In-situ Aerosol Measurement Techniques

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http://www.esrl.noaa.gov/gmd/aero/

Approach

- ***"In this life, we can't measure what we want, so we measure what we can"***
  (Bob Charlson)
- **If we had more time, I would…**
  - discuss what we actually measure
  - describe methods and assumptions used to derive the desired variable
  - discuss the "distance" between physical standards and derived variable

Scope of talk

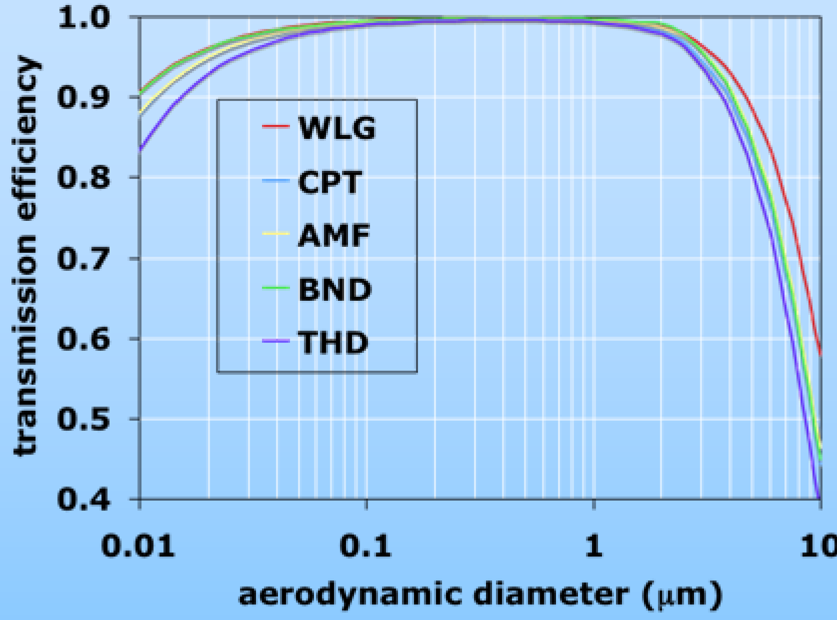
- **40 minutes, including discussion**
- **define "in-situ" to mean methods that draw a sample of air into an analyzer or collection device**
- **Insufficient time to be comprehensive, so spend more time on methods in my area of focus**
  - Microphysical, Radiative, Hygroscopic, Chemical

Aerosol Sampling Issues

- **Key Issues**
  - any change in the chemical thermodynamic state of the sample air will change the aerosol.
  - particle losses (or gains) are size-dependent
- **RH and size control of sampled aerosol**
  - heating vs. dilution vs. diffusion driers
    - inadvertent vs. deliberate heating
    - temperature vs. RH control variable
  - inertial vs. diffusive size control
    - inadvertent vs. deliberate size control
- **Examples of particle loss/gain mechanisms**
  - impaction and diffusion losses in inlet systems
  - scrubbing of organic vapors in dilution air changes equilibrium concentration of volatile species in condensed phase
  - cooling in adiabatic expansion can lead to growth in mass
  - splashing of hydrometeors on inlets in clouds can lead to enhancement of number concentrations
  - sub-isokinetic inlets enhance large particle concentrations through inertial enrichment

Key Questions to Ask about Measurements

- **What is the T, RH, and P of the sample?**
  - as measured
  - as reported
- **What is the T, RH, and P history during sampling?**
  - e.g., hysteresis effects

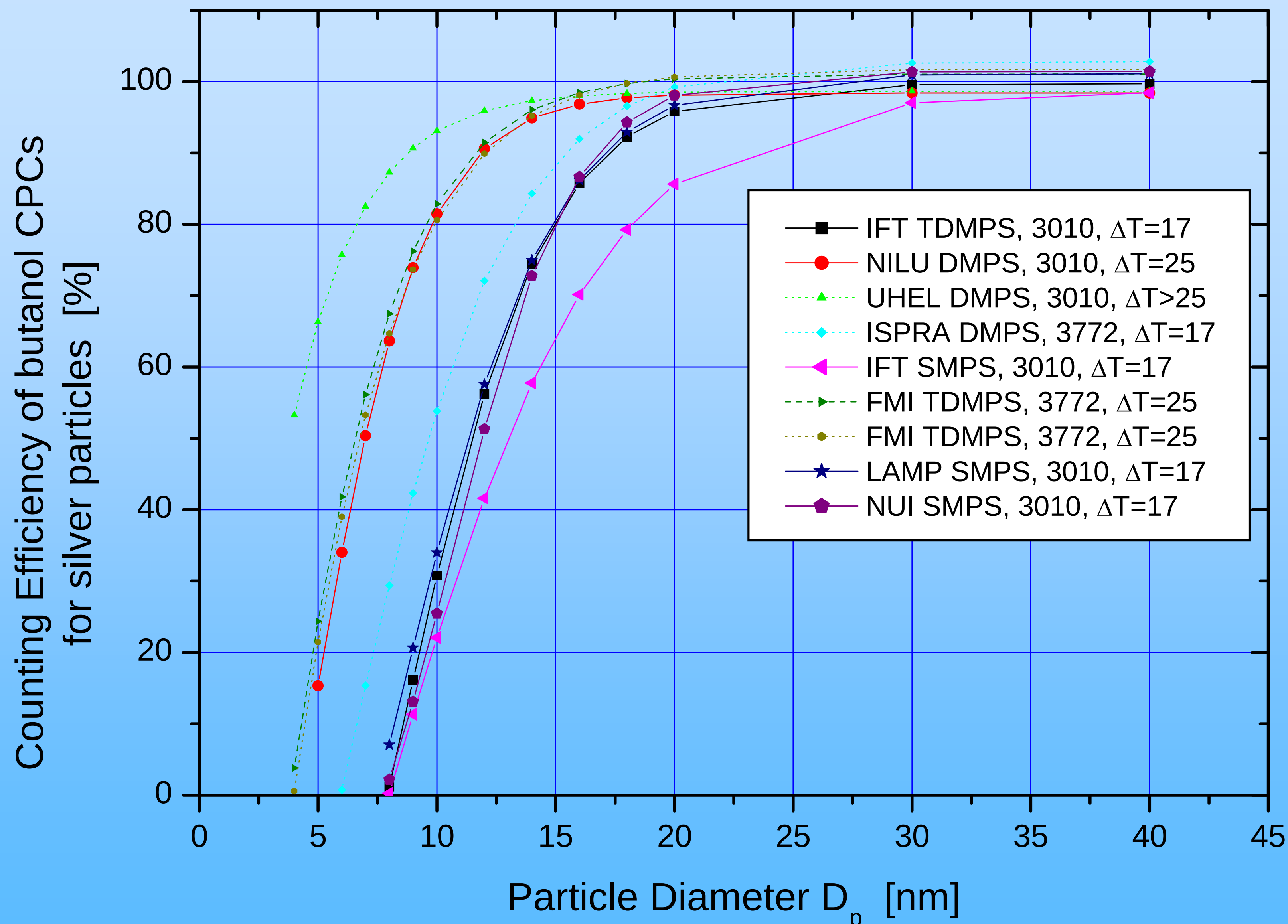


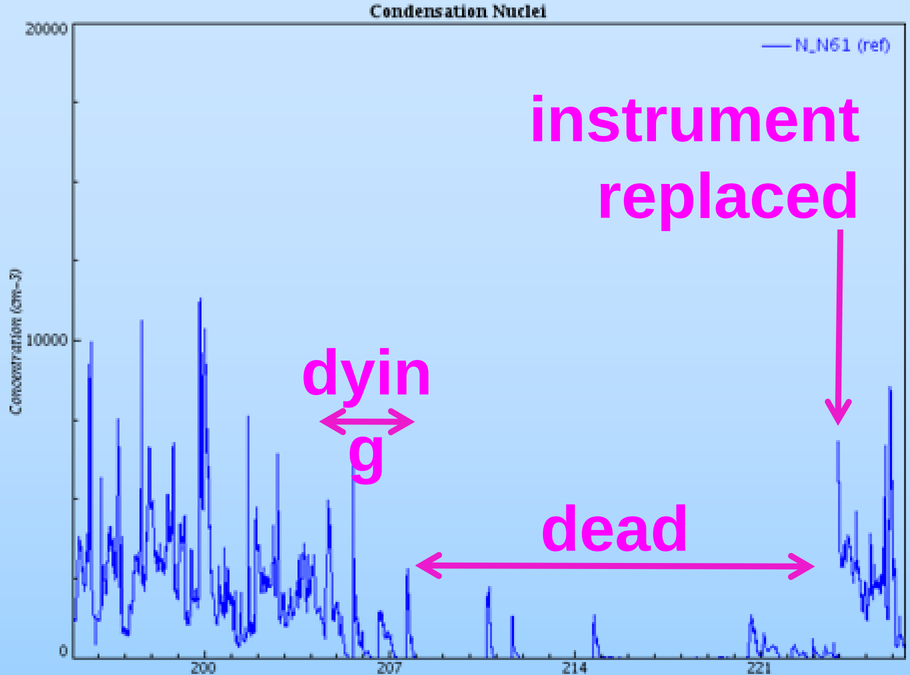
- **What is the size-dependent efficiency of the sample inlet?**

Measurements of number concentration

- **Grow tiny particles to sizes where they are easily detected**
  - butanol vs. water as working fluid
  - expansion vs. continuous operation
- **optical detection**
  - pulse counting from individual particles
  - photometric detection of a cloud of particles
- **absolute calibration**
  - flow rate
  - electrometer measures current from sample of singly-charged particles (hard to do in field)
- **size cut vs. operating parameters (ΔT)**
- **composition effects**
  - butanol-based instruments are relatively insensitive to particle composition
  - lower detection limit of continuous water CPC's is sensitive to particle composition
- **operational considerations**

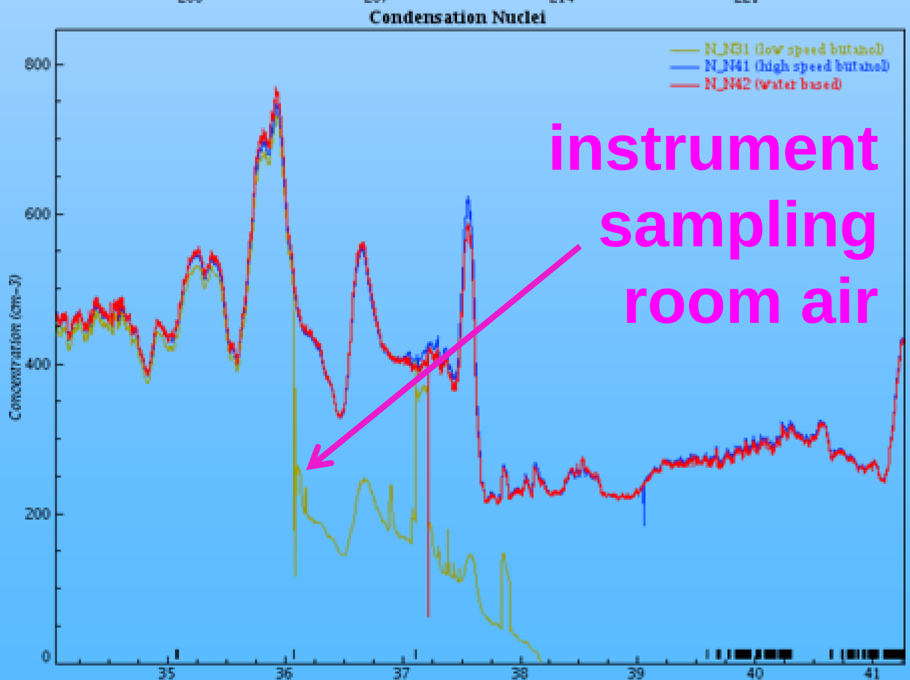
CPC Calibration

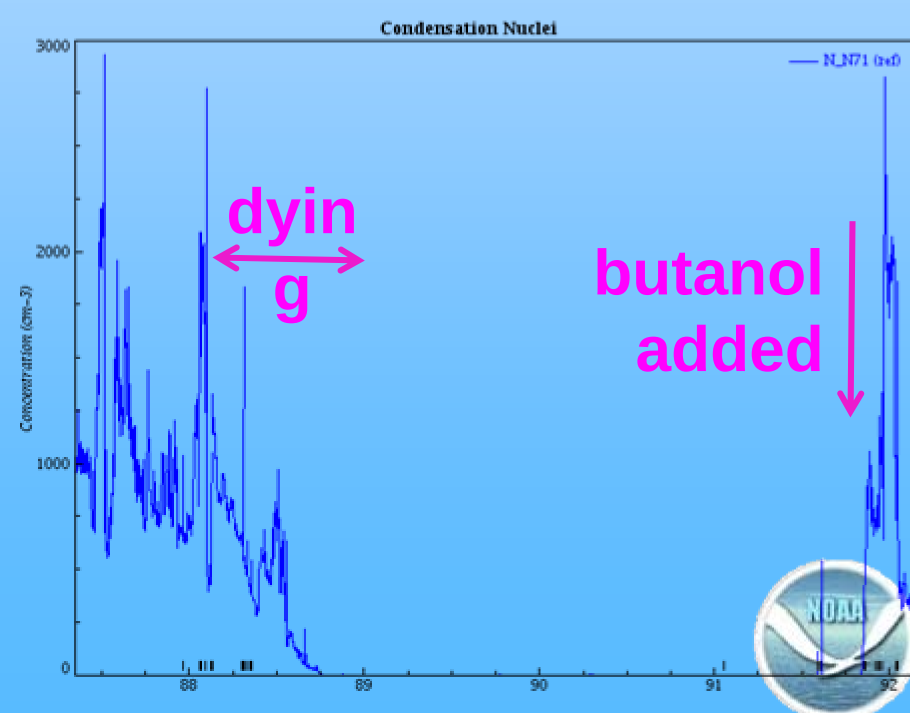




CPC Failures

- butanol drained or contaminated
- inlet disconnected or cracked
- instrument failure





What is the size of a particle?

- **Beware of radius vs. diameter confusion!**
- **Different sizes**
  - optical
  - electrical mobility
  - volume-equivalent sphere
  - aerodynamic
  - vacuum aerodynamic

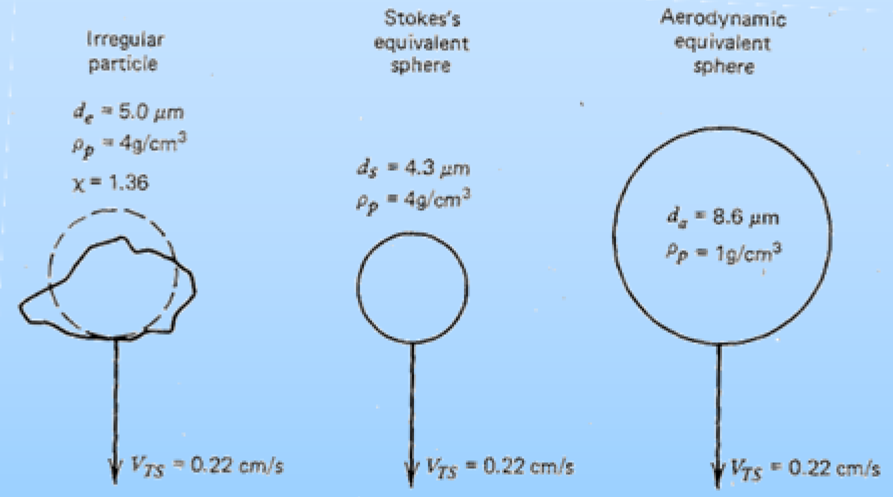


Figure 3.3 An irregular particle and its equivalent spheres.

- **Apparent particle size is affected by morphology, density, and refractive index, depending on the measurement method**

Measurements of Size Distribution

- **DMPS/SMPS**
  - differential mobility particle size spectrometer
  - scanning mobility particle size spectrometer
  - both select a very narrow size range of particles based on their electrical mobility
  - detection is with a CPC
- **APS**
  - aerodynamic particle sizer
  - particles are accelerated and their resulting change in velocity is related to their aerodynamic size
- **OPC**
  - optical particle counter

Particle Mobility Size Spectrometers: Harmonization of Technical Standards and Data Structure for High Quality Long-term Observations of Atmospheric Particle Size Distributions

Alfred Wiedensohler

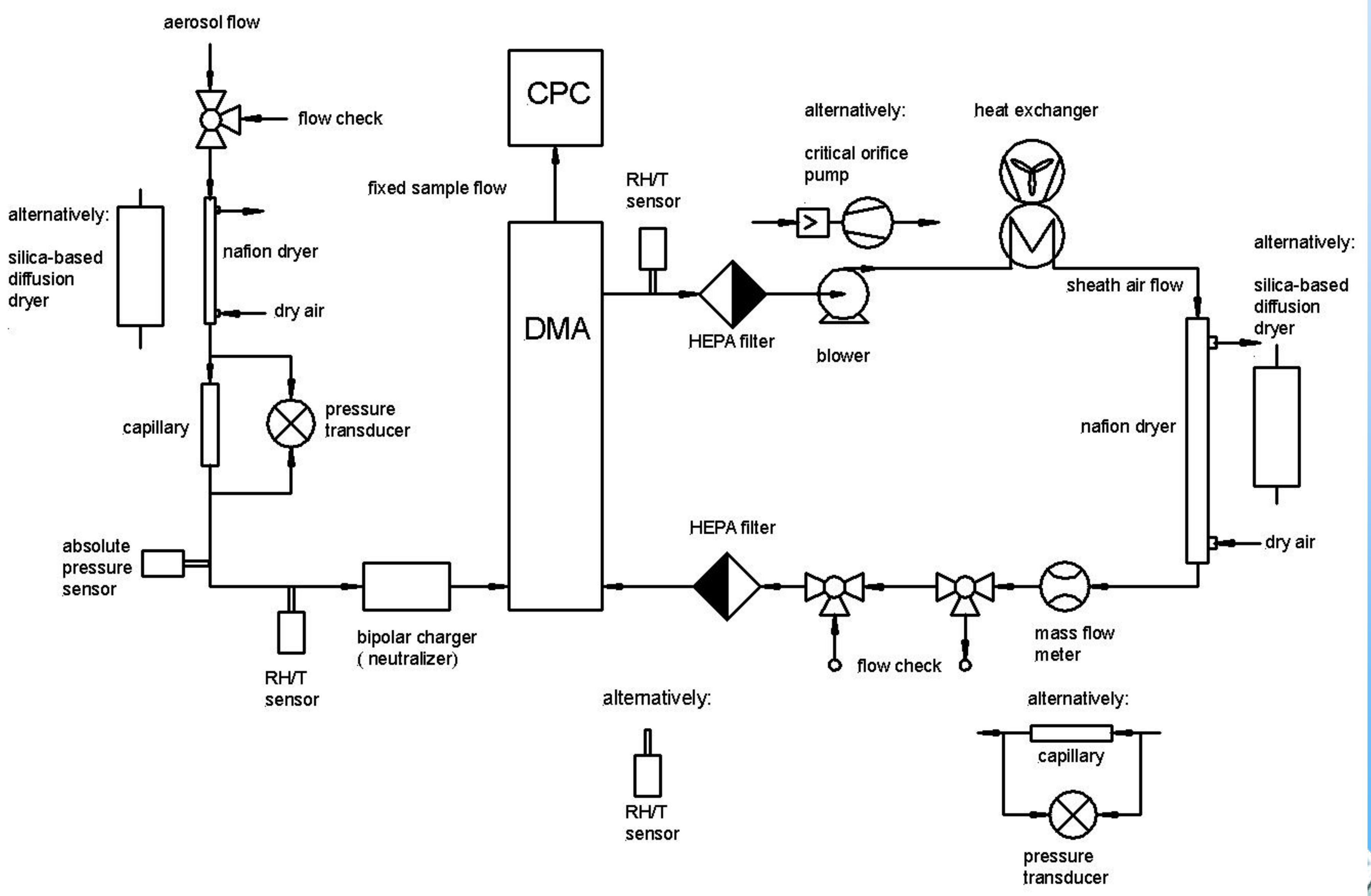
Leibniz Institute for Tropospheric Research

Birmili, Wolfram; Nowak, Andreas; Tuch, Thomas; Wehner, Birgit; Sonntag, Andre; Fiebig, Markus; Asmi, Eija; Laj, Paolo; Sellegri, Karine; Venzac, Herve; Villani, Paolo; Aalto, Pasi; Swietlicki, Erik; Pontus, Roldin; Schmidhauser, Rahel; Gysel, Martin; Weingärtner, Ernest; Riccobono, Francesco; Santos, Sebastiao; Grüning, Carsten; Fallon, Kate; Beddows, David; Monahan, Colin; Marioni, Angela; Williams, Paul; Quincey, Paul; Hüglin, Christoph; Horn, Hans-Georg; Keck, Lothar; Ogren, John; McMurry, Pete

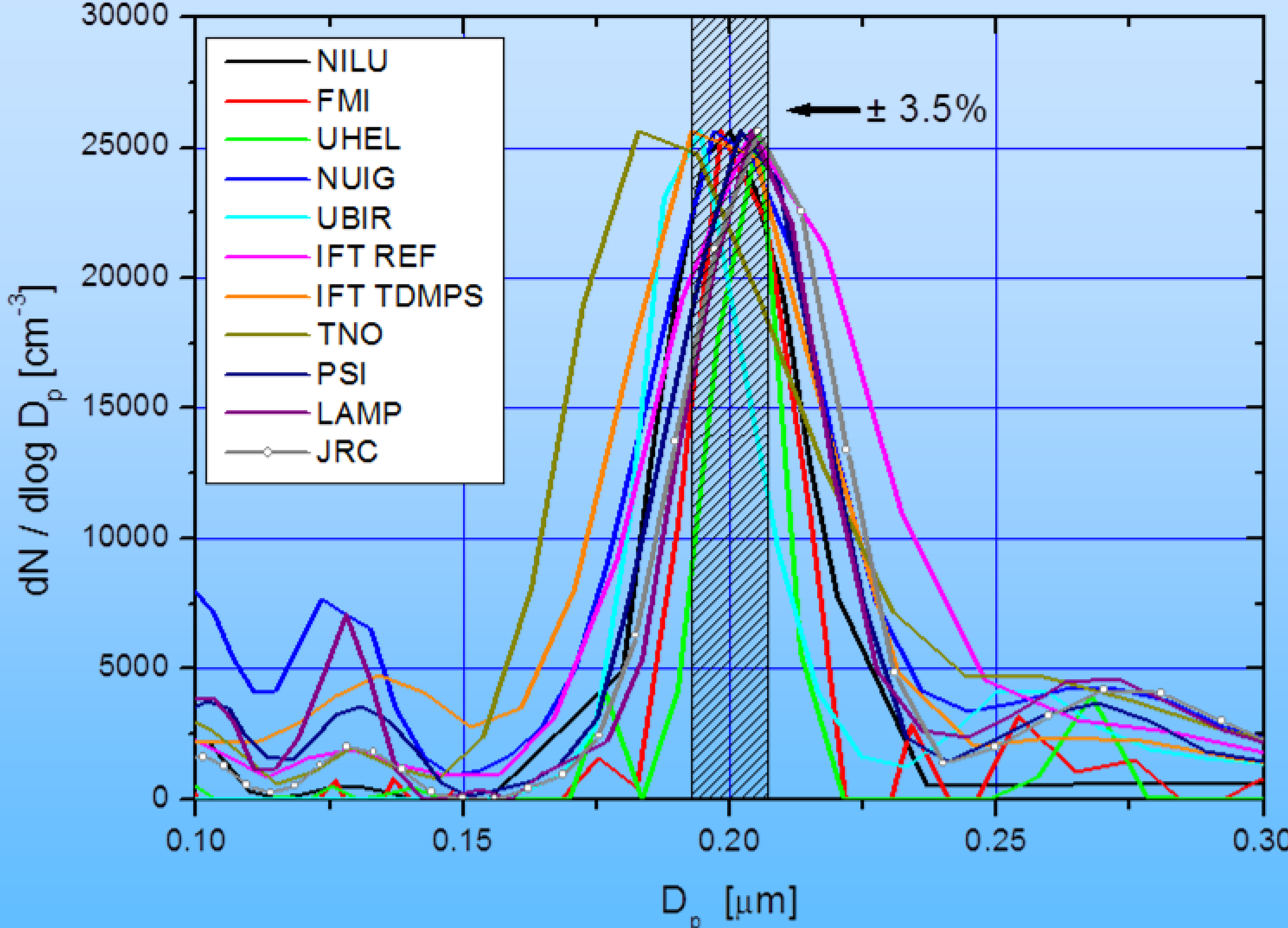
International Aerosol Conference, Helsinki, Finland

September 3, 2010

EUSAAR-Standard SMPS Set-Up

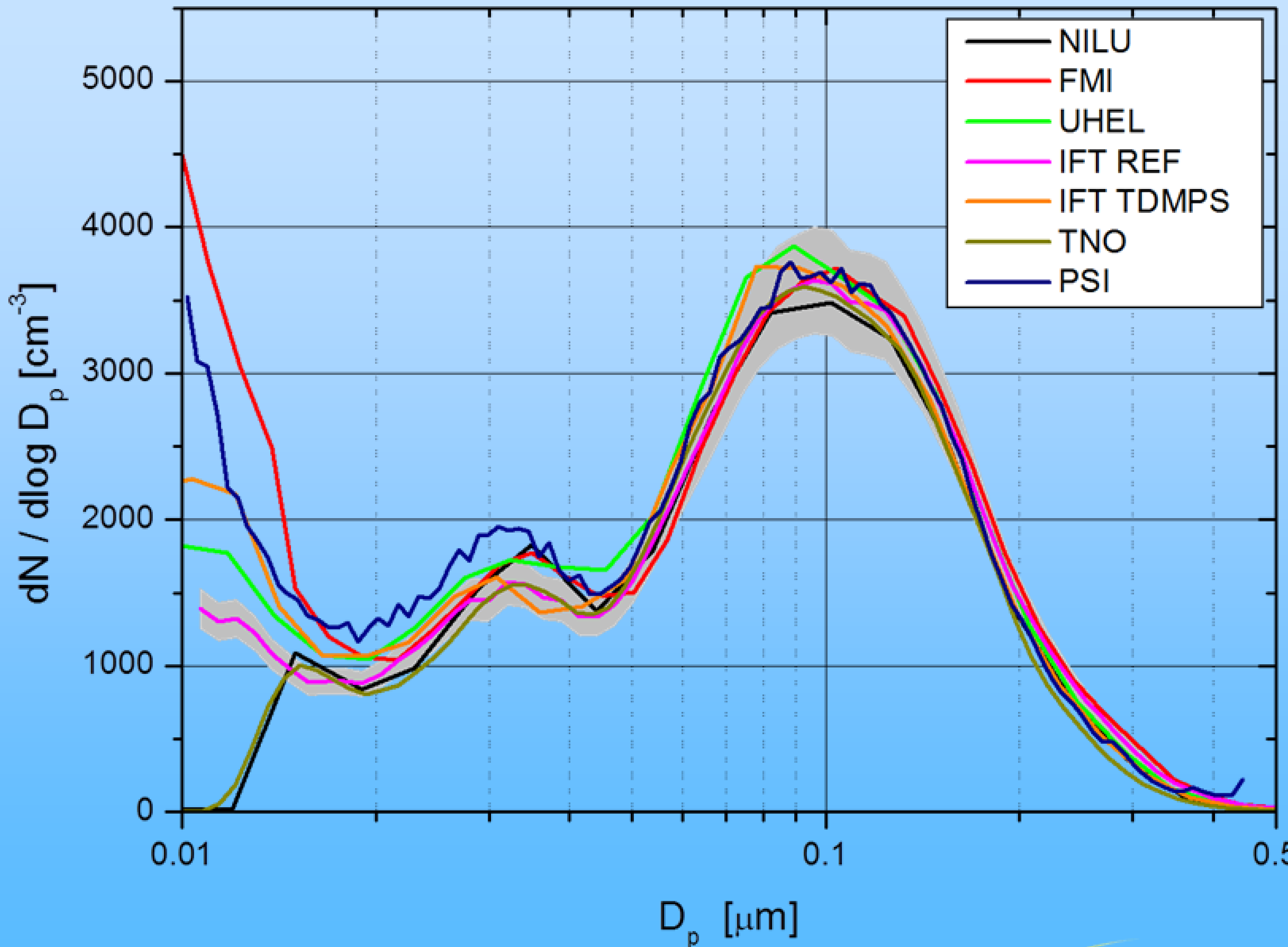


Confirmation of SMPS Sizing

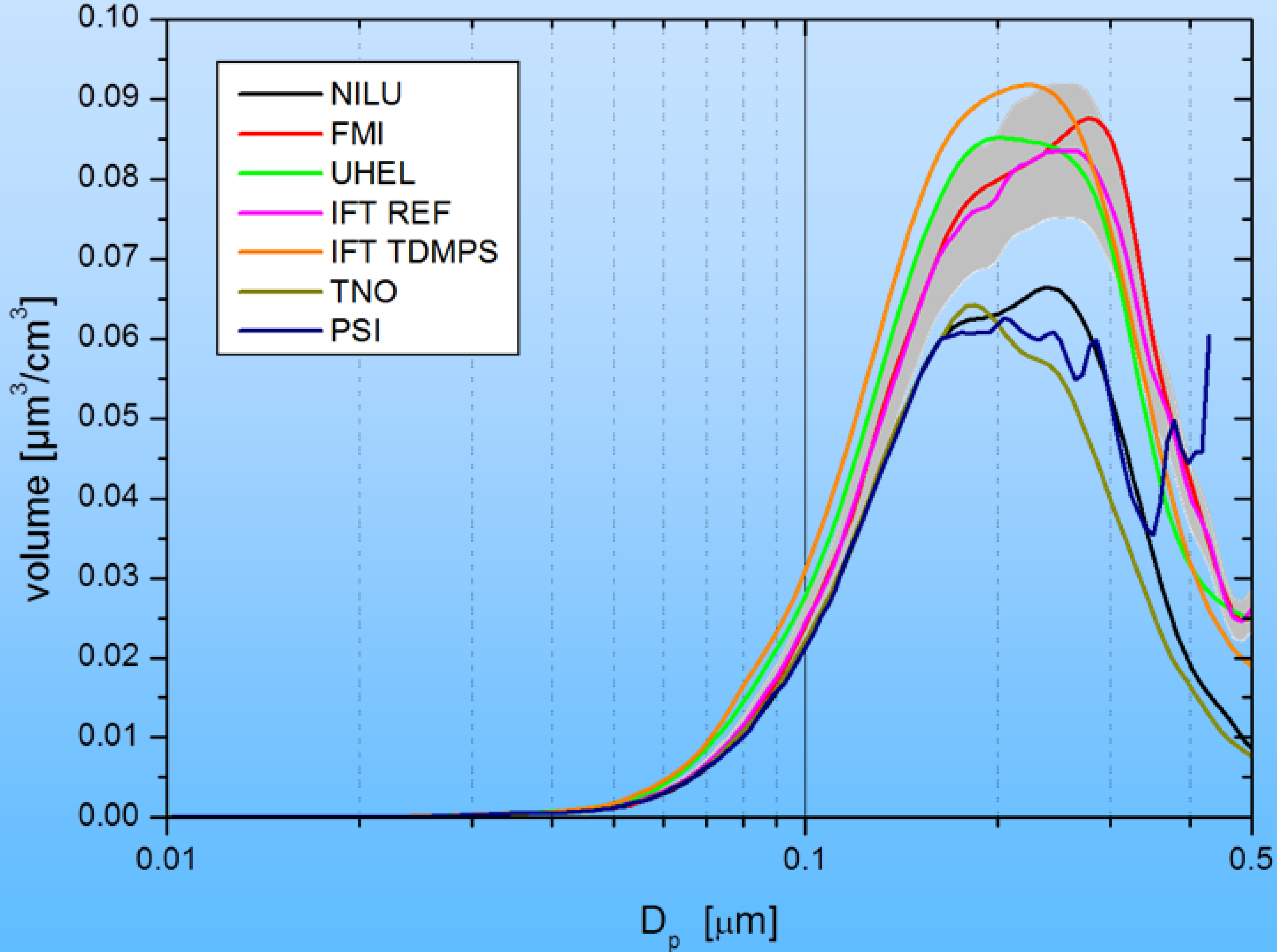


Size of polystyrene latex spheres is measured with an electron microscope

Intercomparison: Number Size Distribution

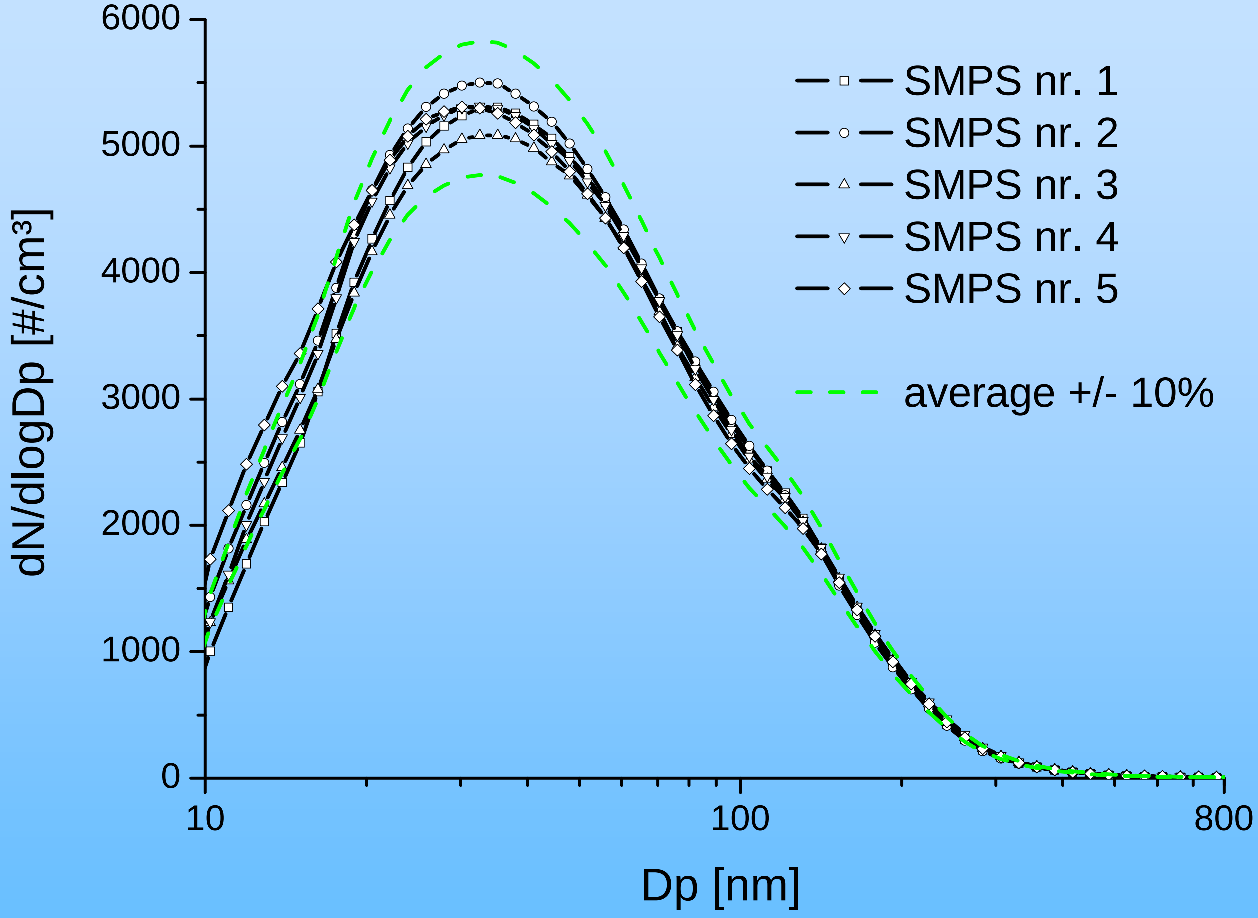


Intercomparison: Volume Size Distribution



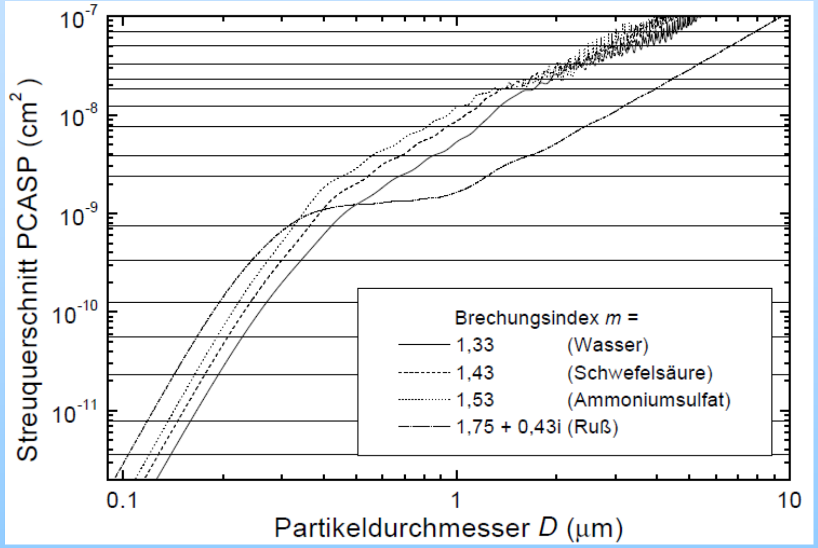
Note difference in intercomparison results compared to number size distribution

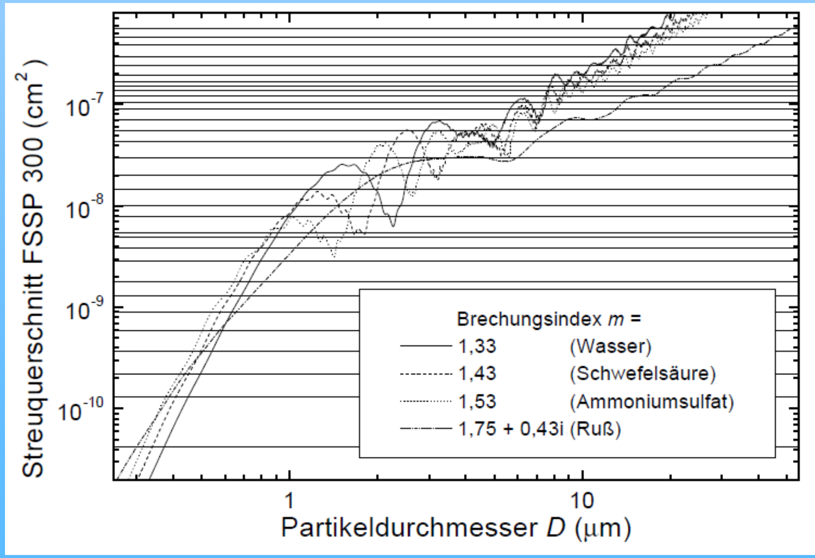
Intercomparison: Number Size Distribution



Experience gained from repeated intercomparison experiments leads to improved agreement among instruments

OPC response functions have ambiguity



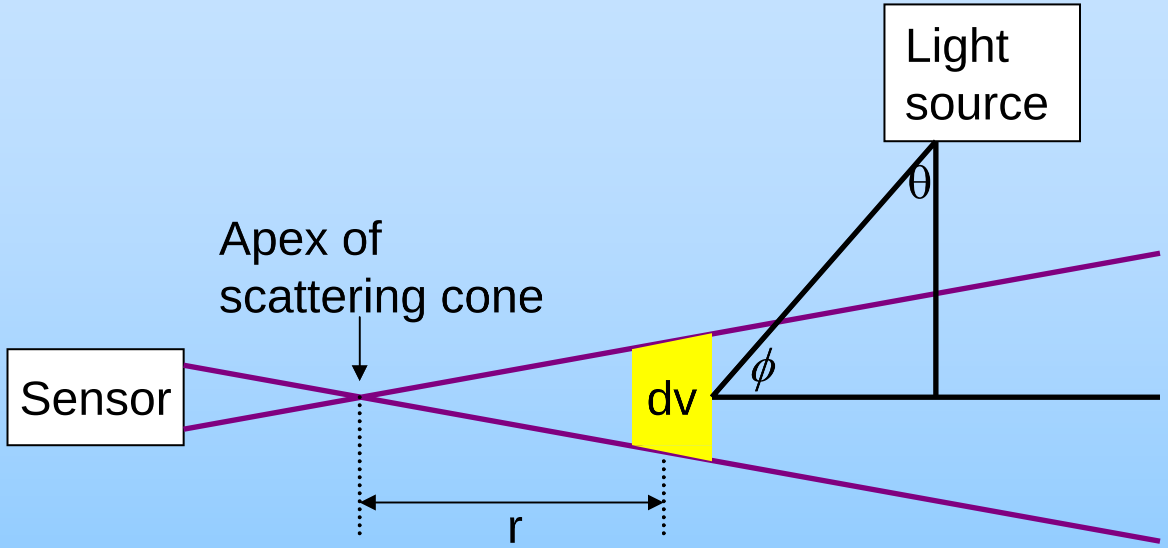


- **Depending on optical geometry and particle refractive index, different particle sizes can produce the same signal in the instrument**
- **Fiebig, 2001, Ph.D. dissertation**

Measurements of Light Scattering Coefficient

- **integrating nephelometer**
- **inverse nephelometer**
  - in photoacoustic absorption instrument
  - cavity ringdown extinction instrument
- **measures count rate from particles as they pass through an illuminated volume**
- **calibrated against known Rayleigh scattering of gases (air, CO_2, CFC-12, He) at measured T&P**
- **errors:** truncation, angular illumination, sample heating

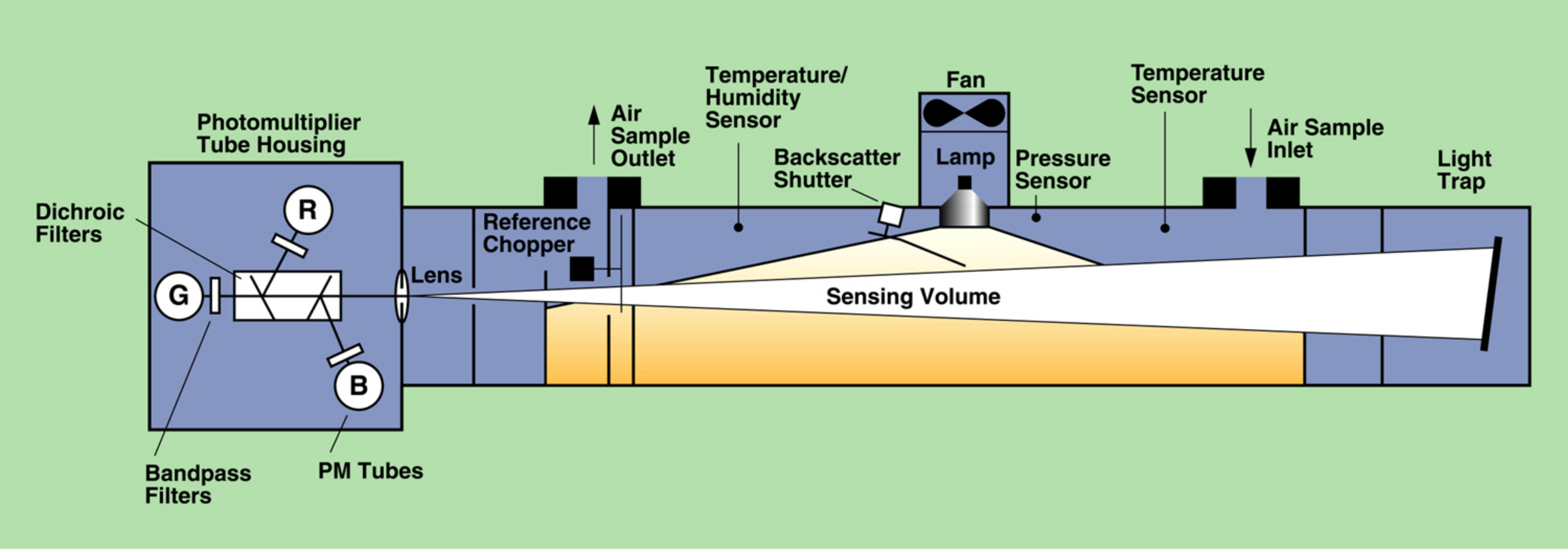
Principle of Integrating Nephelometer



1. Light source intensity is proportional to $\cos\theta$, which gives the $\sin\phi$ weighting in the integrand.
2. Conical viewing volume *dv* increases as r^2, but intensity of light from *dv* reaching sensor follows an inverse-square law. The r^2 and $1/r^2$ dependencies cancel, yielding equal weighting of each linear increment dr.

Source: Butcher and Charlson (1972)

TSI 3563 Integrating Nephelometer



Wavelengths: 450, 550, 700 nm

Bandwidth: 40 nm FWHM

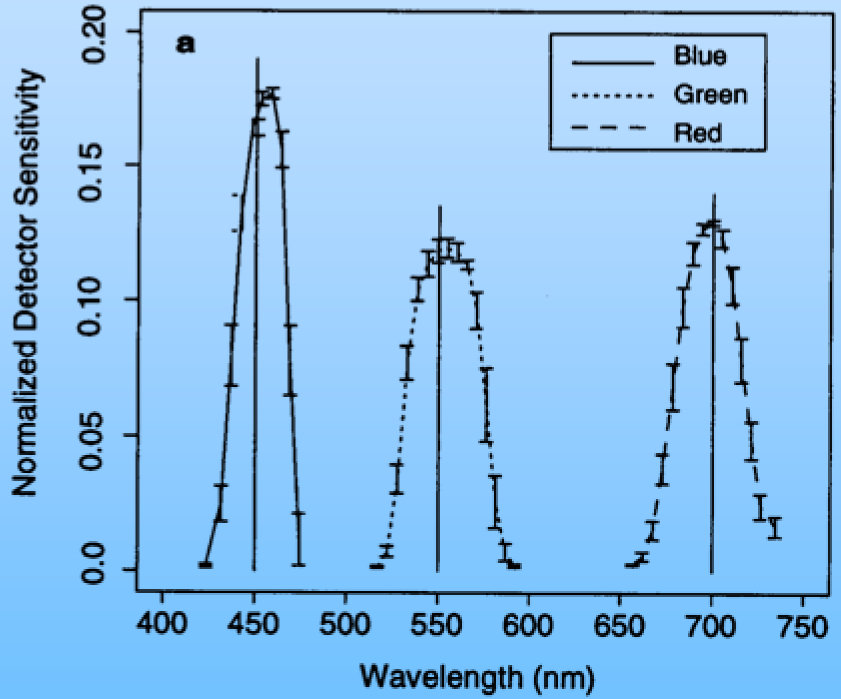
Angular range: 7-170° (total), 90-170° (backscatter)

Sensitivity: 2-3 x 10^{-7} m^{-1} (60-sec average)

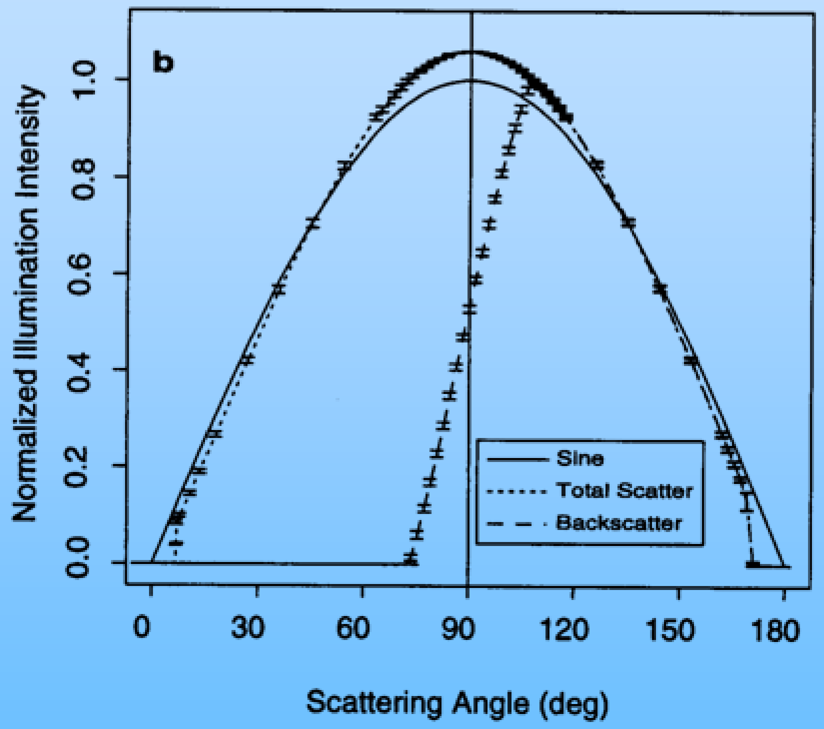
Source: TSI, Inc.

TSI Nephelometer Non-Idealities

wavelength response

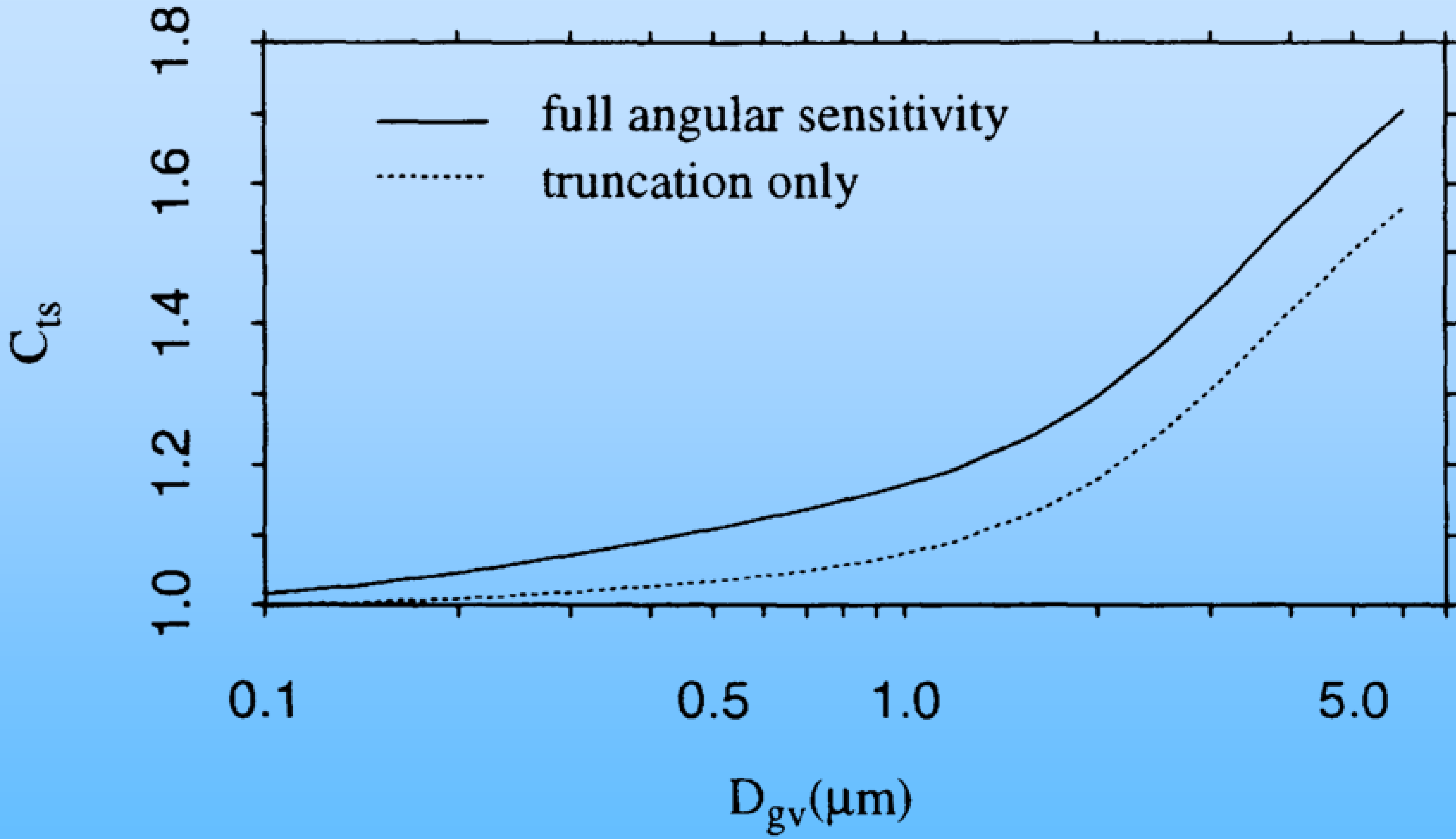


angular response



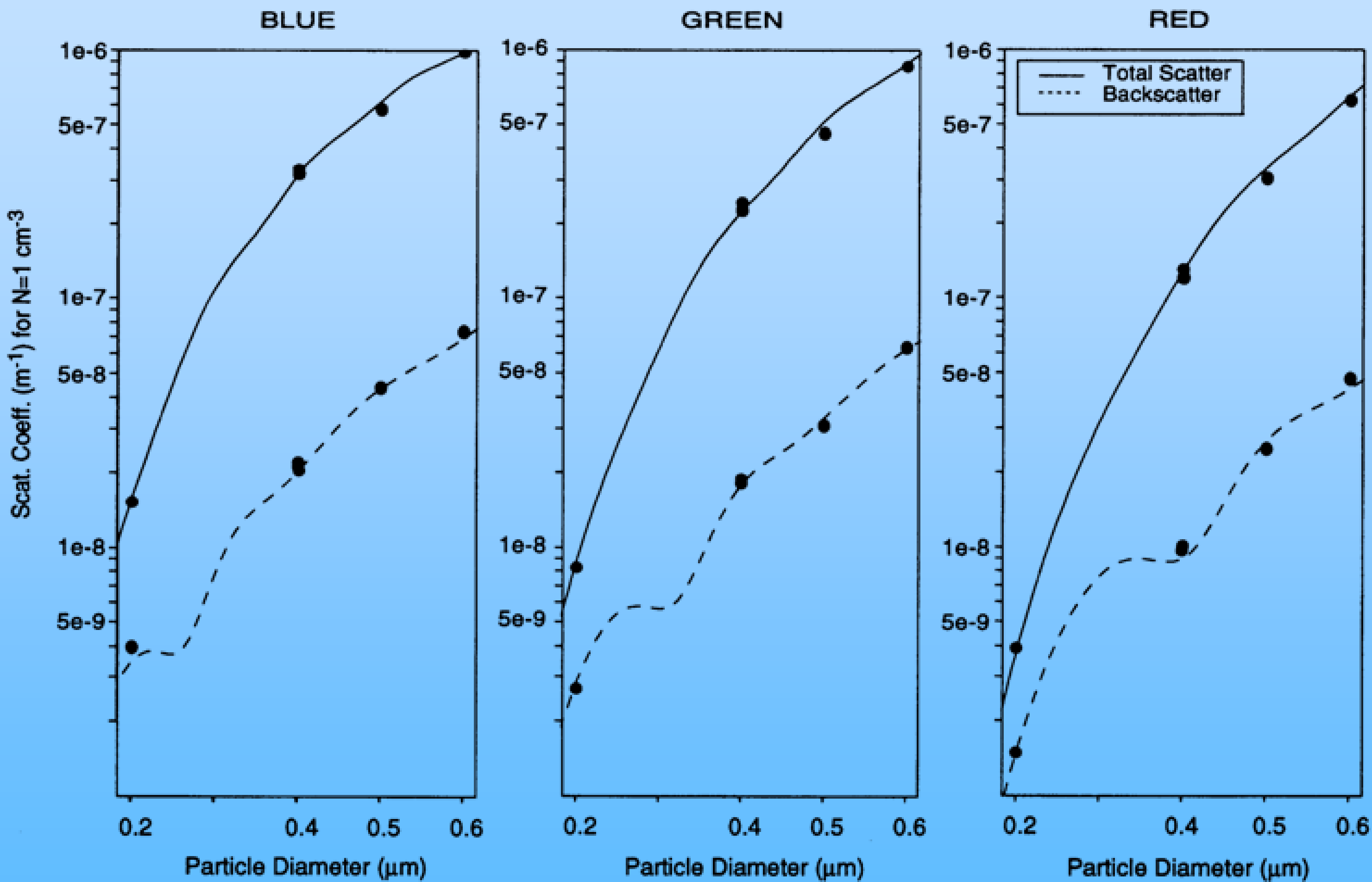
Source: Anderson et al. (1996)

TSI Nephelometer Angular Errors



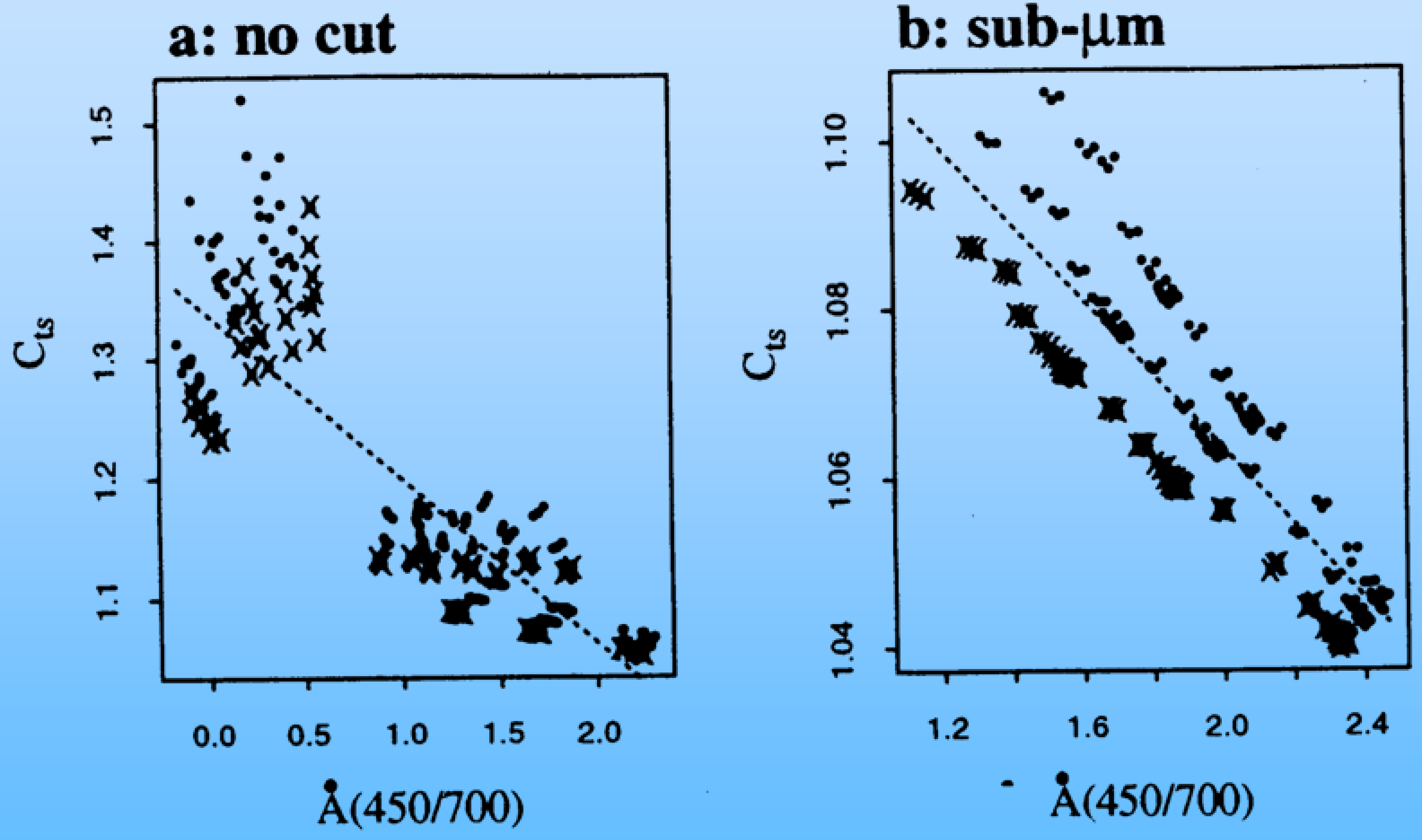
This error is a consequence of calibration with Rayleigh scattering vs. measurement of Mie scattering particles

Measured (points) vs. Calculated (lines)
Response of TSI Nephelometer



Source: Anderson et al. (1996)

Nephelometer Truncation Corrections

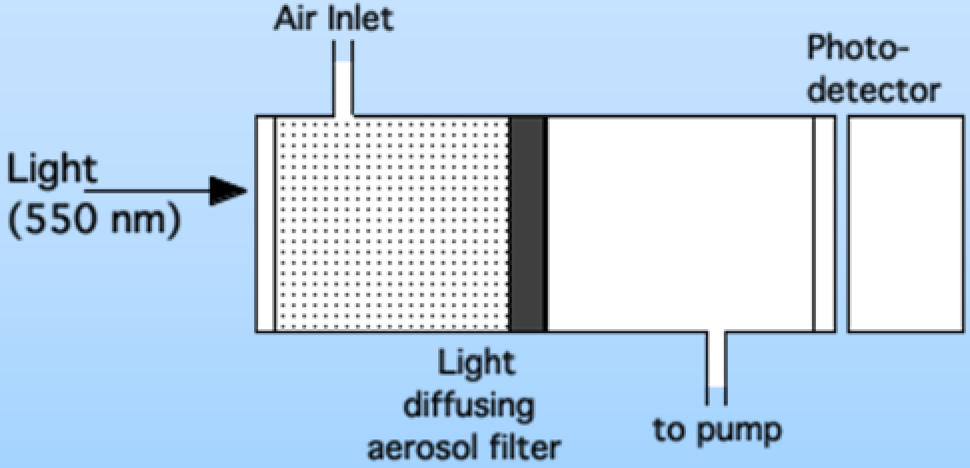


Source: Anderson and Ogren (1998)

Measurements of Light Absorption Coefficient

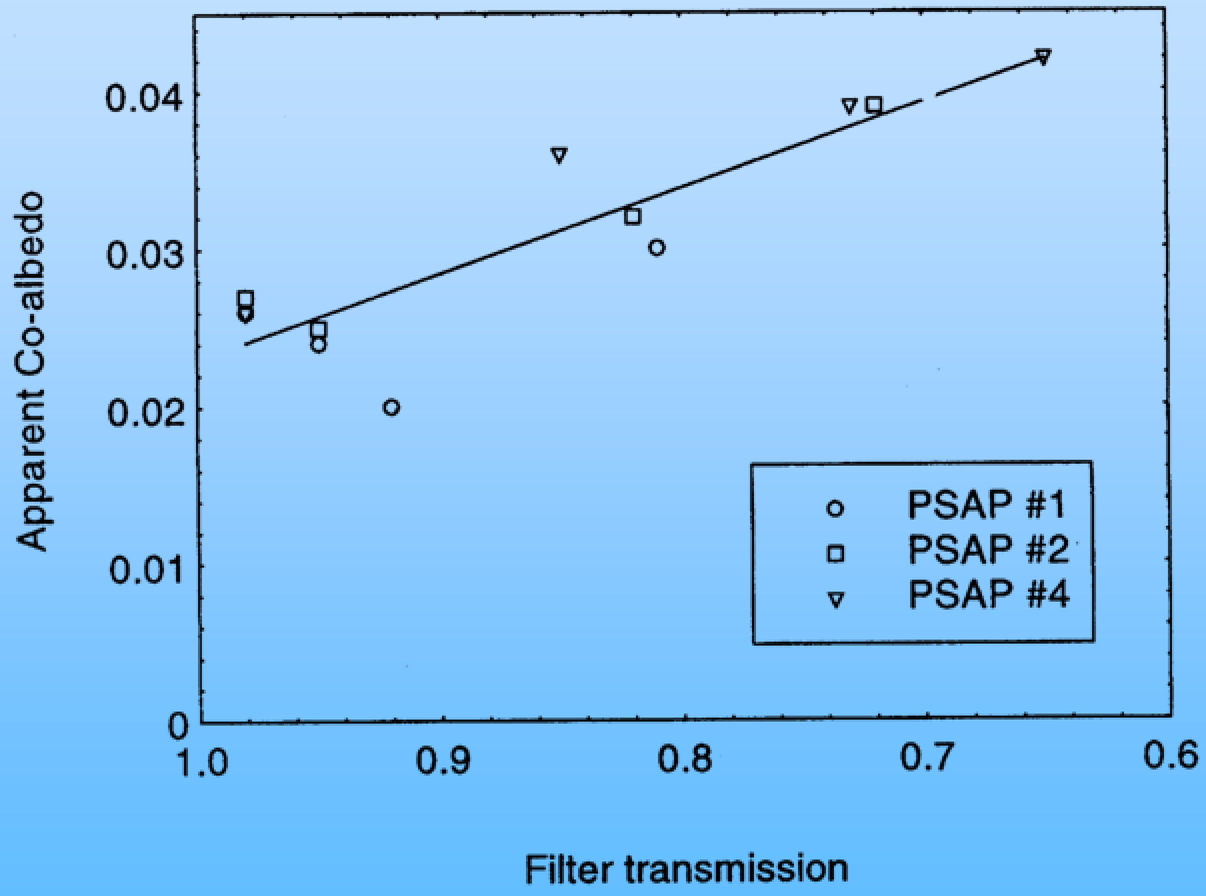
- **Filter-based**
  - PSAP (particle/soot absorption photometer)
  - Aethalometer
    - broadband
    - spectral
  - MAAP (multi-angle absorption photometer)
  - correction schemes
  - comparison results
  - "yellow beads" – sensitivity to liquid aerosols
  - heated inlet (Kondo, 2009, AS&T)
- **"Direct"**
  - photoacoustic
  - photothermal interferometer

Filter Methods for Light Absorption



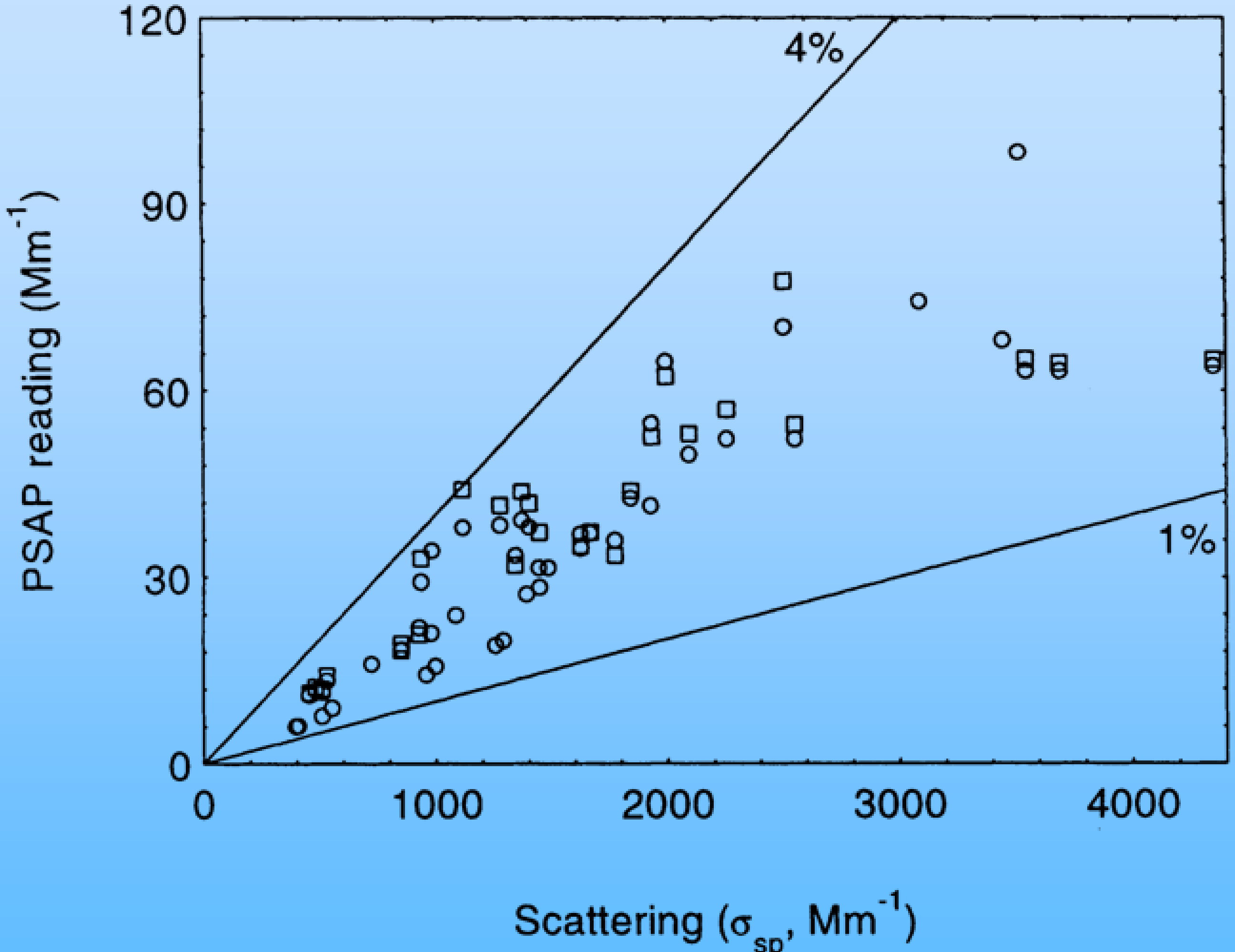
- **Particles are deposited on the filter, which is a light-diffusing, multiple scattering substrate.**
- **Light absorbing particles reduce the light power at the photodetector.**
- **Ideally, light scattering particles don't reduce power.**
- **Variants:**
  - Time-integrated: integrating plate method, integrating sphere, integrating sandwich
  - Continuous: aethalometer, PSAP, MAAP

PSAP Response to Non-Absorbing Particles Depends on Filter Loading



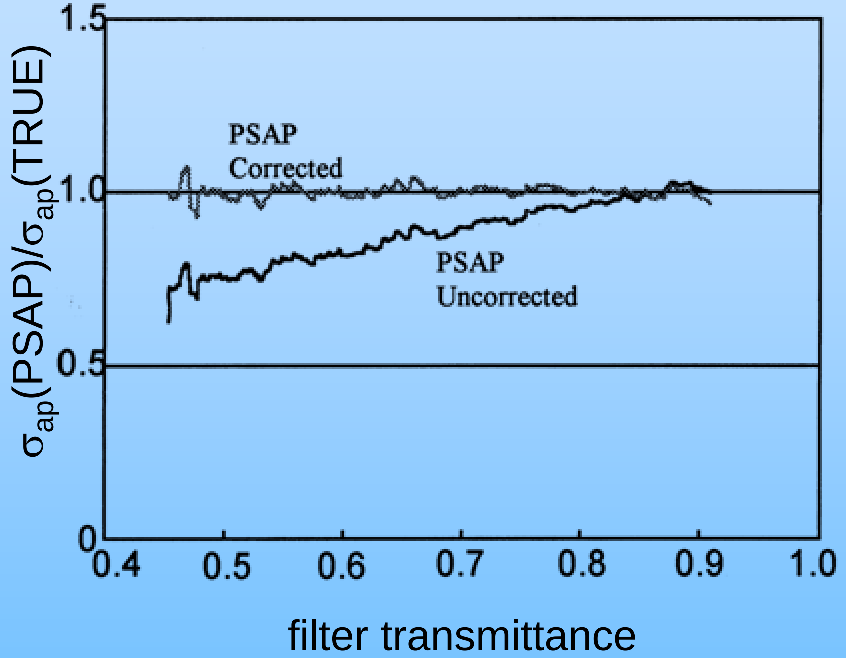
Source: Bond et al. (1999)

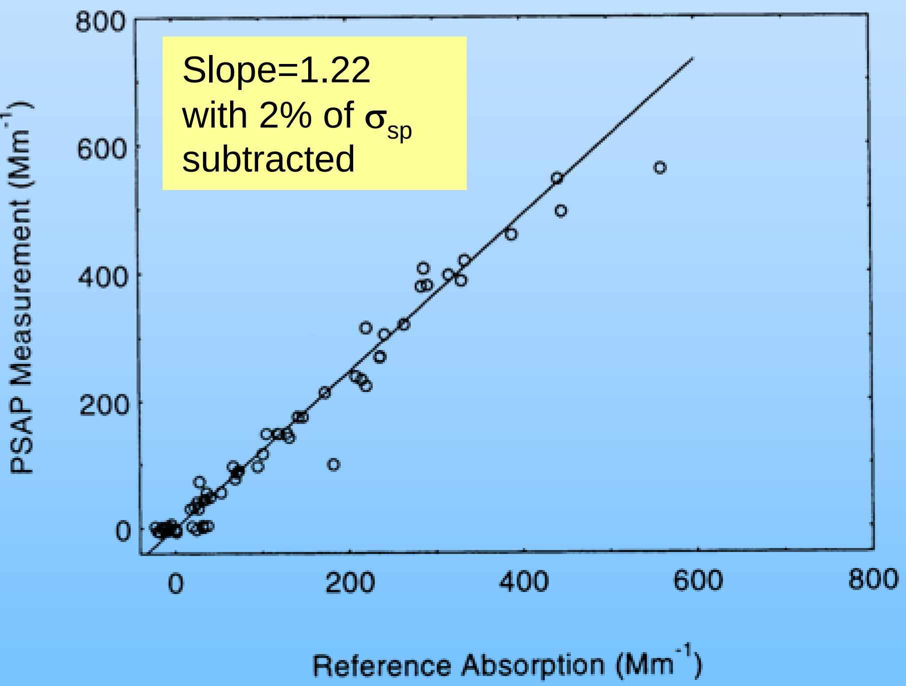
PSAP Response to Scattering



Source: Bond et al. (1999)

Current PSAP Correction Factors

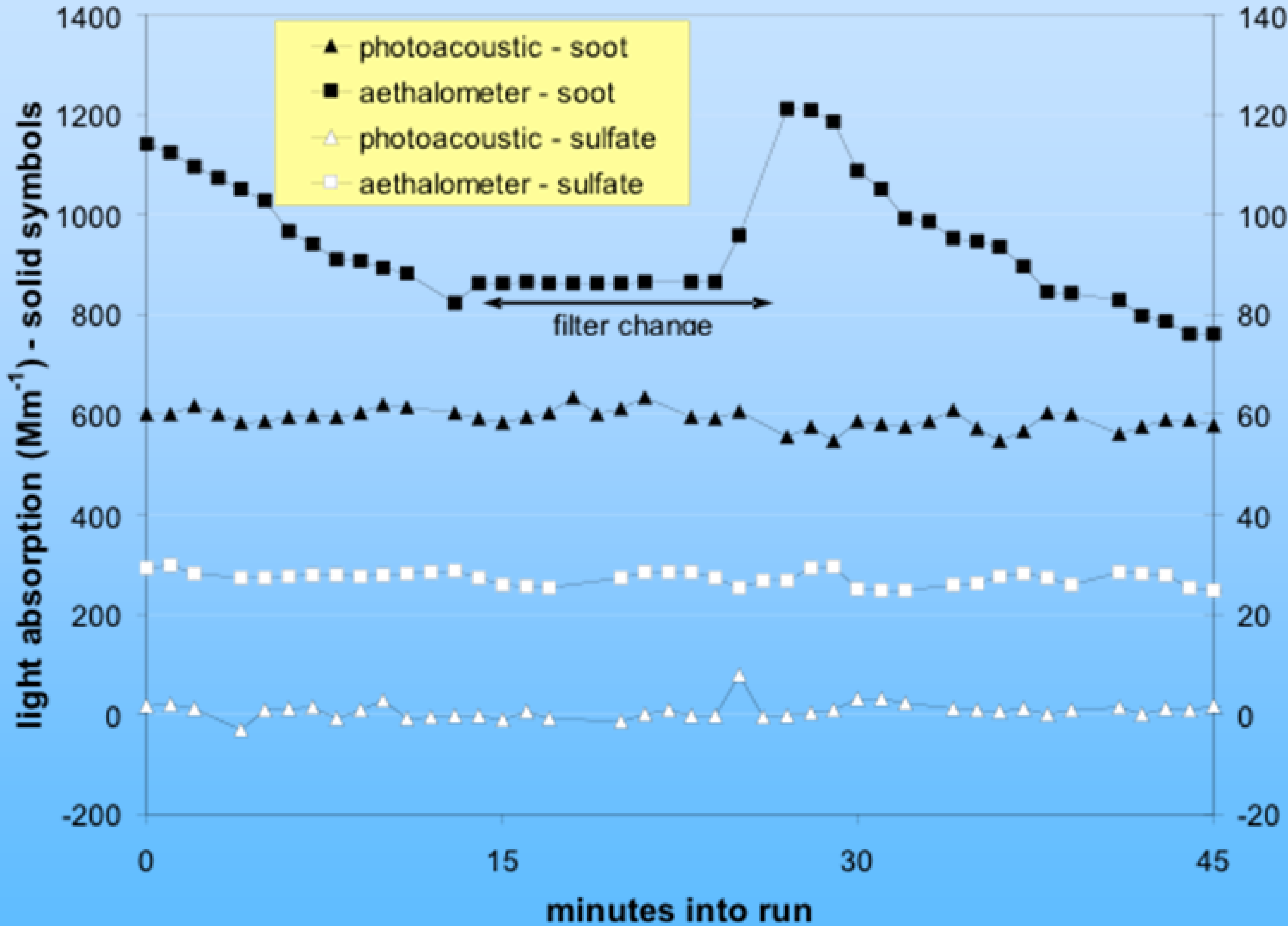




Manufacturer's built-in calibration (Weiss, unpublished)

Bond et al. (1999)

Aethalometer response vs. time



Separate runs with pure soot (σ_{ext}~800 Mm^{-1}) and ammonium sulfate (σ_{ext}~450 Mm^{-1}). Photoacoustic wavelength 532 nm, aethalometer wavelength 521 nm.

Multi-Angle Absorption Photometer

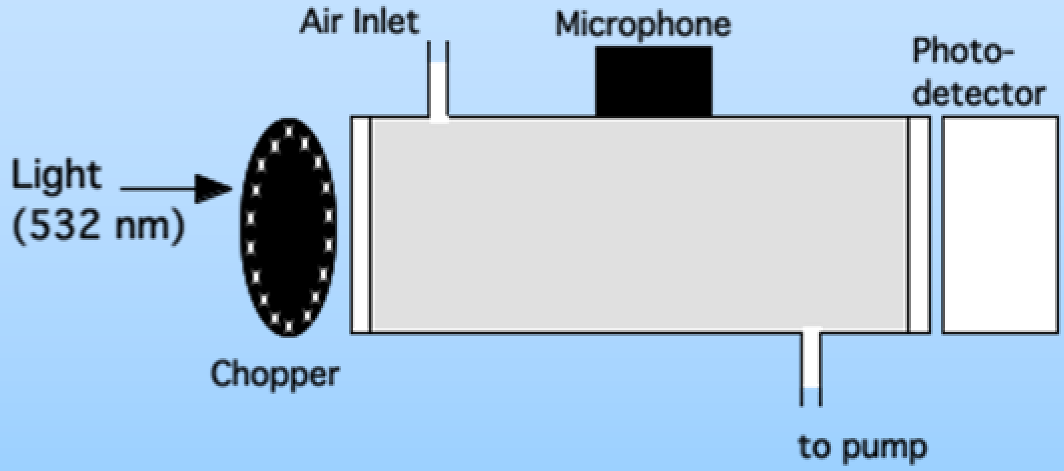
- **"MAAP"**
- **Simultaneously measures light (670 nm) transmitted and reflected by aerosol deposit on filter**
- **A two-stream radiative transfer model is used to derive the aerosol absorption coefficient, accounting for light scattering by particles and filter.**
- **Detection limit ~ 1 Mm^{-1} for 2-minute average at 16.7 lpm flowrate.**

Source: A. Petzold[1] , M. Schönlinner[2] , H.Kramer[2] and H. Schloesser[2]
[1]German Aerospace Center, Oberpfaffenhofen, Germany
[2]ESM Andersen Instruments, Erlangen, Germany

Summary of Filter-based Absorption

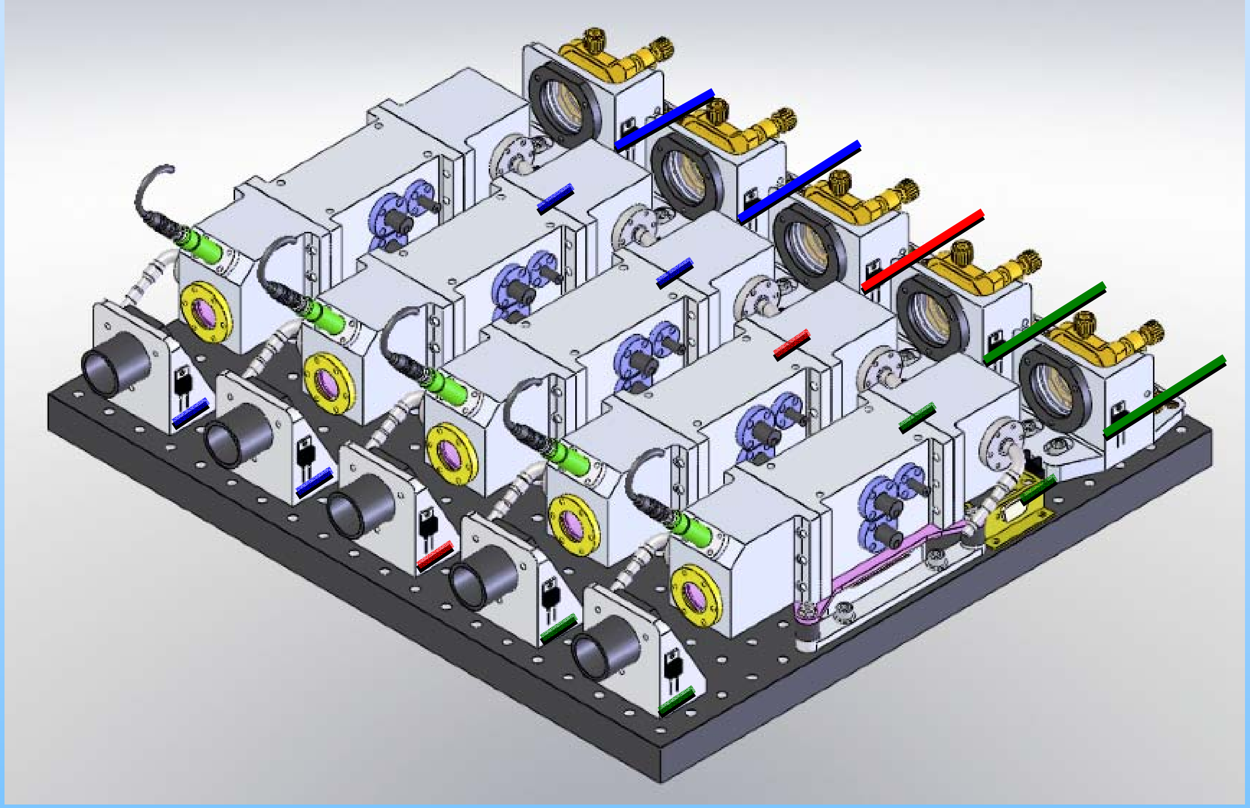
- **Filter spot size and flow rate must be individually calibrated for each instrument**
- **Corrections are required for non-ideal responses of instrument to**
  - scattering by particles (requires scattering measurement)
  - attenuation of light by deposited particles ("shadowing")
- **Correction schemes**
  - PSAP: Bond (1999, AS&T)
  - Aeth: Collaud Coen (2010, AMT)
  - MAAP: done internally, Petzold (2004, J. Aerosol Sci.)
  - improvements are coming

Photoacoustic Absorption Measurement



- **Laser light is power modulated by the chopper.**
- **Light absorbing aerosols convert light to heat, producing a sound wave. No response to light scattering.**
- **Microphone signal at chopper frequency is a measure of the light absorption.**
- **Calibrated by absorption by gases (NO_2, O_3), monodisperse particles, or light extinction**

NOAA 5-Channel Photoacoustic Spectrometer (PAS)



405 nm: ambient + thermo-denuded (0.5 Mm^{-1})

532 nm: ambient + humidified (0.75 Mm^{-1})

660 nm: ambient (1.5 Mm^{-1})

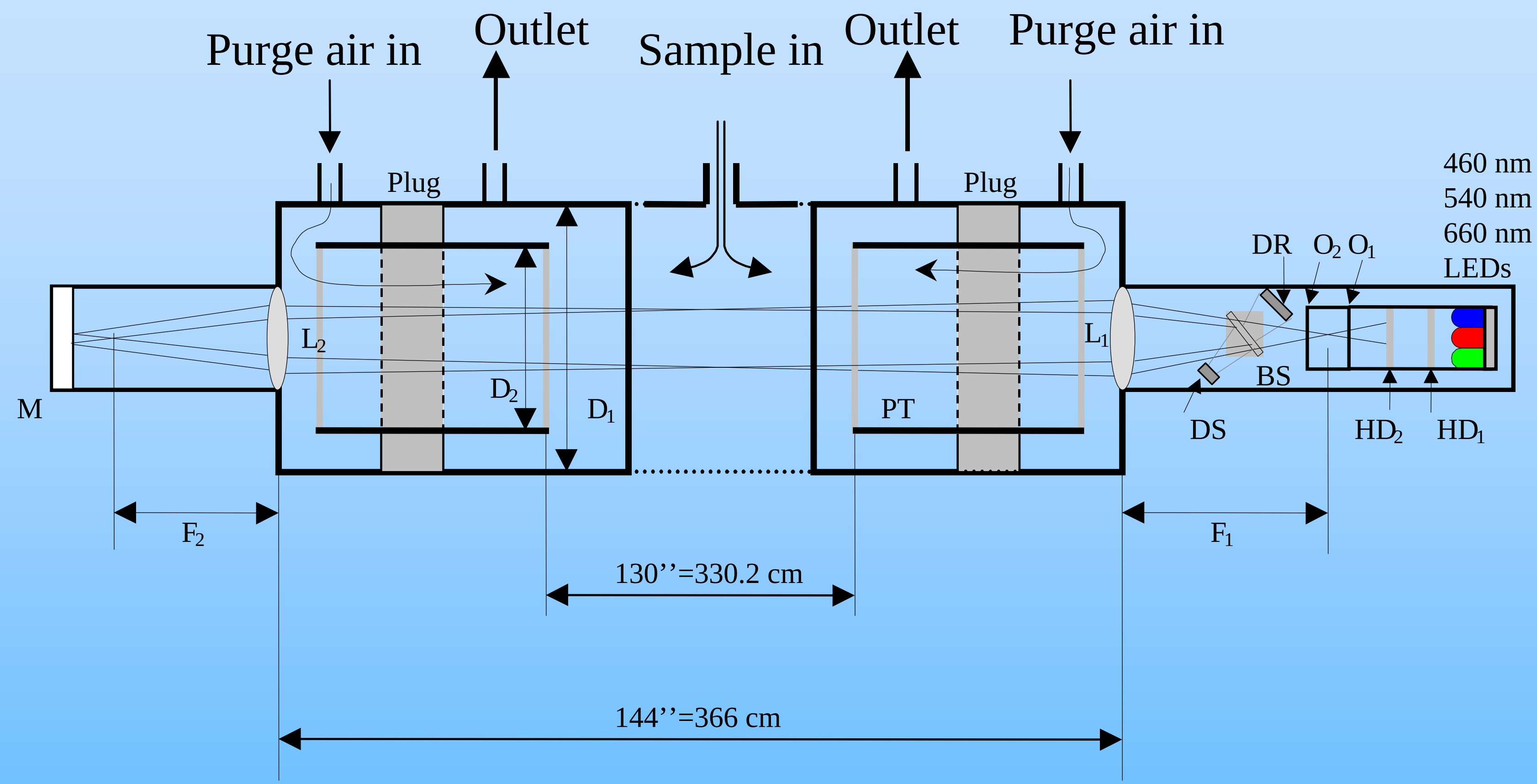
(2σ detection limits for 1 Hz data in parentheses)

Source: D. Lack, 2010, personal communication

Measurements of Extinction Coefficient

- **long-path cell (Virkkula, 2005, AS&T)**
- **cavity ring-down (Baynard, 2007, AS&T)**
- **cavity assisted phase shift (Massoli, 2010, AS&T)**
- **Fundamental calibration is geometric path length**
- **measure difference in light extinction between sample air and filtered sample air**

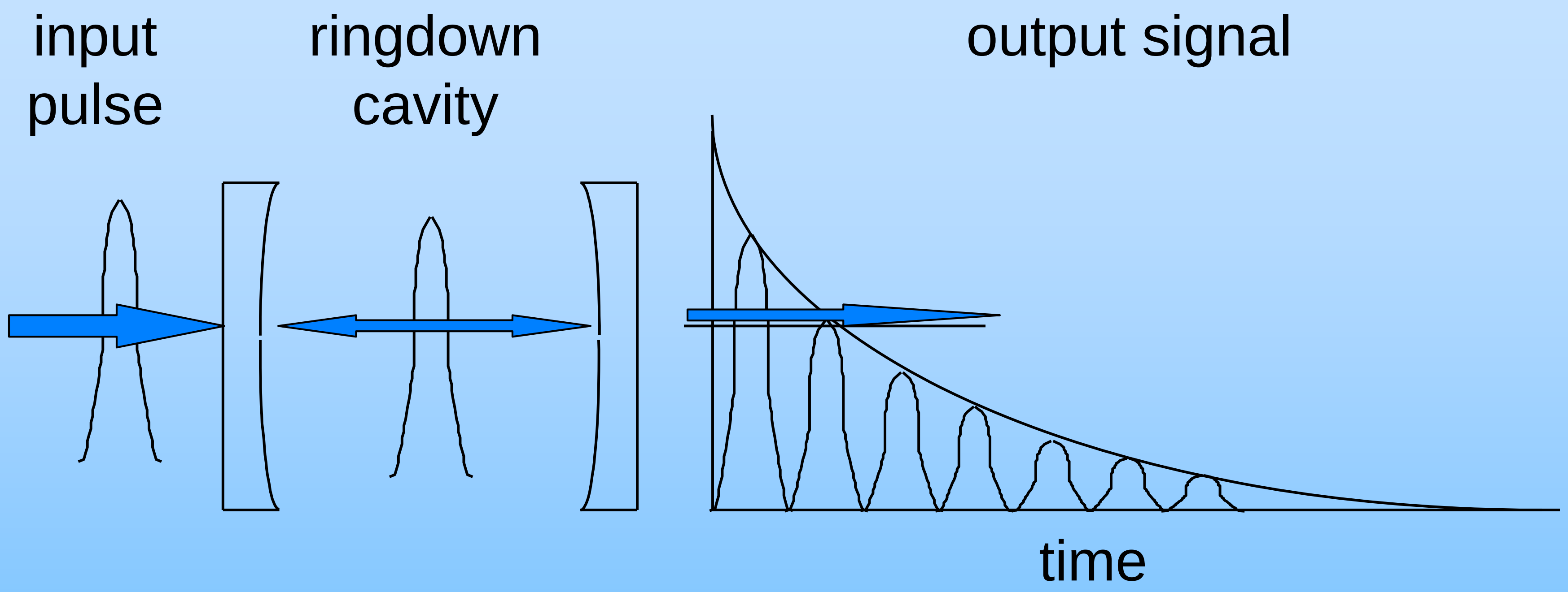
U.W. Optical Extinction Cell



L = 660 cm

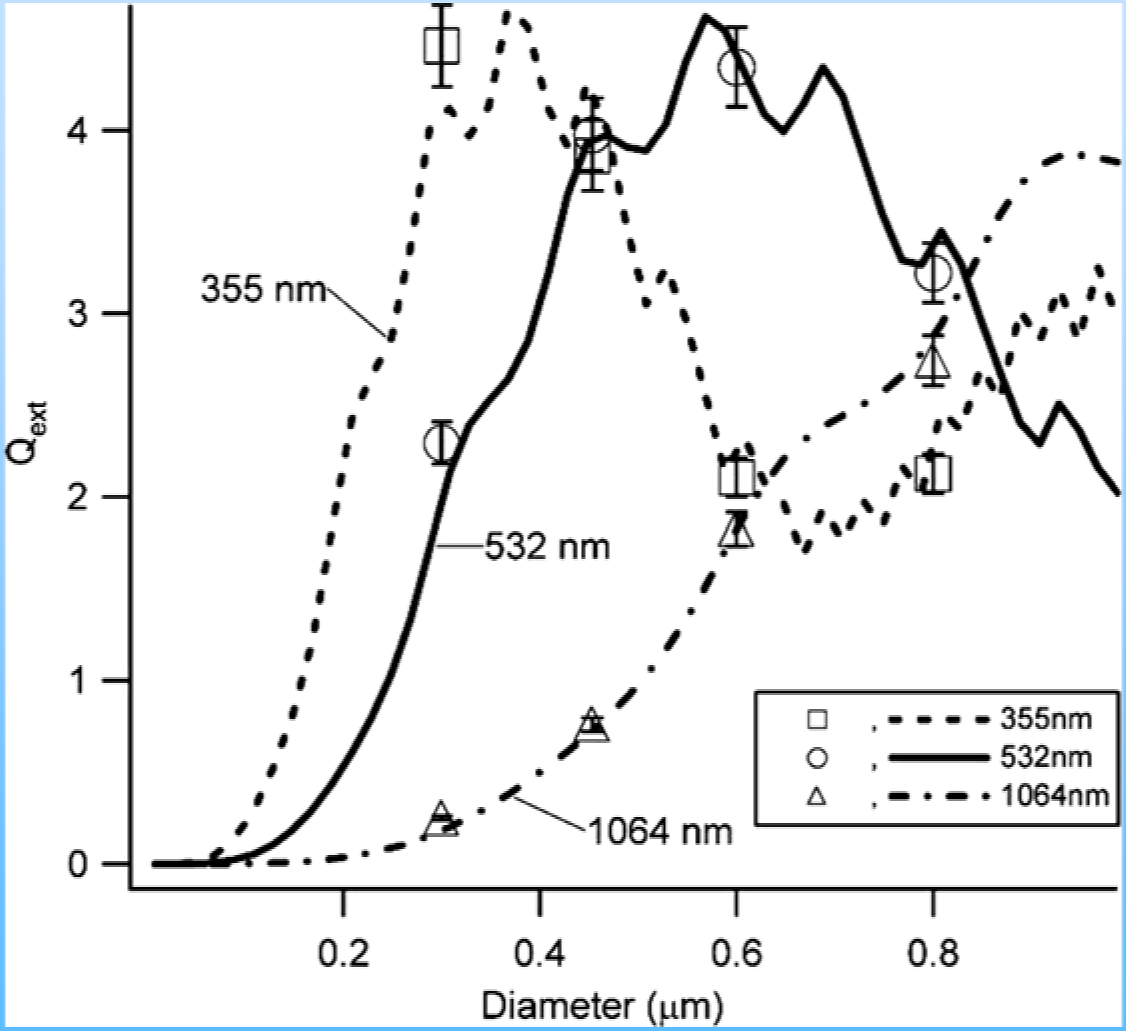
Source: Virkkula et al. (2005)

What is Cavity Ringdown (CRD)?



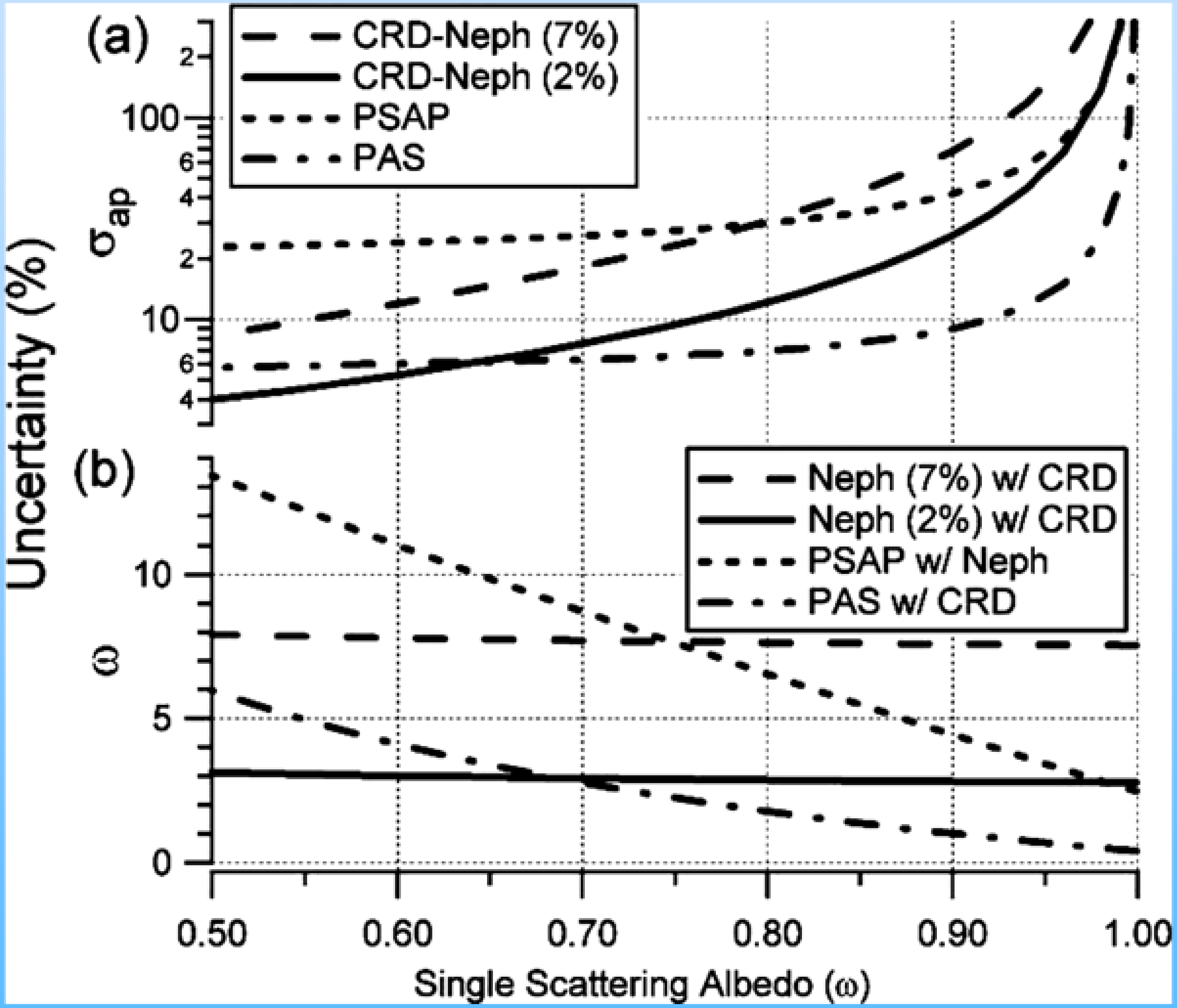
- input pulse width ~ 20 nanoseconds
- mirror reflectivity > 99.995%
- ring-down time 5-100 microseconds
- extinction coefficient derived from fitting an exponential function to decay of output signal
- some variants measure scattering coefficient simultaneously

CRD Accuracy Confirmation



- **measurements of spheres of known size and refractive demonstrate accuracy of CRD instrument**
- **Baynard, 2007, AS&T**

Uncertainty of Absorption and SSA

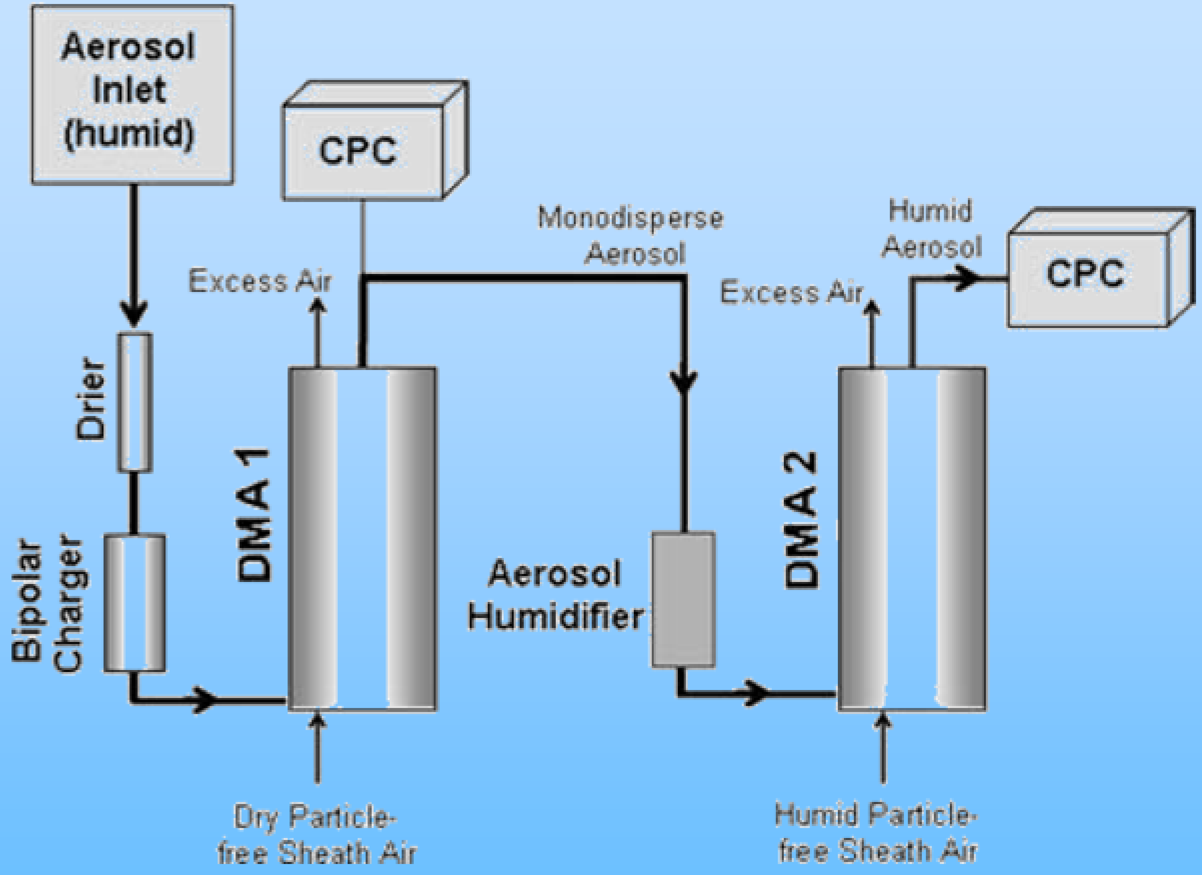


- **CRD + photoacoustic give the lowest uncertainties**
- **Baynard, 2007, AS&T**

Hygroscopic Growth Measurements

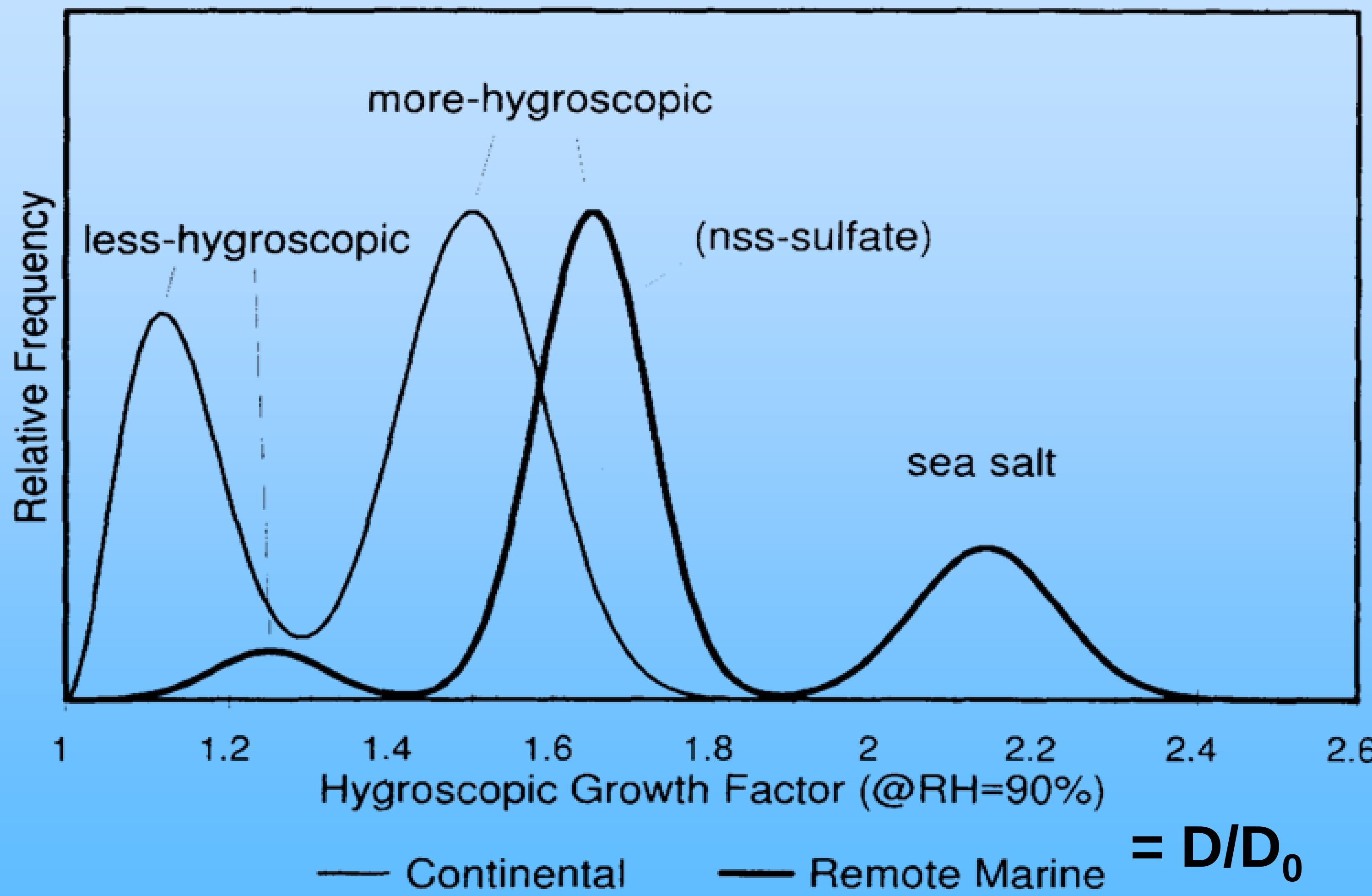
- **Diameter growth**
  - HTDMA
- **Scattering growth**
  - humidograph
- **CCN concentration**
  - expansion
  - axial temperature gradient
    - dT scanning
    - flow scanning
  - parallel plate
- **Mixed methods**
  - SMPS + CCNC

Humidified Tandem
Differential Mobility Analyzer (HTDMA)



- **DMA #1 selects particles of a single size, D_0**
- **Monodisperse particles are conditioned at a higher RH**
- **DMA #2 measures the size distribution of the humidified particles**

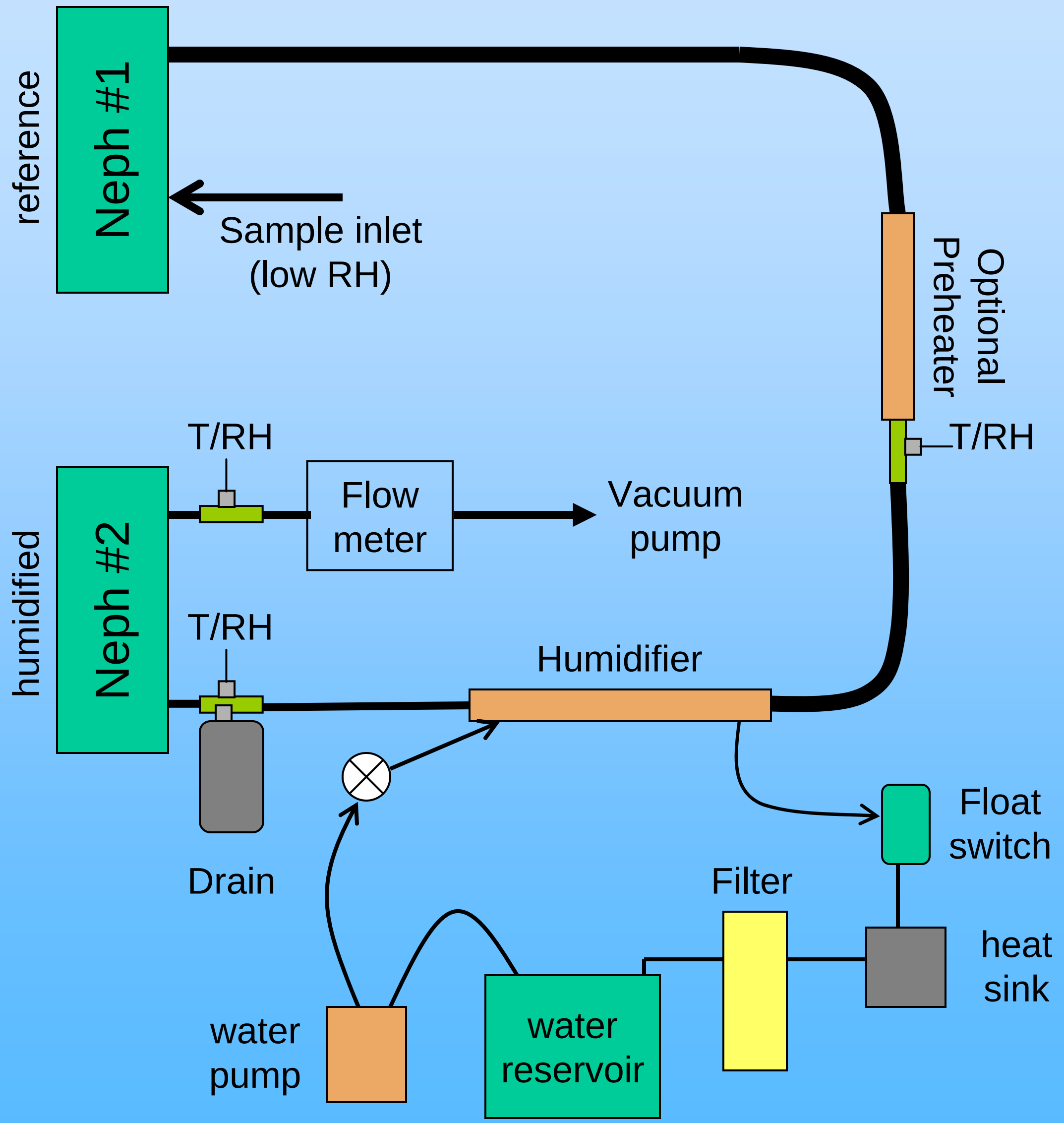
HTDMA Hygroscopic Growth Curves



= D/D_0

Source: Berg et al (JGR, 1998)

Humidograph flow diagram



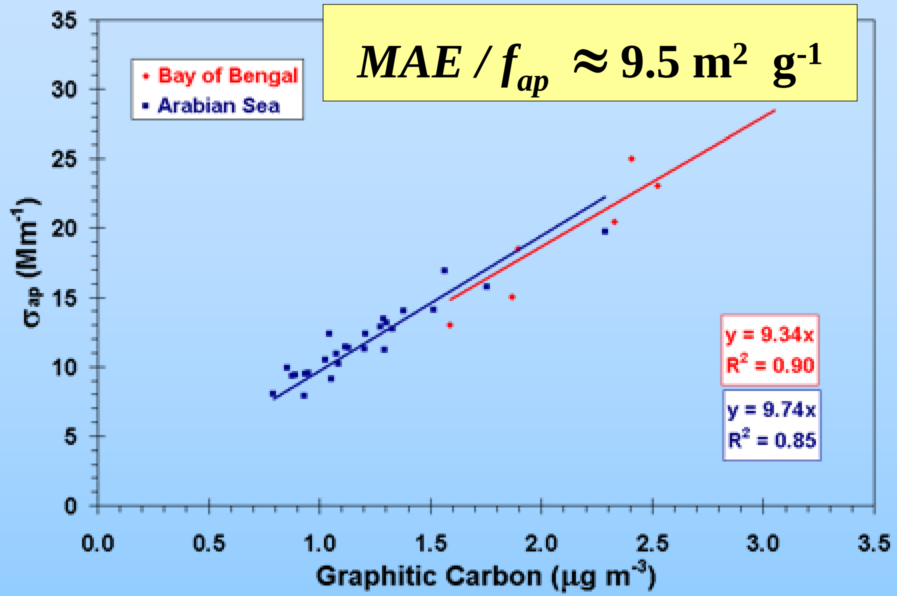
- **A humidified nephelometer measures RH-dependence of light scattering**
- **Heated water flows past a water-permeable membrane to humidify the air**
- **Sample RH is controlled by the temperature of the heated water**

Measurement Methods - Chemical

- **Ion chromatography**
- **Wet-chemical**
- **X-ray spectroscopy**
- **Atomic absorption spectroscopy**
- **Mass spectroscopy**
  - single particles
    - PALMS
    - TSI
  - size-resolved
    - AMS
- **Major ions**
- **Trace metals**
- **Elemental composition**
- **Elemental carbon**
- **Black carbon**
- **Brown carbon**
- **Organic carbon**
- **Organic molecular composition**
- **Chow review paper (2008, JAWMA)**

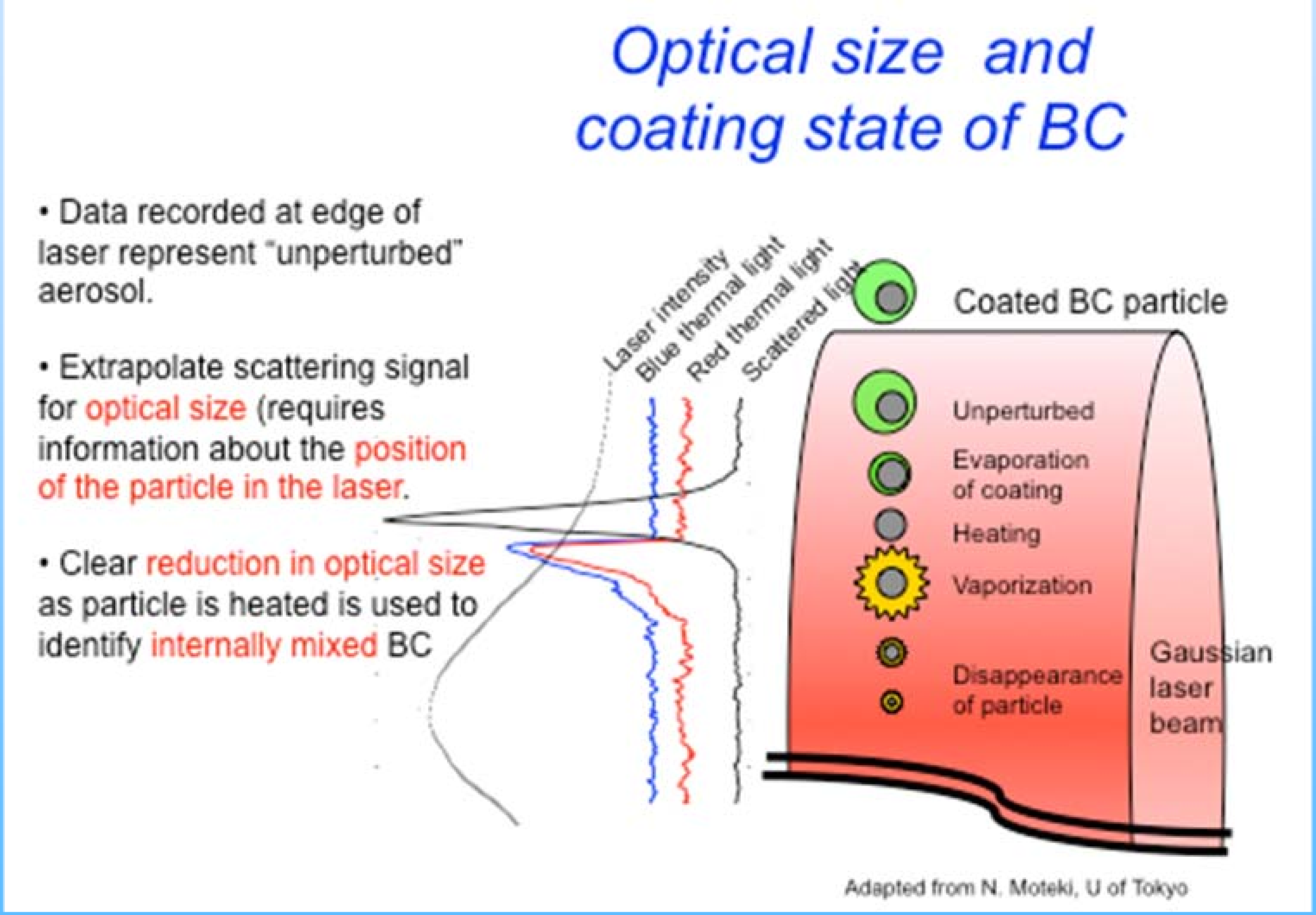
Black Carbon and Light Absorption

- **Optical methods for determining BC really measure σ_{ap} (PSAP, aethalometer, MAAP, photoacoustic, …)**
- **BC = σ_{ap} x f_{ap} / MAE**
  – f_{ap} = fraction of light absorption due to BC
  – *MAE* = mass absorption efficiency of BC ($m^2\ g^{-1}$)
- **Climate forcing calculations require σ_{ap}**



- **Empirical relationships, like the one show above for the Indian Ocean, are required to determine BC from σ_{ap} (WMO/GAW report #153)**

Measurement of BC + Coatings using the <u>Single Particle Soot Photometer (SP2)</u>



Source: J. Schwarz, personal communication

Measurements not Discussed

- **CCN concentration vs. supersaturation**
  - – expansion
  - – parallel plate
    - Hudson
  - – axial temperature gradient
    - DMT
- **Mass concentration**
  - – beta attenuation
  - – TEOM
  - – gravimetric

Parting Thoughts about In-situ Measurements

- **Common feature**
  - sample air is brought into an instrument through an inlet
- **Common weakness**
  - sampling changes the chemical and/or physical properties of the particles
- **Common strength**
  - ability to measure known substances under controlled conditions, which ties the measurements closely to physical or chemical standards