Atmospheric Aerosol Physics, Physical Measurements, and Sampling

Integrating Nephelometer & Absorption Photometer

São Paulo School of Advanced Science on Atmospheric Aerosols:
properties, measurements, modeling, and effects on climate and health

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European Center for Aerosol Calibration

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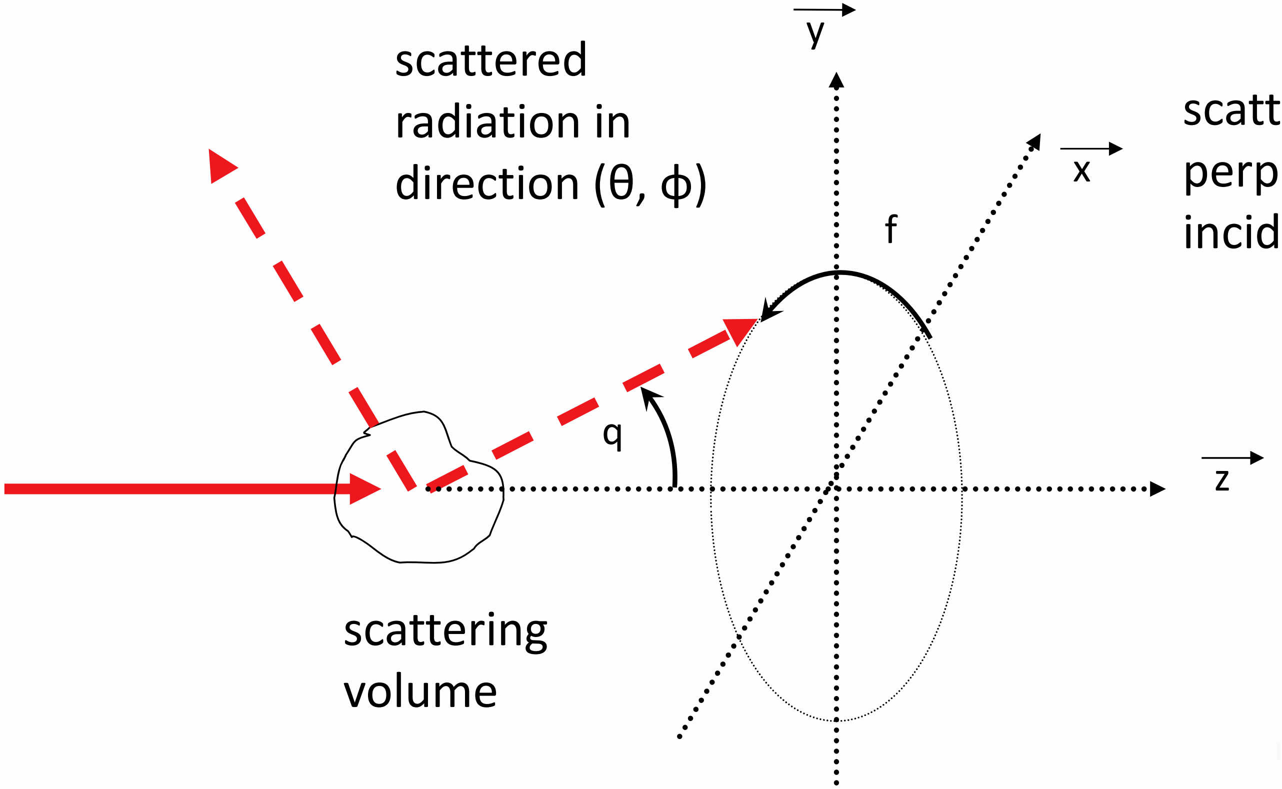
Principle of an Integrating Nephelometer

Integrating Nephelometer

- The original application of the instrument was for estimating the horizontal visibility at night for wartime military operations (Beuttel and Brewer, 1949).
- Since that time, numerous other applications of the integrating nephelometer have been found.
- Integrating nephelometers produce a signal that is closely related to the spectral scattering coefficient.
- Currently, it is used to determine that particle light scattering and backscattering coefficient.

Principle of Light Scattering



scattered
radiation in
direction (θ, ϕ)

scattering plane (x,y)
perpendicular to
incident radiation (z)

incident
radiation I_0^λ

scattering
volume

Scattering coefficient of light in a small volume:

- The spectral scattering coefficient σ_s^λ can be defined with the help of the scattering function $f^\lambda(\theta, \phi)$.

$$\boxed{f^{\lambda}(\theta,\varphi) = \frac{p^{\lambda}(\theta,\varphi)}{4\pi} \cdot \sigma_s^{\lambda}}$$

- $f^\lambda(\theta,\phi)$ gives the energy that is scattered into an increment of solid angle $d\Omega$ in direction (θ,ϕ). The dimension *of* $f^\lambda(\theta, \phi)$ is $m^{-1}sr^{-1}$.
- The scattering angle θ is measured from the initial direction of illumination.
- The integral of $f^\lambda(\theta, \phi)$ over all directions is the spectral scattering coefficient.

$$\boxed{\sigma_s^{\lambda} = \int_0^{\pi}\int_0^{2\pi} f^{\lambda}(\theta,\varphi)\sin(\theta)\,\mathrm{d}\varphi\,\mathrm{d}\theta}$$

- The problem for constructing a Nephelometer is the correct integration including the term $\sin(\theta)$ over the angular range $0 \le \theta < \pi$.
- Nephelometer doing this integration are called Integrating Nephelometer

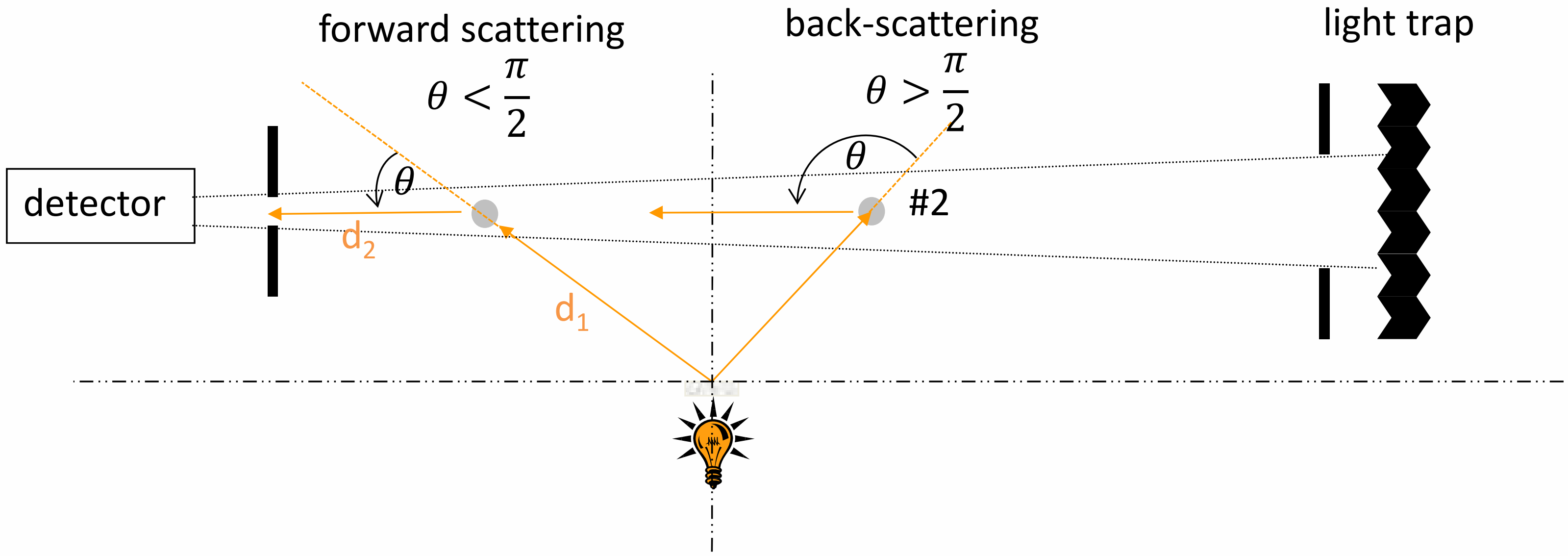
Integration for spherical particles

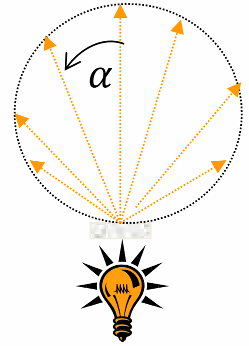
For spherical particles the scattering function simplifies to

$$\boxed{f^{\lambda}(\theta,\varphi) = f^{\lambda}(\theta)}$$

$$\boxed{\sigma_s^{\lambda} = 2\pi\int_0^{\pi} f^{\lambda}(\theta)\cdot\sin(\theta)\cdot\mathrm{d}\theta}$$

Schematic illustration of an nephelometer with opal glass diffuser



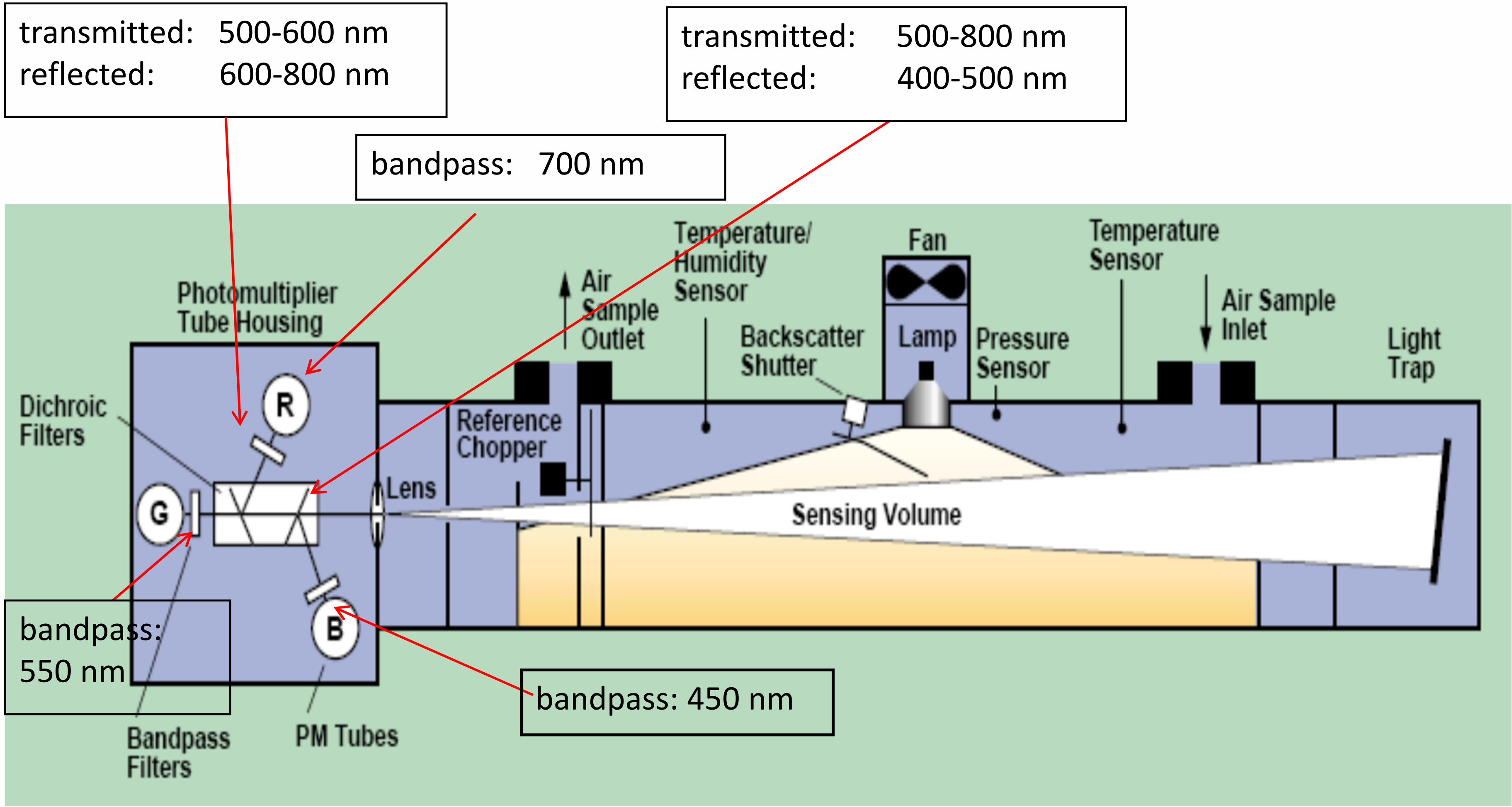


$I(\alpha) \sim cos(\alpha)$

How does this configuration make the right integration?

- Integration over θ is substitute by integration along the length of the measurement cell
- The sinus is generated by the Lambertian radiation characteristics of the light source
- The decrease of intensity with the square of distances (d_1 and d_2) is compensated by the opening of the cone (field of view of detector)

TSI Integrating Nephelometer model 3563



transmitted: 500-600 nm
reflected: 600-800 nm

transmitted: 500-800 nm
reflected: 400-500 nm

bandpass: 700 nm

bandpass: 550 nm

bandpass: 450 nm

Calibration

Nephelometer Calibration

The measured scattering coefficient (photon frequency C_{meas} x calibration factor K_2) is the sum of:

σ_{sp} … Particle scattering

σ_{air} … Rayleigh scattering of the air molecules

W … Wall scattering

$$\boxed{\sigma_{\mathrm{sp}} + \sigma_{air}(T,p) + W = K_2 C_{\mathrm{meas}}}$$

The particle scattering coefficient is then

$$\boxed{\sigma_{\mathrm{sp}} = K_2 C_{\mathrm{meas}} - W - \sigma_{air}(T,p)}$$

And the backscattering coefficient can be calculated to

$$\boxed{\sigma_{\mathrm{bsp}} = K_2 C_{\mathrm{meas,b}} - W_b - K_4 \cdot \sigma_{air}(T,p)}$$

Two particle-free gases are used to calibrate the integrating nephelometer: one low (air)and one high span gas (CO_2)

Step 1: Scattering and backscattering is measured with particle free air. The measured signal is the sum of Rayleigh scattering of air molecules and the wall scattering.

$$\boxed{\sigma_{\mathrm{sp}} = 0 \rightarrow K_2 C_{\mathrm{meas,air}} = W + \sigma_{air}(T,p)}$$

$$\boxed{\sigma_{\mathrm{bsp}} = 0 \rightarrow K_2 C_{\mathrm{meas,air,b}} = W_b + K_4 \cdot \sigma_{air}(T,p)}$$

Step 2: Scattering is measured with CO_2. The measured signal is the sum of Rayleigh scattering of CO_2 molecules and the wall scattering

$$\boxed{\sigma_{\mathrm{sp}} = 0 \rightarrow K_2 C_{\mathrm{meas,CO_2}} = W + \sigma_{CO_2}(T,p)}$$

$$\boxed{\sigma_{\mathrm{bsp}} = 0 \rightarrow K_2 C_{\mathrm{meas,CO_2,b}} = W_b + K_4 \cdot \sigma_{CO_2}(T,p)}$$

- There are four unknown parameters: K_2, K_4, W, W_b
- Theses parameters can be calculated by the previous set of four equations.

K_2 … the calibration slope

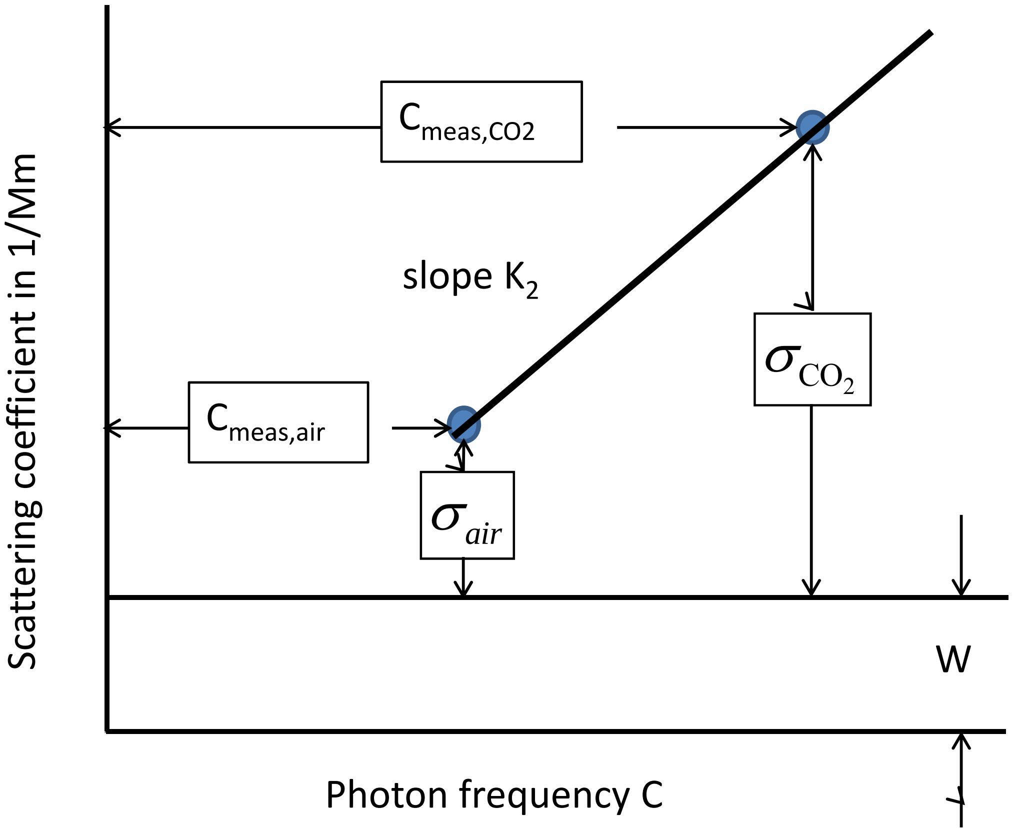
K_4 … calibration factor for backscattering. Ideally $K_4=0.5$

W … wall scatter constant for total scatter

W_b … wall scatter constant for backscatter

The calibration factor K_2 is then:

$$K_2 = \frac{\sigma_{CO_2} - \sigma_{air}}{C_{meas,CO_2} - C_{meas,air}}$$



The calibration factor for K4 (back-scattering) calculated similarly (not show):

Rayleigh scattering constants of air and CO_2

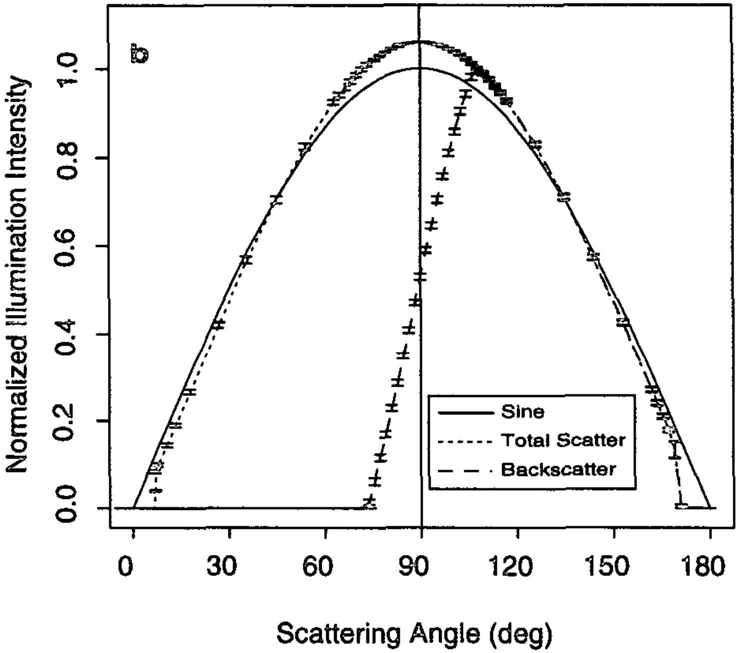
Gas	$\sigma_{s,R}$ 10^{-6} m^{-1}	λ µm	P hPa	T C
Air	27.40	0.45	1013	0
	12.28	0.55		
	4.68	0.70		
CO_2	86.01	0.45	1013	0
	30.48	0.55		
	11.61	0.70		

Rayleigh backscattering coefficients are half of the value of the total scattering coefficient.

Correction & Ångström Exponent

Angular Truncation and Imperfect Illumination Function

- The opal glass diffuser is not a perfect sin(θ)!
- Light scattered at angles smaller 7°and larger 170°can not be measured.
- These systematic uncertainties are combined in the illumination function Z(θ).
- The illumination function has to be considered in calibrations and data evaluation.



Ångström Exponent

Spectral behavior of particle scattering often is described by the Ångström exponent

$$\boxed{\frac{\sigma_s^{\lambda_1}}{\sigma_s^{\lambda_2}} = \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha}}$$

The Ångström exponent depends on particle size distribution (aerosol type)

- urban aerosol: $1.5 < \alpha < 2.5$
- rural aerosol: $1.0 < \alpha < 1.5$
- mineral dust : $-0.1 < \alpha < 0.5$
- Sea salt: $0.2 < \alpha < 0.5$

Particle Light Absorption

Particle Light Absorption

- Absorption is the process by which the energy of a photon is taken up by another subject (here particles).
- The photon is destroyed.
- In the atmosphere, light is absorbed by both gas molecules and by aerosol particles.
- Absorption by gases is usually weak compared to absorption by aerosol particles.
- The use of Absorption Photometers is:
  - to measure the particle light absorption coefficient
  - to estimate a corresponding particle mass concentration of Black Carbon

Difference of Extinction Minus Scattering

Difference of Extinction Minus Scattering

The ‘extinction minus scattering’ method is based on **first principles** of optics. The basic equation is

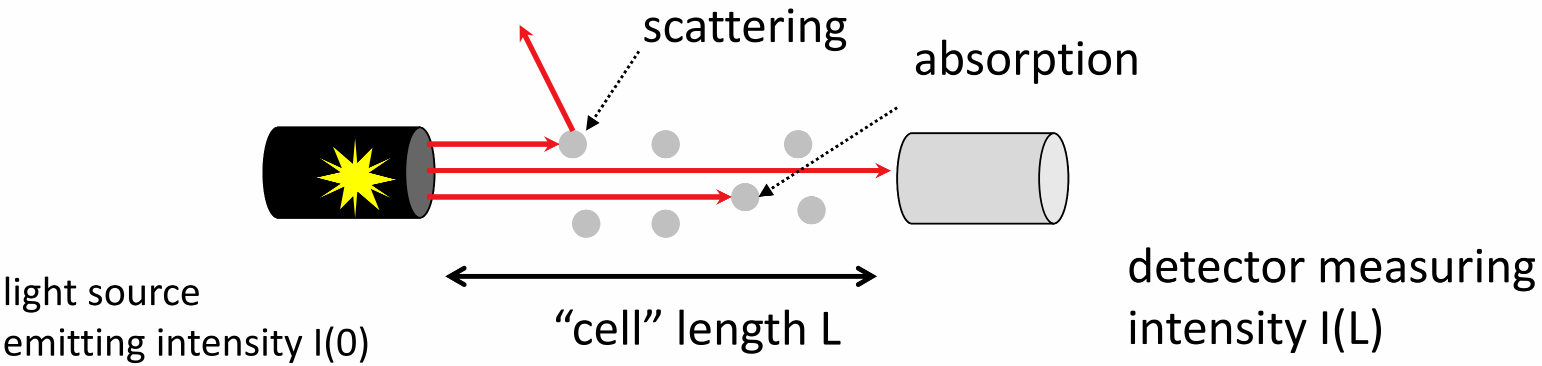
$$\boxed{\sigma_{abs} = \sigma_{ext} - \sigma_{sca}}$$

particle light extinction coefficient

particle light scattering coefficient

- Two concurrent measurement of extinction and scattering coefficients are needed.
- An instrument for measuring the particle light scattering coefficient was shown in the lecture *Integrating nephelometers*.
- The principle of an extinction measurements is shown in the following.

Principle of extinction measurements



The extinction coefficient is derived from the Lambert-Beer law:

$$\boxed{\frac{I(L)}{I(0)} = e^{-\sigma_{ext} \cdot L} \quad \Leftrightarrow \quad \sigma_{ext} = \frac{-\ln \frac{I(L)}{I(0)}}{L}}$$

- The extinction coefficient is given in unit of 1/m.
- Measuring extinction at low aerosol particle concentrations requires cell lengths up to to several hundreds meters.

Error propagation

- From error propagation follows, that the uncertainty of the absorption coefficients is

$$\Delta\sigma_{abs} = \sqrt{(\Delta\sigma_{sca})^2 + (\Delta\sigma_{ext})^2}$$

- The absolute uncertainty is constant for all concentrations. (It just depends on the instrumental uncertainties of both instruments)
- Span between extinction and scattering changes with concentration and single scattering albedo ($ssa = \sigma_{sca}/\sigma_{ext}$).

Examples:

1. Low particle light extinction and scattering coefficients with relative larger uncertainties

σ_{ext} =20 #/Mm; $\sigma_{\mathrm{sca}s}$ =18 #/Mm; $\Delta\sigma_{\mathrm{ext}}$=2 #/Mm; $\Delta\sigma_{\mathrm{sca}}$=1.8 #/Mm → $\Delta\sigma_{abs}$=2.7#/Mm

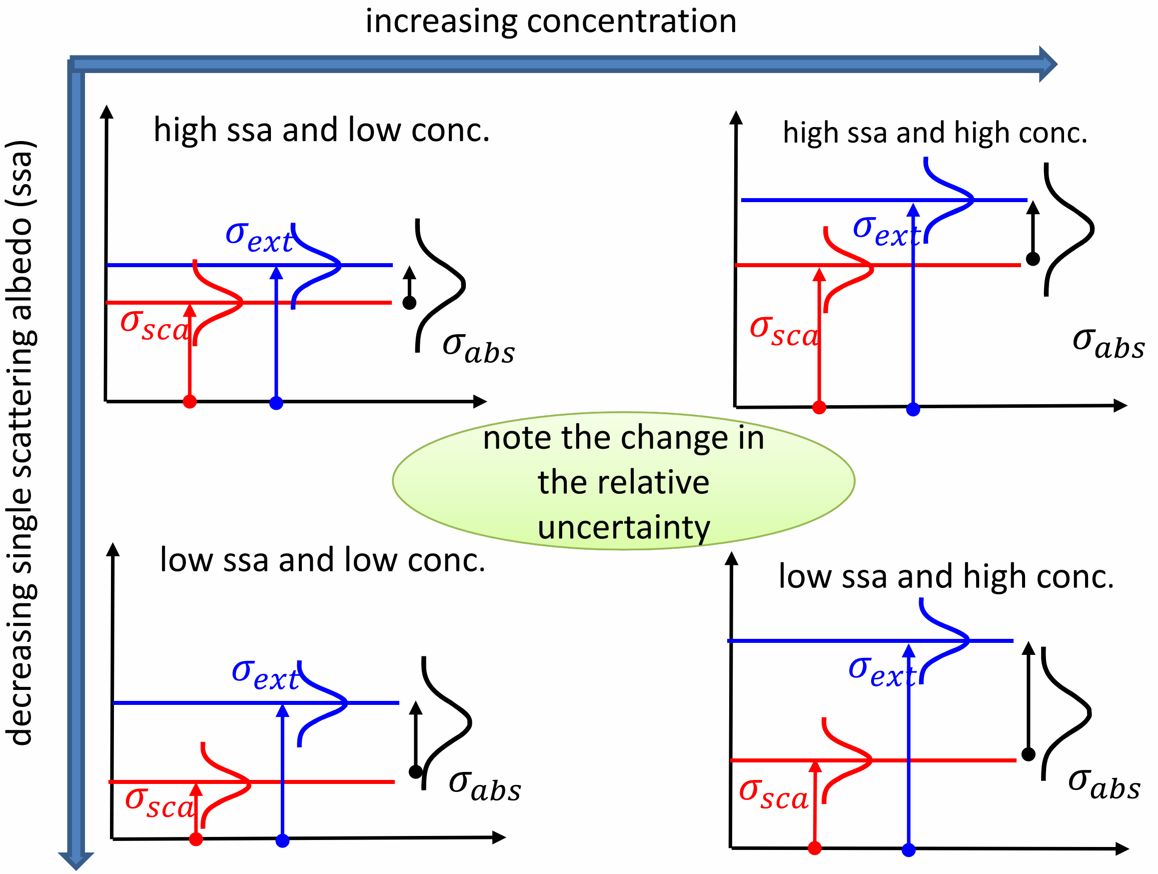
→ σ_{abs}=20-18 #/Mm = 2 +/- 2.7 #/Mm

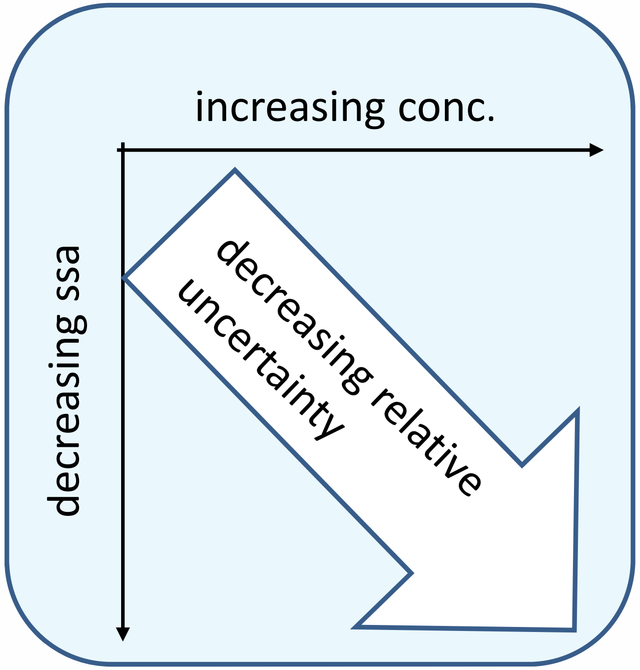
2. High particle light extinction and lower scattering coefficients with relative small uncertainties

σ_{ext} =100 #/Mm; $\sigma_{\mathrm{sca}s}$ =50 #/Mm; $\Delta\sigma_{\mathrm{ext}}$=5 #/Mm; $\Delta\sigma_{\mathrm{sca}}$=2.5 #/Mm → $\Delta\sigma_{abs}$=5.6 #/Mm

→ σ_{abs}=100-50 #/Mm = 50 +/- 5.6 #/Mm

Relative uncertainty as function of concentration and single scattering albedo





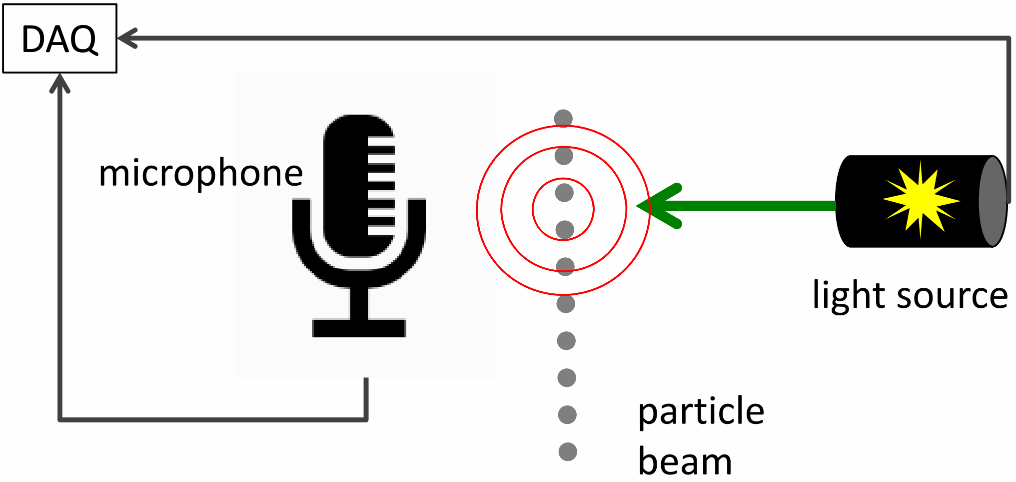
The higher the concentration and the lower the single scattering albedo, the better the performance of extinction minus scattering systems.

Photo Acoustic Sensor

Photo Acoustic Sensor (PAS)

- An on-off modulated laser beam passes a particle beam. The laser is on-off modulated with frequency f.
- The laser radiation is partly absorbed by the particles and heats the particles.
- By thermal conductivity the surrounding air is heated periodically.
- The periodic heating of the air causes an acoustic wave with frequency f, the laser modulation frequency.

$$P_{acoustic} \propto P_{therm} \propto \sigma_{abs}$$



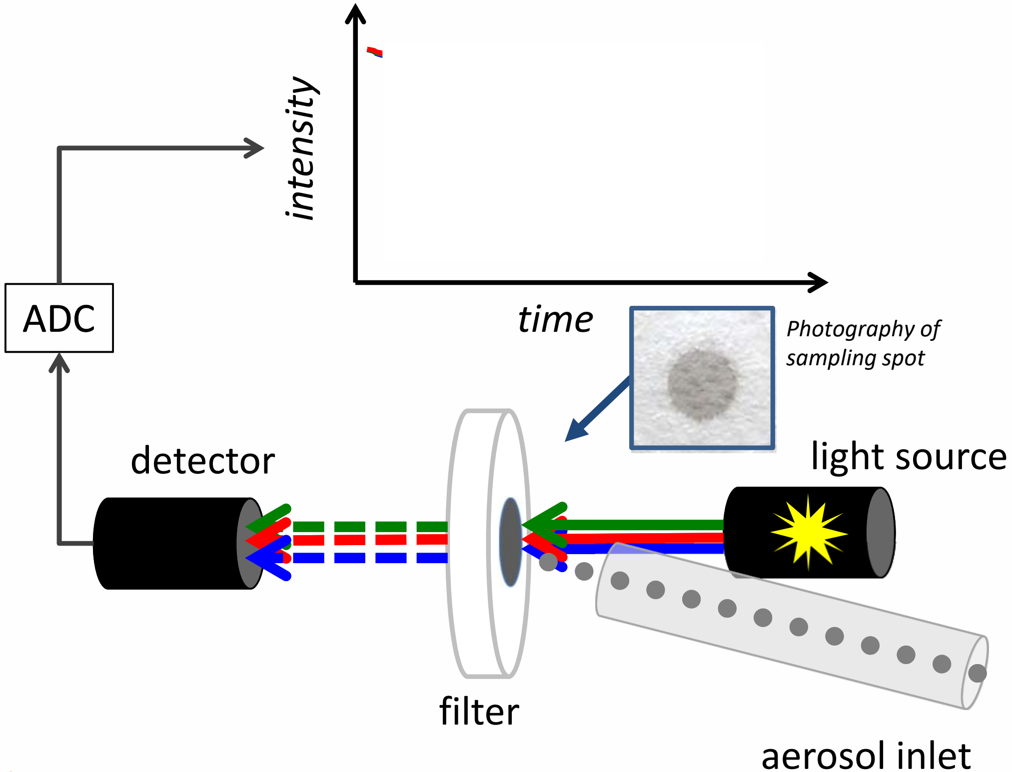
- The intensity of the acoustic ware is measure using a microphone.
- The particle absorption coefficient is proportional to the acoustic intensity.

- Requires calibration to determine the proportionality between absorption coefficient and acoustic intensity.
- Calibration with gases or particle with well known absorption coefficients.
- Sensitive to background noise.
- Volatile organic compounds on the particles can evaporate when heated by the laser beam. The thermal energy of the particle and thus the intensity acoustic wave is reduced by the latent heat.

Filter-Based Absorption Photometers

Filter-Based Absorption Photometers

- A fibre filter is loaded with particles
- **Transmitted intensity** through system of **particle and filter** is measured
- Intensities for one or more wavelengths are recorded

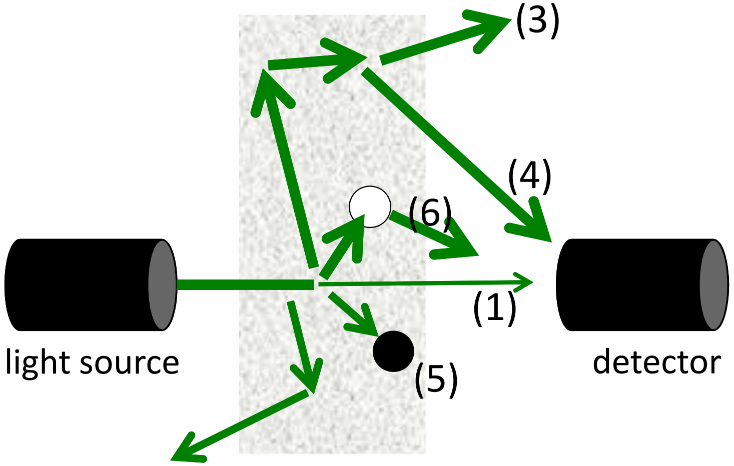


Isn't that a setup similar to measuring particle extinction?

Radiative transfer through a particle free filter

Light is scattered several times by the filter matrix

1. very little light passes the filter without scattering
2. light is scattered back
3. light is scattered forward
4. multiple scattered light reaches the detector



Radiative transfer through a particle loaded filter

Additionally to scattering by the particle free filter matrix, light is scattered and absorbed by particles

5. light is absorbed by particles
6. light is scattered by particles (additionally to scattering by the filter)

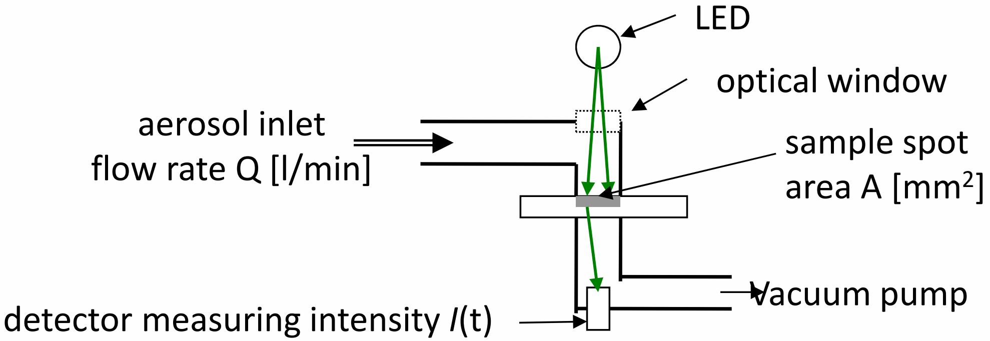
- The exact description of the radiation transfer is complicated. The following is a simplified description of the main points.

- Light scattering by the filter is order of magnitudes larger than scattering by particles. The internal radiation field does not change much by loading with particles.
  ➜The effect of additional particle scattering on the transmission of light is greatly reduced.

- Because of multiple scattering by the filter, the light path length inside the filter is larger than the filter thickness.
  ➜ The light path enhancement factor depends on filter type and amounts between two and four.

- Light absorbed by particles reduces light transmittance. Furthermore, the enhanced light path length causes a higher probability for a photon to be absorbed by particles.
  ➜ Light absorption is magnified by the light path enhancement factor.

Determining the particle light absorption coefficient using an Absorption Photometer



LED

optical window

aerosol inlet
flow rate Q [l/min]

sample spot
area A [mm^2]

Vacuum pump

detector measuring intensity *I*(t)

While loading the filter with particles the intensity *I*(t) and is measured and Attenuation is calculated by $ATN = -ln(\tau)$

Here, *dl* is the increment of the column of air sucked through the filter is $dl = \frac{Q}{A} \cdot dt$

Substituting the path length *l* by time *t* (equation from previous slide)

$$\sigma_{atn}(l) = \frac{d\ ATN(l)}{dl} \quad \Rightarrow \quad \sigma_{atn}(t) = \frac{Q}{A}\frac{d\ ATN(t)}{dt}$$

Then, the absorption coefficient is (c.f. equation from previous slide):

$$\sigma_{abs} \approx \frac{\sigma_{atn} - f_1 \cdot \sigma_{sca}}{f_2}$$

Aethalometer AE31 & AE33

Aethalometer AE31

- The functional principle of the Aethalometer is similar to that of the PSAP.
- The Aethalometer AE31 measures the absorption coefficient at 7 wavelengths

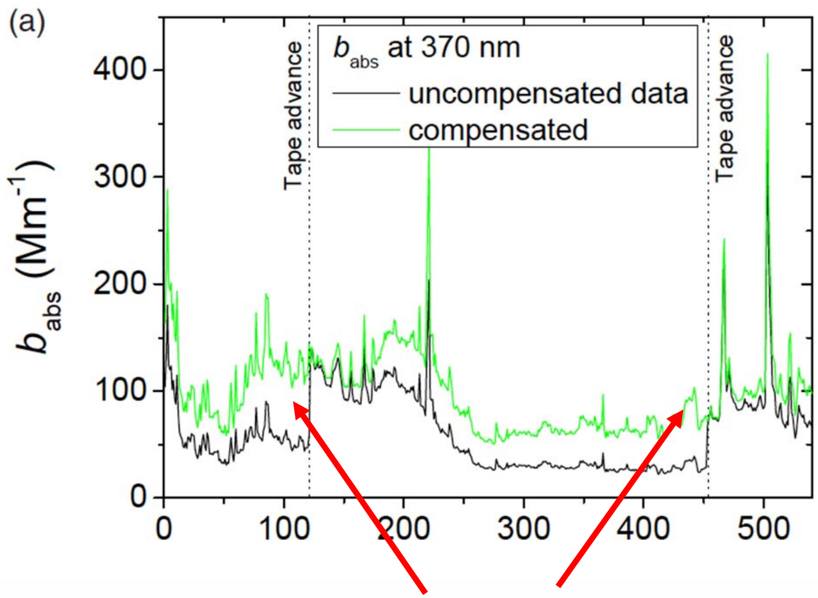
  → 370, 470, 520, 590, 660, 880, and 950 nm
- The calibration is different to the PSAP because of the use of a different filter tape.
- The calibration function of the instrument is:

$$\sigma_{abs} \approx \frac{\sigma_{atn}}{3.5\ (\pm 25\%)}$$

- Cross sensitivity to particle scattering can be neglected.
- The light path enhancement factor varies a lot depending on aerosol type.
- A loading effect was omitted in the calibration function, since the uncertainty due to the a priori unknown aerosol type is comparable large.

Aethalometer AE33

- The aethalometer AE33 is a further development of the AE31.
- The main feature is the dual spot technology to compensate for loading effects.



The particle light absorption coefficient is calculated by $\sigma_{abs} = \frac{d\ OD(t)}{d\ t}$,

with an empirically determined loading function of the form: $ATN = \frac{1}{k}\left(1 - e^{-k\ OD}\right)$.

The compensation parameter *k* is determined by the dual spot technology (shown on next slide).

Without compensation: Jump in time series occurs, when changing to an new, unloaded spot

Drinovec, et al. The "dual-spot" Aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation, Atmos. Meas. Tech., 8, 1965-1979, https://doi.org/10.5194/amt-8-1965-2015, 2015.

Aethalometer AE33 dual spot compensation

- Two spots are loaded simultaneously with different aerosol flows Q_1 and Q_2, respectively. T
- Therefore, one spot has a higher loading than the other spot.

$$ATN_1 = \frac{1}{k}\left(1 - e^{-k\,OD_1}\right)$$
$$ATN_2 = \frac{1}{k}\left(1 - e^{-k\,OD_2}\right)$$

- ATN_1 and ATN_2 are measured. k, OD_1 and OD_2 are unknown.
- Can we solve this system of two equations for OD_1 and OD_2?

- We have one more information! The ratio of the optical depth equals the flow ratio:

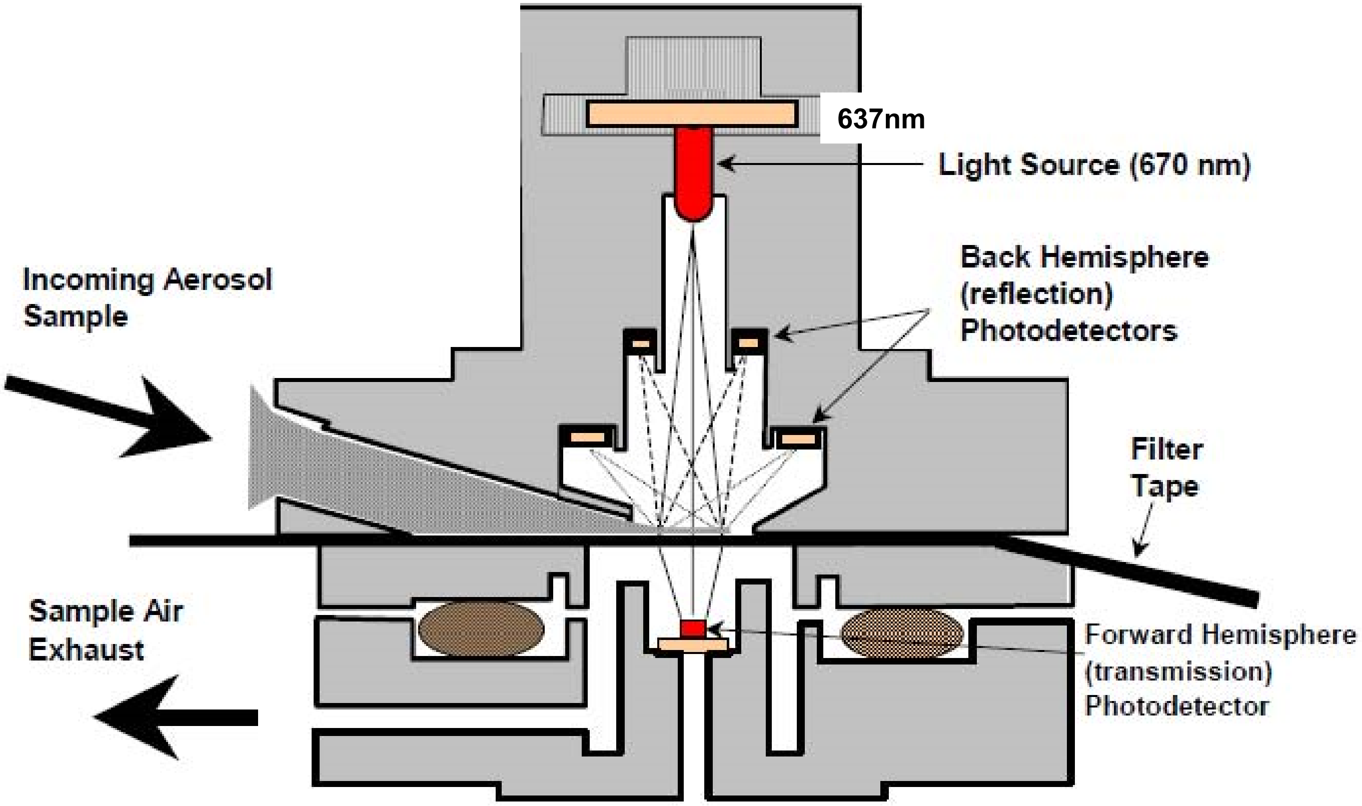
$$\frac{Q_1}{Q_2} = \frac{OD_1}{OD_2}$$

- Now it is just mathematics to solve the equation for k, and OD_1 and OD_2.
- Combining the information from two spots, a compensation for the loading effect can be derived while collecting particles and taking data.

Multi-Angle Absorption Photometer

Multi Angle Absorption Photometer (MAAP)

- The MAAP is another instrument with a build in loading correction.
- Intensities are measured in forward and in backward direction.



Petzold et al. 2004 JAS 421-441

- Scattering artifacts are reduced.
- Method is based on radiative transfer calculations.
- Calculation of the absorption coefficient requires a rather complex algorithm (not explained here).
- The MAAP overcomes most problems, which occur for PSAP and Aethalometer.

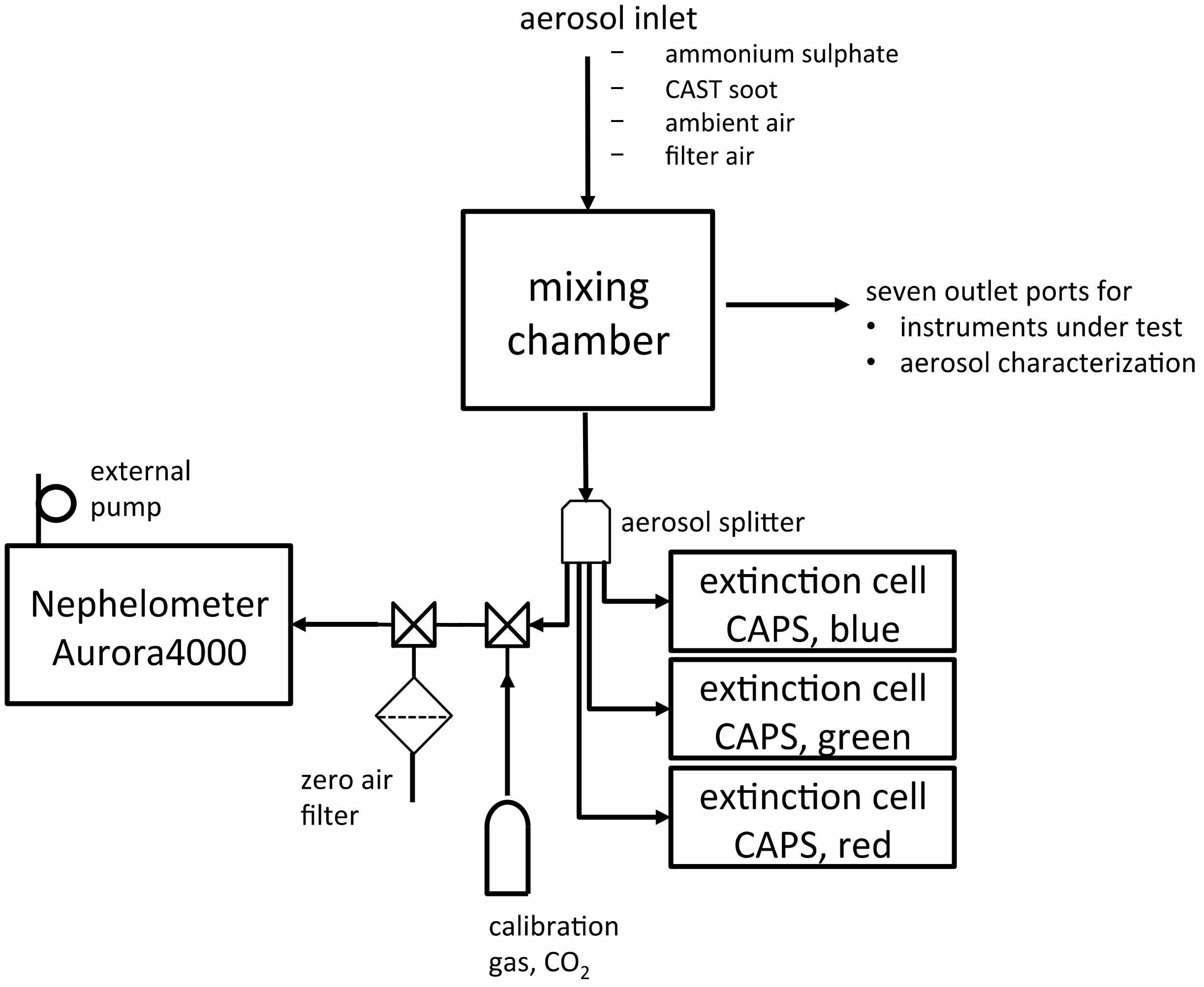
Summary

Comparison chart of particle absorption measurements systems

Method	Time resolution	Advantages	Disadvantages	Detection limit $\sigma_{abs}\ [Mm^{-1}]$	Application
Extinction minus scattering	Seconds	Fundamental optical method	High uncertainy at high ssa and low concentration. Two instrument must be calibrated very carefully.	$\approx$ 10	Laboratory Reference for calibrating other instruments Field experiments only possible under certain favourable conditions.
Photoacoustic Sensor	A few seconds	Can be calibrated with absorbing gases	Biased when evaporation takes place (latent heat). Requires special calibration gases.	<10	Laboratory Field experiments
Filter based PSAP, AE31, MAAP, AE33	Seconds to minutes	Inexpensive Easy maintenance	Requires corrections High uncertainty for high single scattering albedos	$\approx$ 0.5	Laboratory Field experiments Long term measurments (monitoring)

Calibration of Absorption Photometers

Calibration setup for absorption photometers



aerosol inlet

- ammonium sulphate
- CAST soot
- ambient air
- filter air

mixing chamber

seven outlet ports for

- instruments under test
- aerosol characterization

external pump

Nephelometer Aurora4000

aerosol splitter

extinction cell CAPS, blue

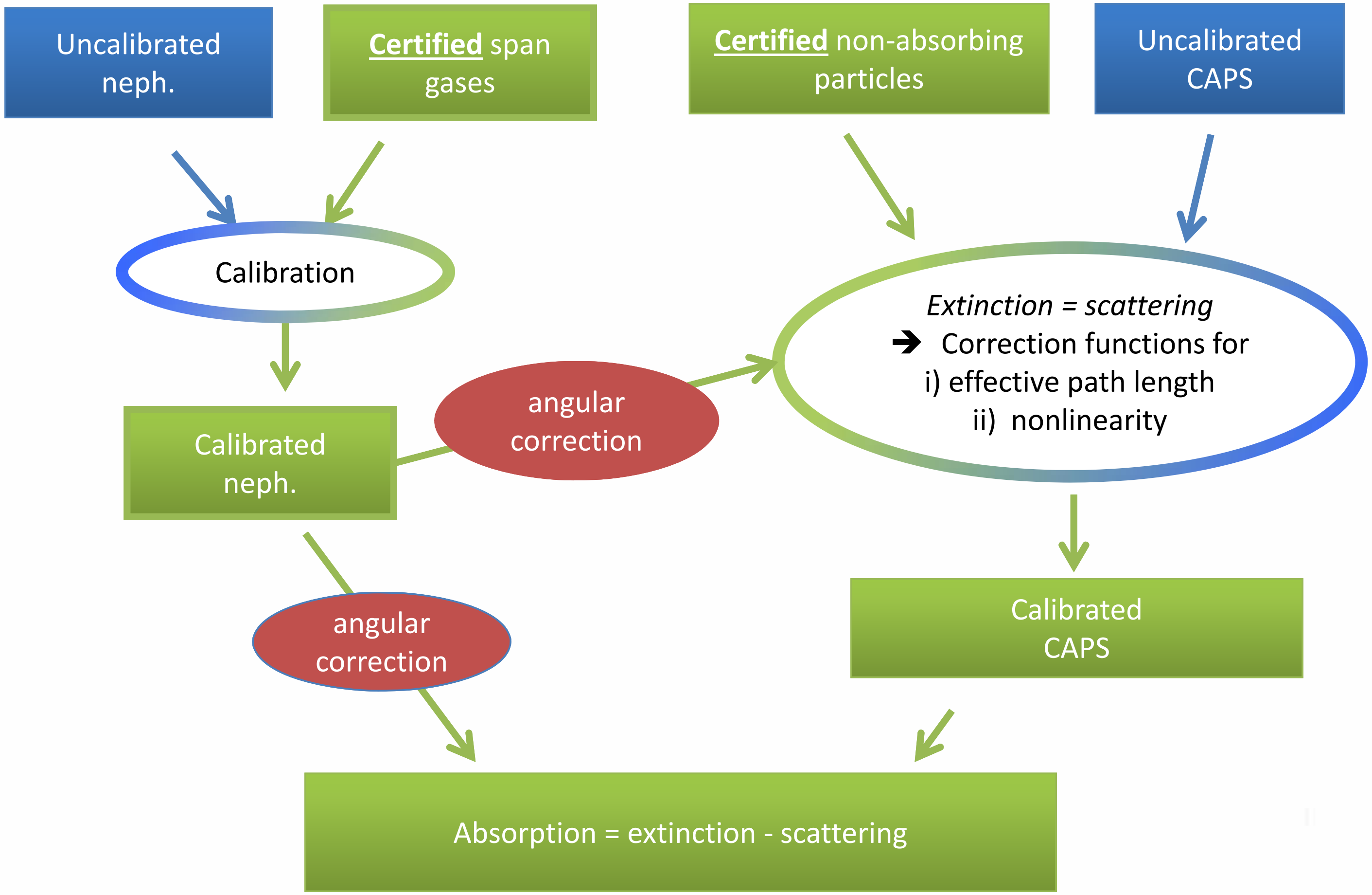
extinction cell CAPS, green

extinction cell CAPS, red

zero air filter

calibration gas, CO_2

Workflow for the Method “Extinction minus Scattering”



Uncalibrated neph.

Certified span gases

Certified non-absorbing particles

Uncalibrated CAPS

Calibration

Extinction = scattering

➔ Correction functions for

i) effective path length

ii) nonlinearity

Calibrated neph.

angular correction

Calibrated CAPS

angular correction

Absorption = extinction - scattering

Uncertainty of Absorption for Existing Reference Setup