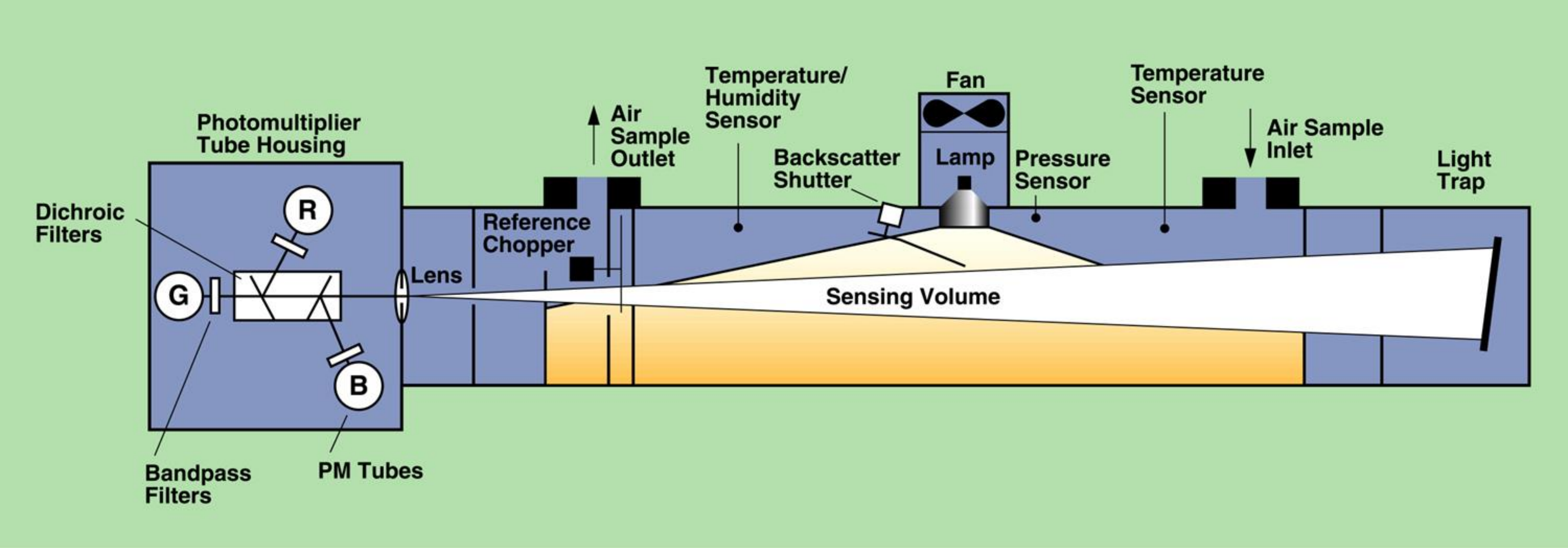




pulsed laser cavity-ringdown spectrometer

stack opacity monitor

Nephelometer: Measuring light scattering



The nephelometer is an instrument that measures aerosol light scattering. It detects scattering properties by measuring light scattered by the aerosol and subtracting light scattered by the gas, the walls of the instrument and the background noise in the detector.

Aerosol Chemical Composition

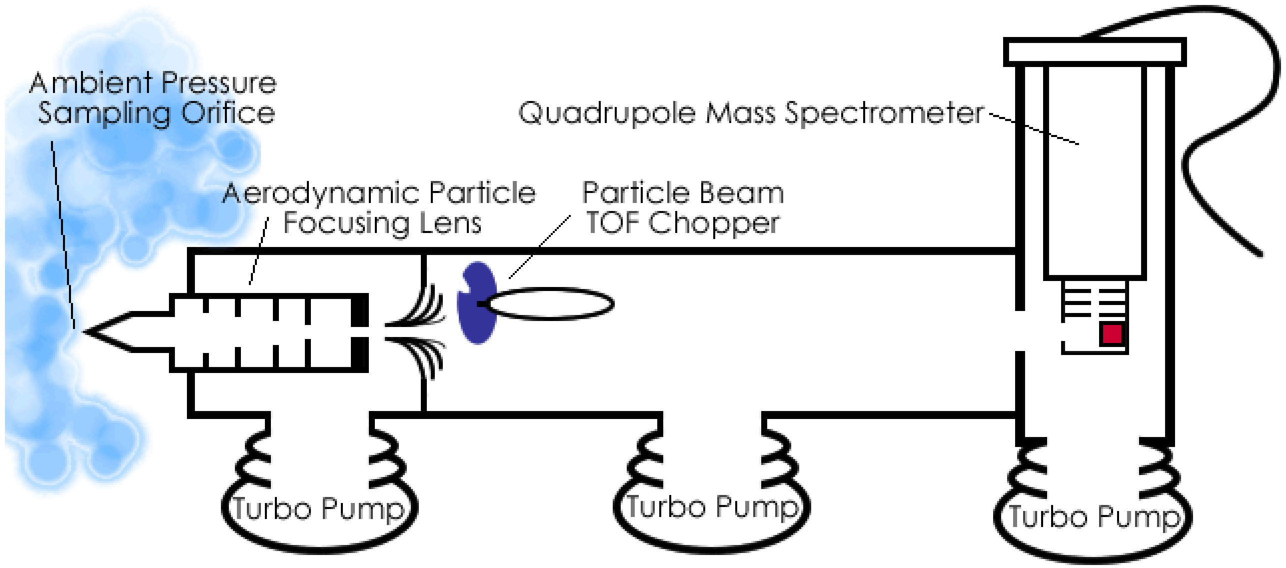
- National networks include CSN (Chemical Speciation Network) –mostly urban locations; and IMPROVE – mostly rural & remote locations
- Like with Mass Concentration, the routine network measurements are 24 hour samples collected on filters and analyzed post-sampling in the laboratory. Many networks collect three different filters:

1. A Teflon filter which is analyzed for total mass and elements using XRF (X-Ray Fluorescence)
2. A Nylon filter (preceeded by gas denuders) which is “digested” and analyzed for major ionic species (i.e., sulfate, nitrate, ammonium, etc.)
3. A pre-baked quartz filter which is analyzed for total carbonaceous material and the empirically defined Elemental Carbon (EC) and Organic Carbon (OC) fractions.

Continuous Chemical Composition

- Mass Spectrometry (many types, very active research field) – next slides
- Particle- Into Liquid-Sampling (PILS) – can be couple with Ion Chromatography, Total Organic Carbon detection, etc.
- A variety of analyzers or systems for one or more chemical fraction, like carbon, sulfate, or nitrate.

Aerosol Mass Spectrometer (AMS)



- For an excellent review of this and other instruments that measure aerosol composition using mass spectrometry see:
  - http://cires.colorado.edu/~jjose/Papers/2010-09_IAC_Aerosol_MS_Tutorial.pdf
  - Aerodyne Research, Incorporated

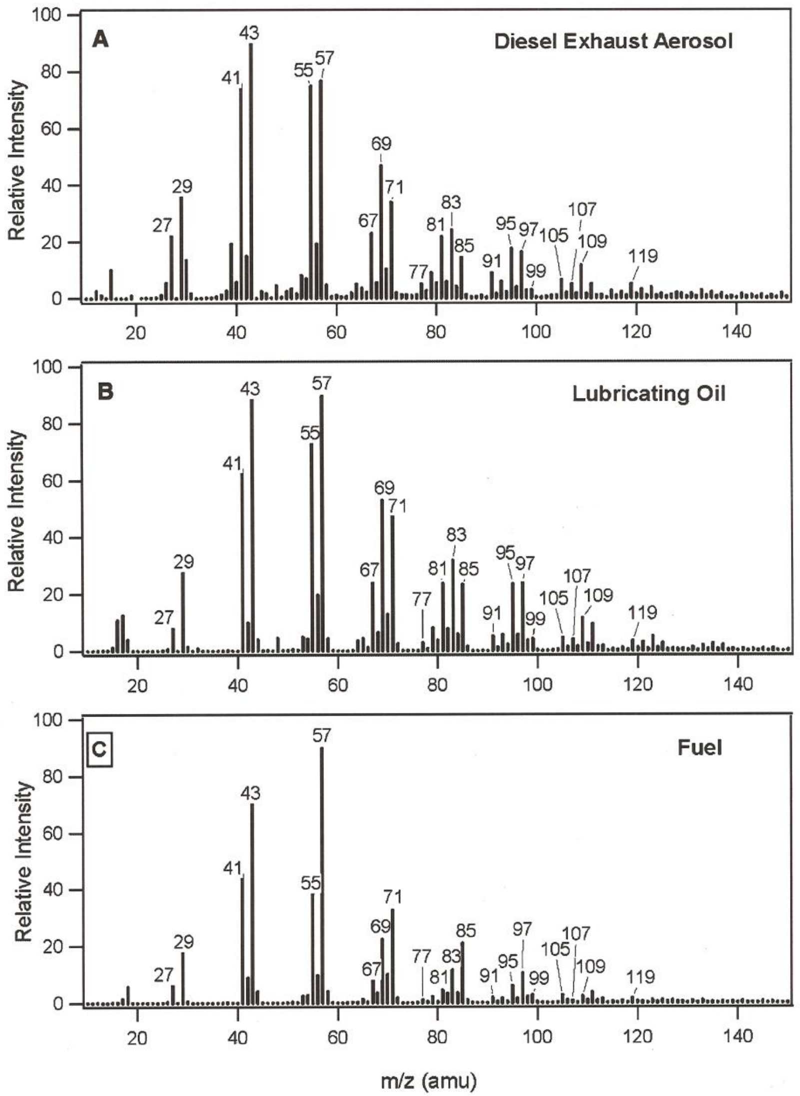


FIGURE 21. AMS mass spectra obtained from diesel bus exhaust (**A**), pure lubricant oil (**B**), and pure diesel fuel (**C**) aerosols. The lubricant oil and diesel fuel spectra were obtained from lab aerosols and the diesel bus exhaust spectrum is an average of PM exhaust mass spectra obtained during all the diesel vehicle chases performed with the mobile laboratory during the New York City measurement campaign. (Aerosol Science & Technology: Canagaratna et al.: Chase studies of particulate emissions from in-use New York City vehicles. (38) 555–573. Copyright 2004. Mount Laurel, NY, Reprinted with permission.)

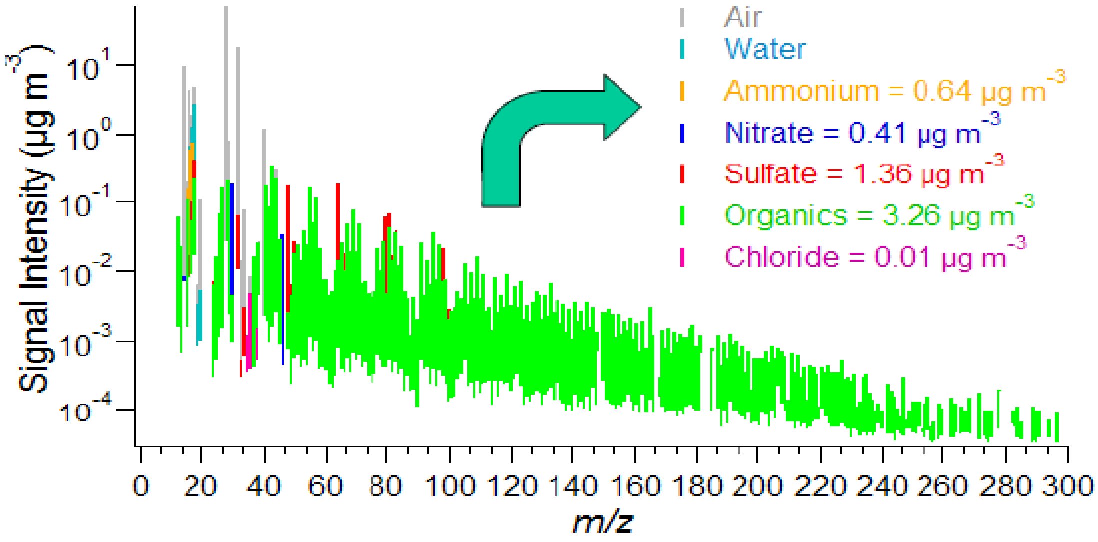
Field observations

Lab

Lab

Canagaratna et al., Mass Spec Rev, v26, P185-222,2007.

AMS mass spectrum from ambient aerosol



- Since the AMS uses electron impact ionization and high temperature, species are modified as they are desorbed and ionized.
- Luckily, marker species and co-varying peaks can be found that uniquely identify compound classes.
- A high-resolution Time-Of-Flight Mass Spectrometer (TOFMS) has been developed for use with the AMS, thus allowing for elemental analyses such as C:O. In the TOFMS, an E field accelerates ions of different mass to the same kinetic energy ½ m v^2. Larger mass ions travel at slower v than lighter ions. For each ion, measure the travel time between two laser beams, get v, and then m.