Development of a new photothermal interferometer for the in-situ measurement of carbonaceous aerosols

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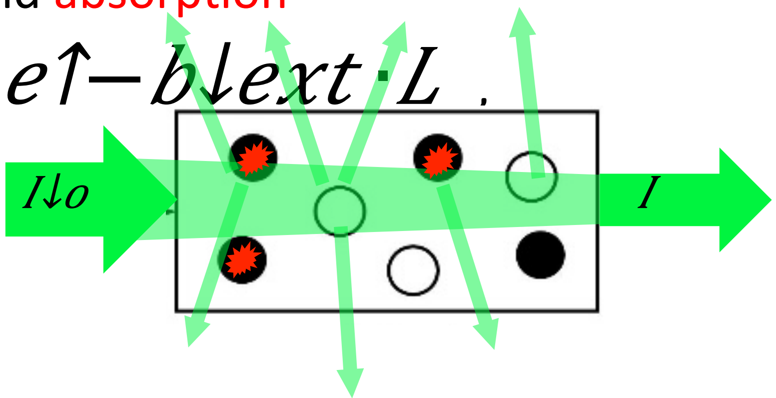
Some motivation….

- Radiation interacts with particles via scattering and absorption

$$\text{Beer–Lambert law:} \quad I = I_o \cdot e^{-b_{ext} \cdot L}$$



b_{ext} = Extinction coefficient

= Scattering coeff. + absorption coeff.

= $b_{sca} + b_{abs}$

- Carbonaceous aerosols (e.g. BC) are very efficient light absorbers

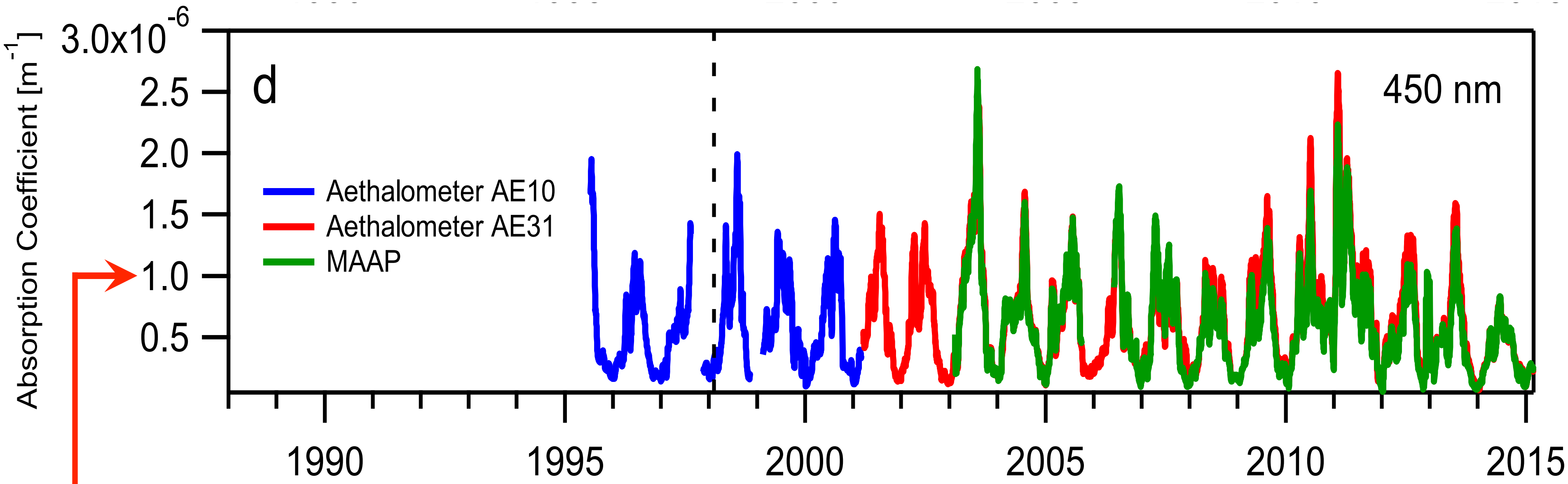
  BC Mass concentration: $M(BC) = b_{abs} / MAC$

- Carbonaceous aerosols are highly relevant for our health.

- Aerosol light absorption also affects climate:

  BC is the second most important anthropogenic climate forcer after CO_2.
  (Bond et al., 2013)

b_{abs} Data from Jungfraujoch



$b_{abs} = 10^{-6}\ m^{-1}$

This corresponds to ~ 100 ng m^{-3} BC (for a MAC = 10 m^2g^{-1})

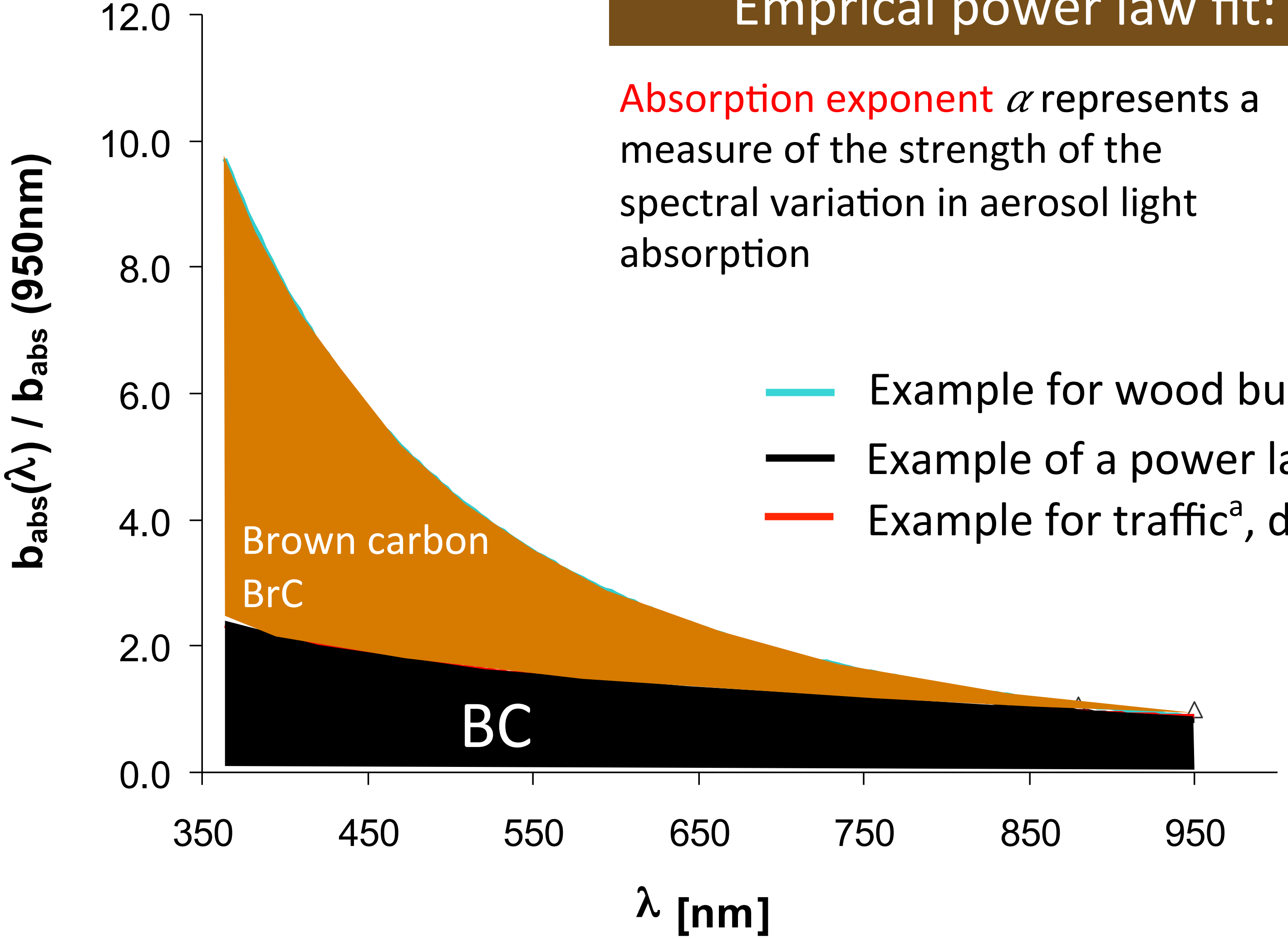
Bukowiecki et al., AAQR, 2015

Source Apportionment using the spectral variation of aerosol absorption (b_{abs})

n|w

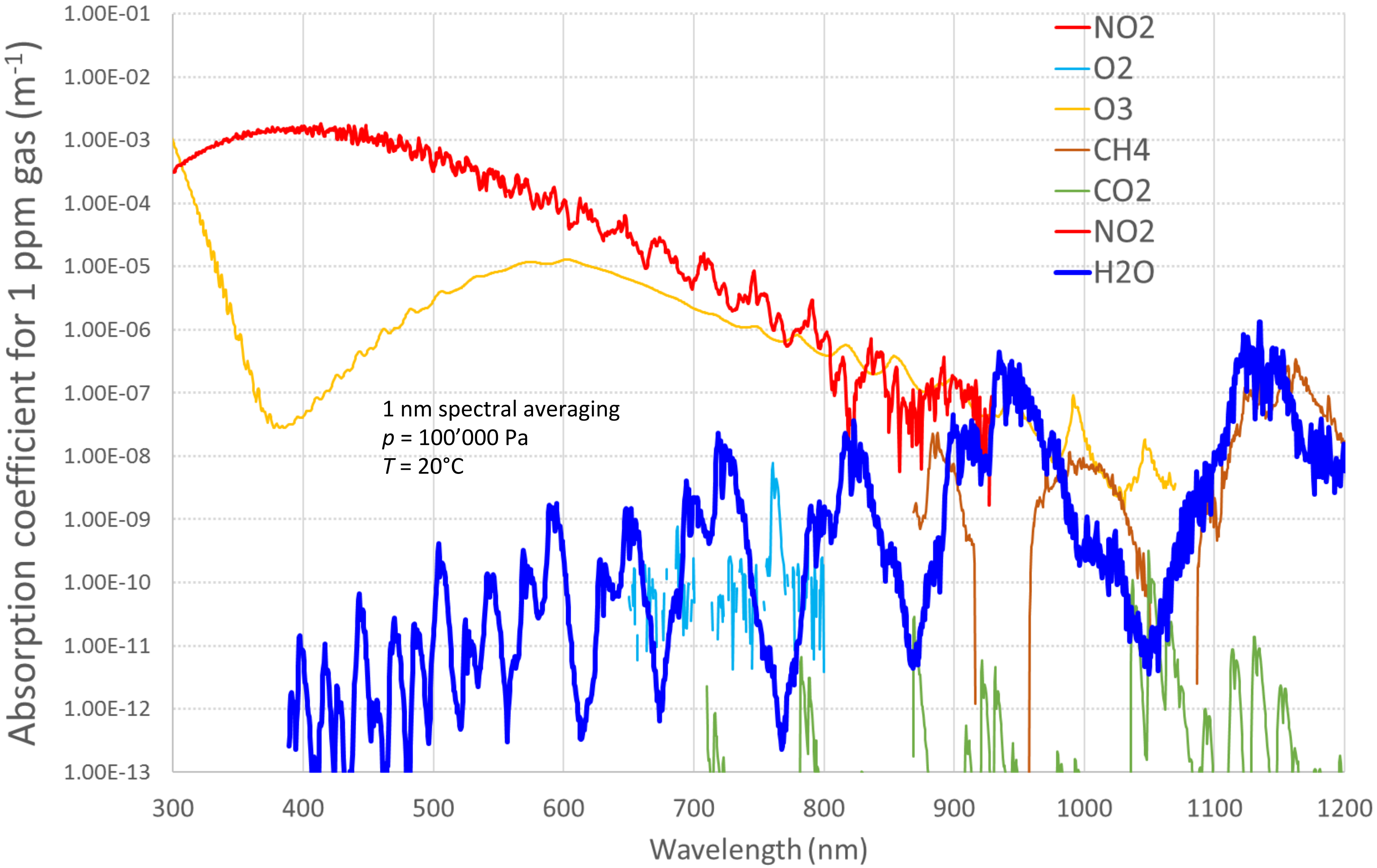
Emprical power law fit: $b_{abs} \propto \lambda^{-\alpha}$

Absorption exponent α represents a measure of the strength of the spectral variation in aerosol light absorption



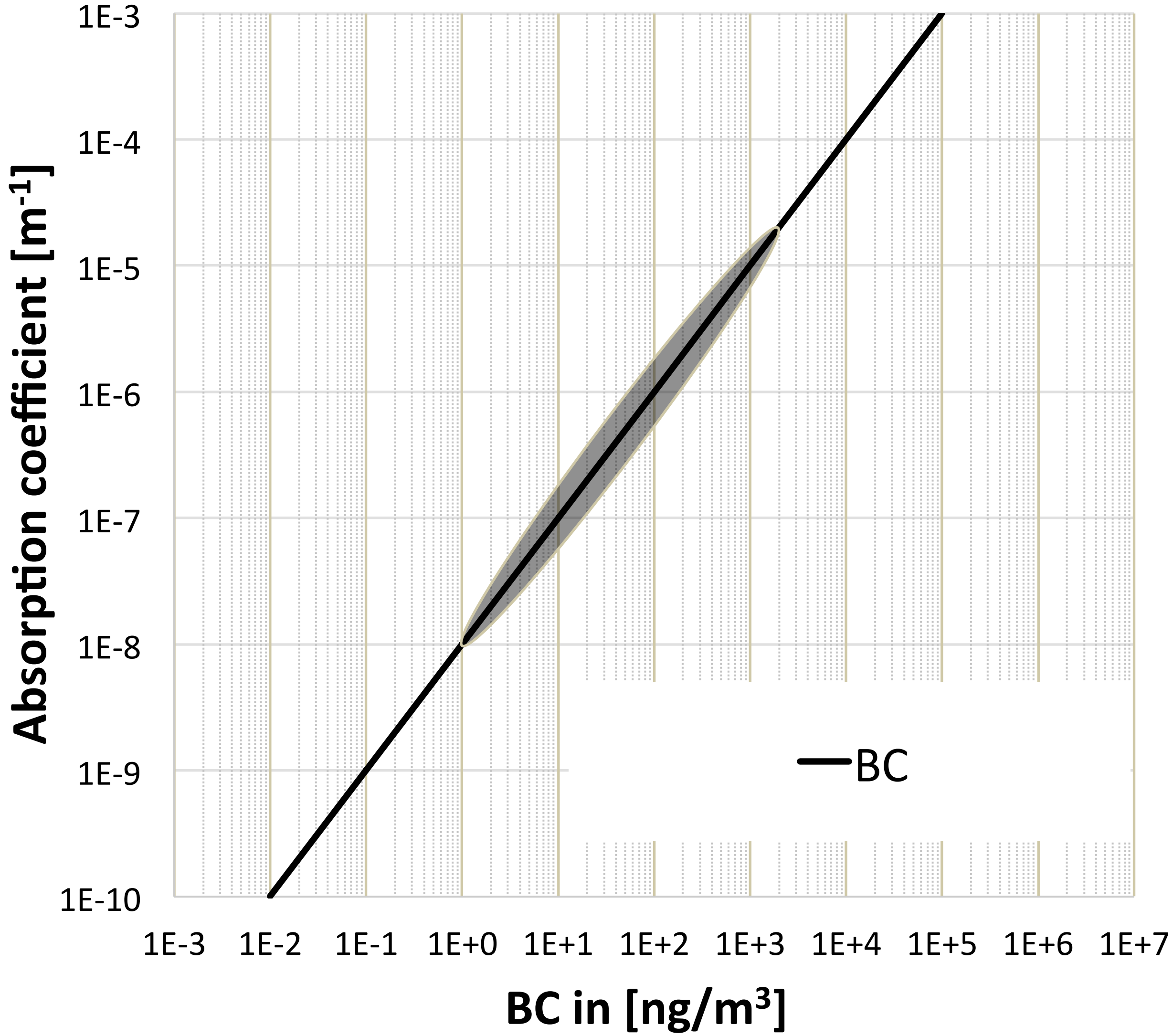
[a] Kirchstetter *et al*. 2004
[b] Schnaiter *et al*. 2003

Light absorbing gases in our atmosphere our friend and foe



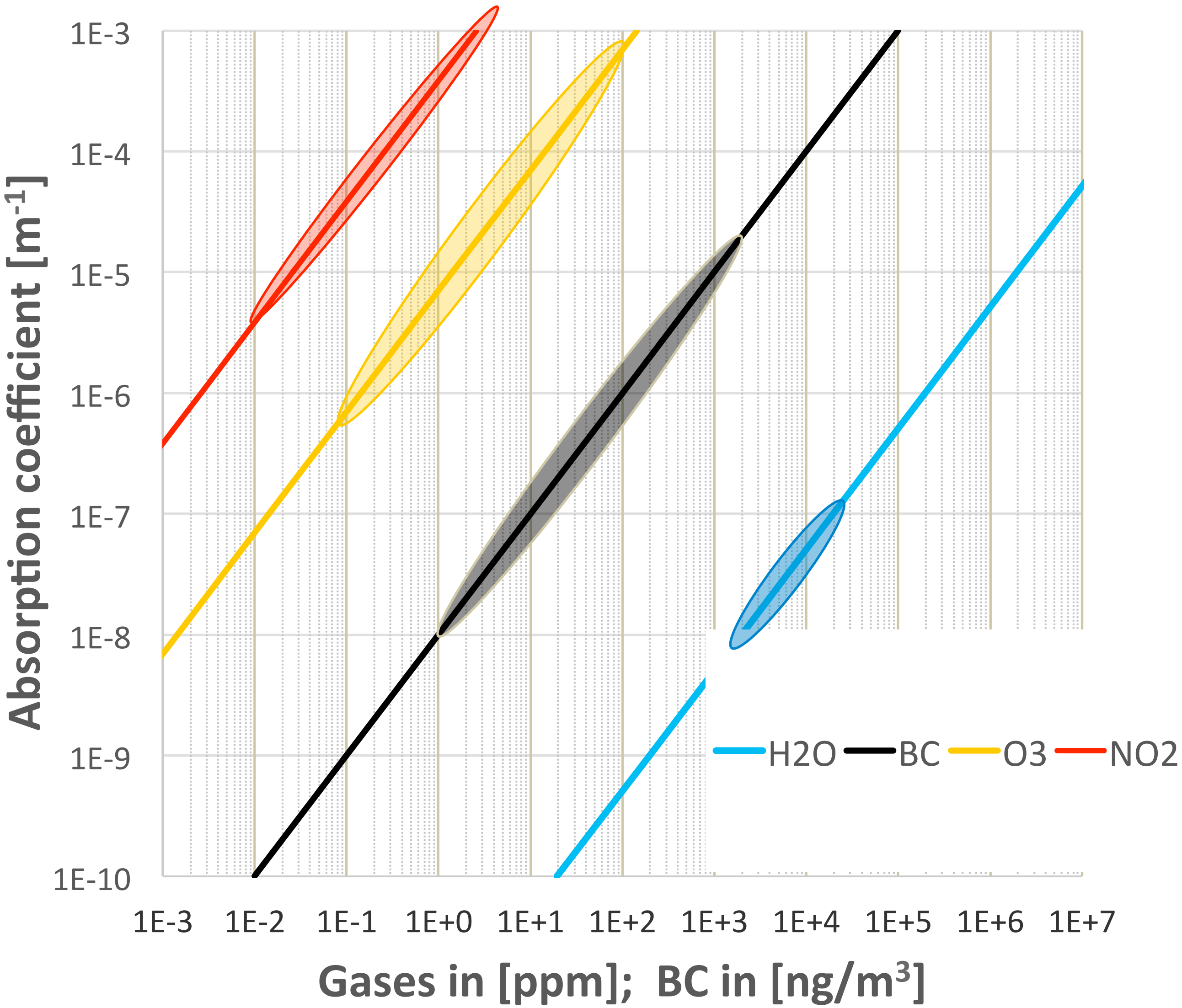
Distinct absorption lines in the IR

Light absorption from Black Carbon (BC)



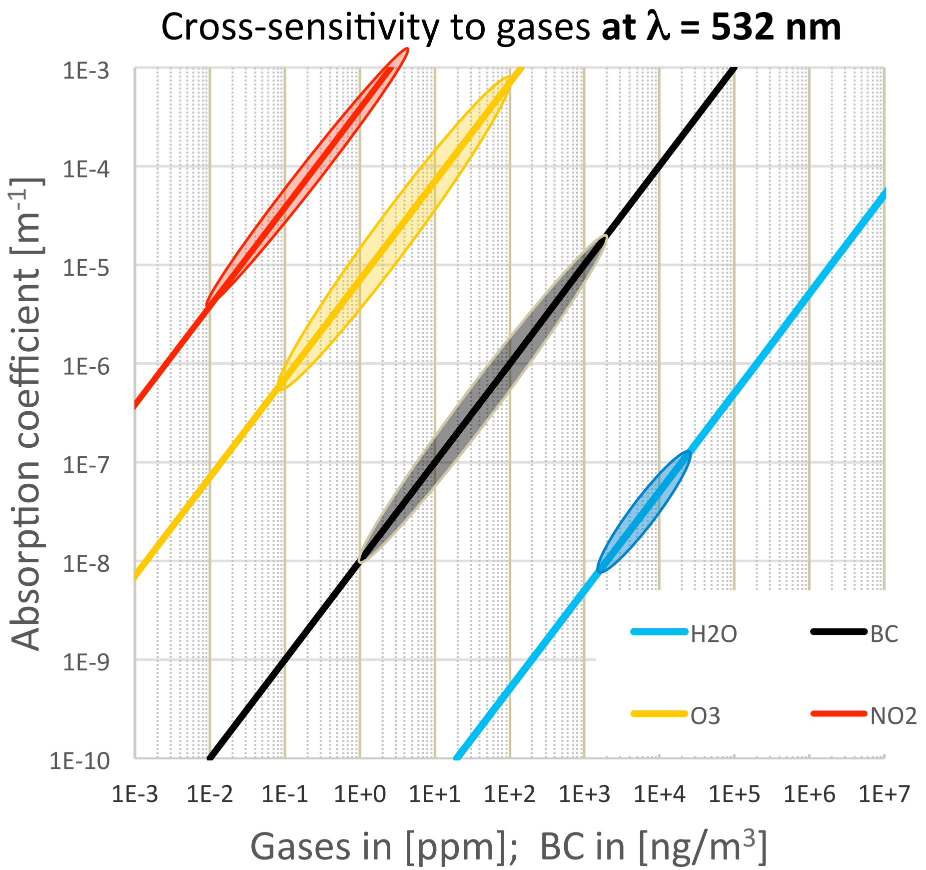
Cross-sensitivity to gases at λ = 532 nm

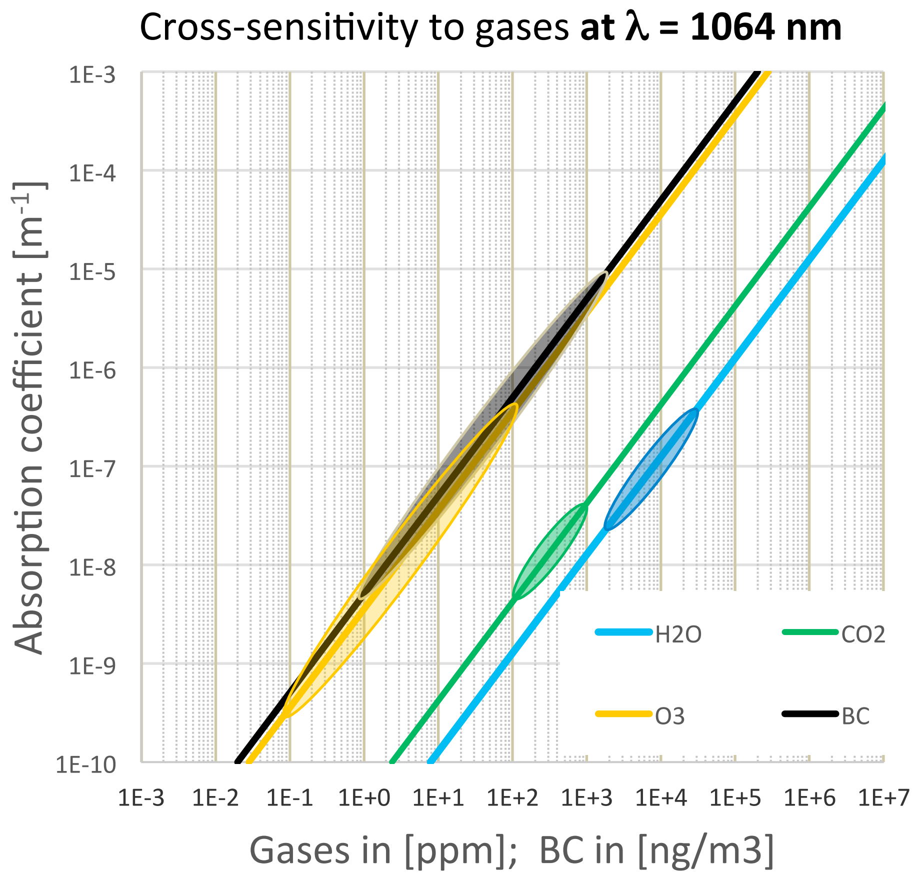
Ovals show the typical ambient concentrations of the respective species.



e.g. 1 μg/m³ BC ≡ 0.03 ppm NO2

Cross-sensitivity to gases





The presence of absorbing gases can lead to measurement artefacts in the determination of equivalent BC mass, but also present an opportunity for the calibration of in-situ instruments.

Commercially available techniques to measure aerosol light absorption:

	Method / *Instrument*	Manufacturers	Time resolution	Advantage	Disadvantage	Detection limit [2] b_{abs} [Mm^{-1}]	BC mass [$ng\ m^{-3}$]
Filter based	*MAAP* [1]	Thermo Scientific	A few minutes	High sensitivity, simple, robust	Low accuracy, prone to filter-based artefacts	~ 0.5	~ 50
	Aethalometer	Magee Scientific					
	TAP *PSAP* [1]	Brechtel/Radiance Research Inc.					
	FP	Haze Instruments					
In-situ	Photoacoustics:		A few seconds	In-situ, fast response, can be calibrated with absorbing gases	Limited sensitivity Evaporation artefact from volatiles on light absorbing particles		
	Micro Soot	AVL GmbH				~ 50	~ 5000
	PASS [1]	DMT, USA				< 10	< 1000
	PAX	DMT, USA				< 10	< 1000
	Differential: "Extinction minus scattering"	Various combinations	Seconds	In-situ	Problematic when aerosol light scattering prevails	< 1	< 100

[1] no longer available, but many instuments are still in operation

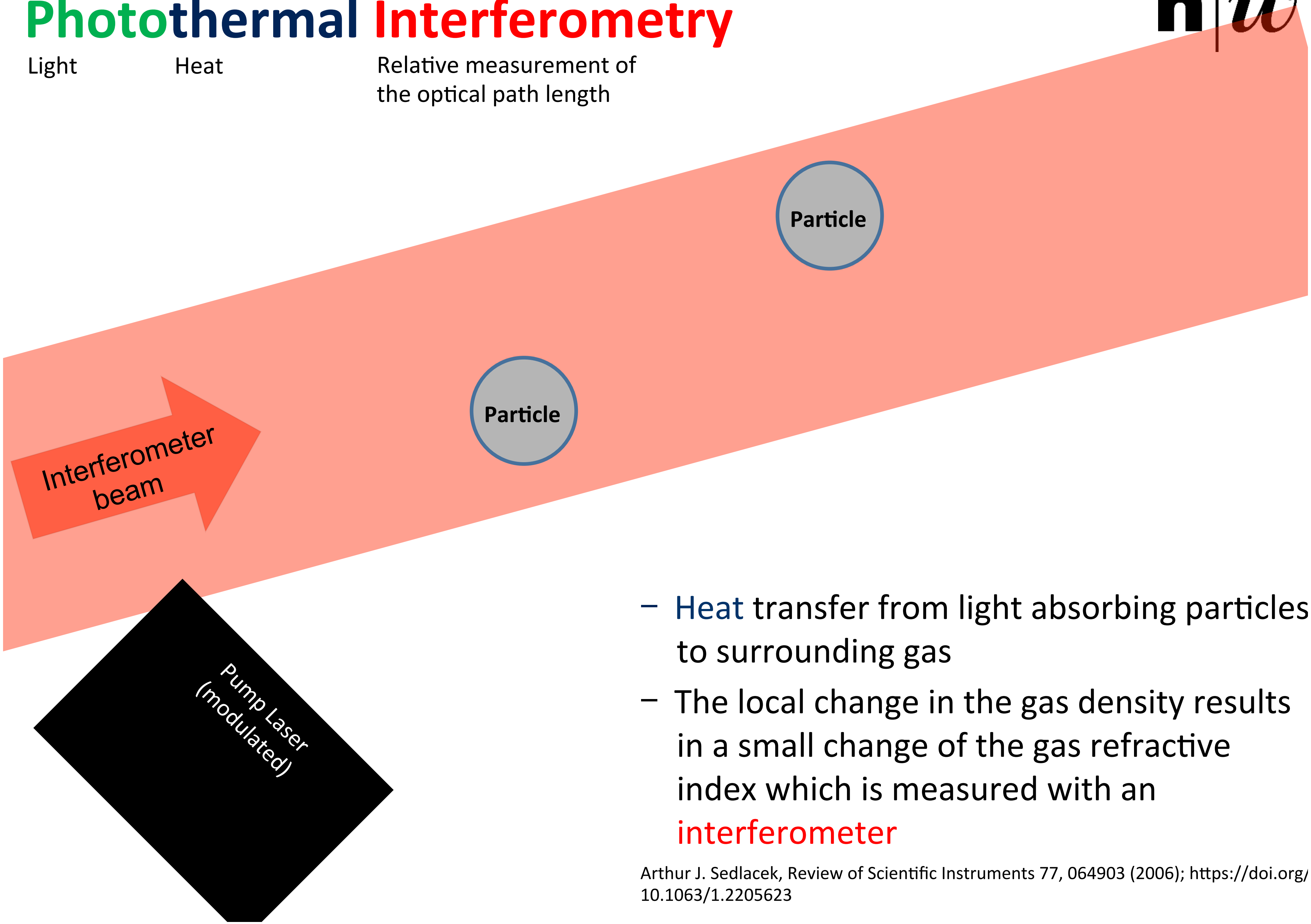
[2] for an integration time of a few minutes

Current aerosol absorption measurement techniques are prone to artefacts causing uncertainties:

- filter photometers – filter based artefacts
- photo-acoustic instruments – affected by evaporation of water and organics
- extinction-minus-scattering method – uncertain at high SSA

Photothermal Interferometry

Light Heat Relative measurement of the optical path length



- Heat transfer from light absorbing particles to surrounding gas
- The local change in the gas density results in a small change of the gas refractive index which is measured with an interferometer

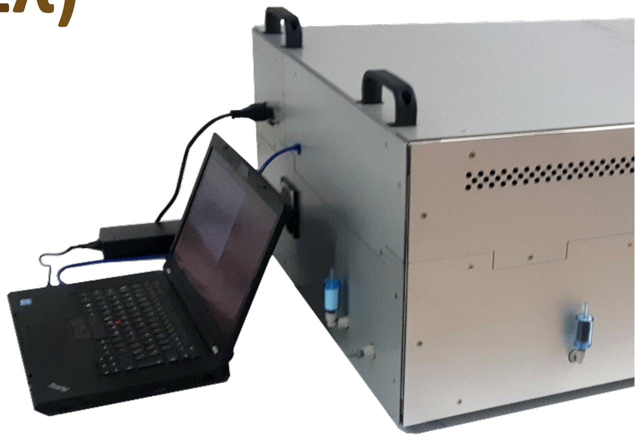
Arthur J. Sedlacek, Review of Scientific Instruments 77, 064903 (2006); https://doi.org/10.1063/1.2205623

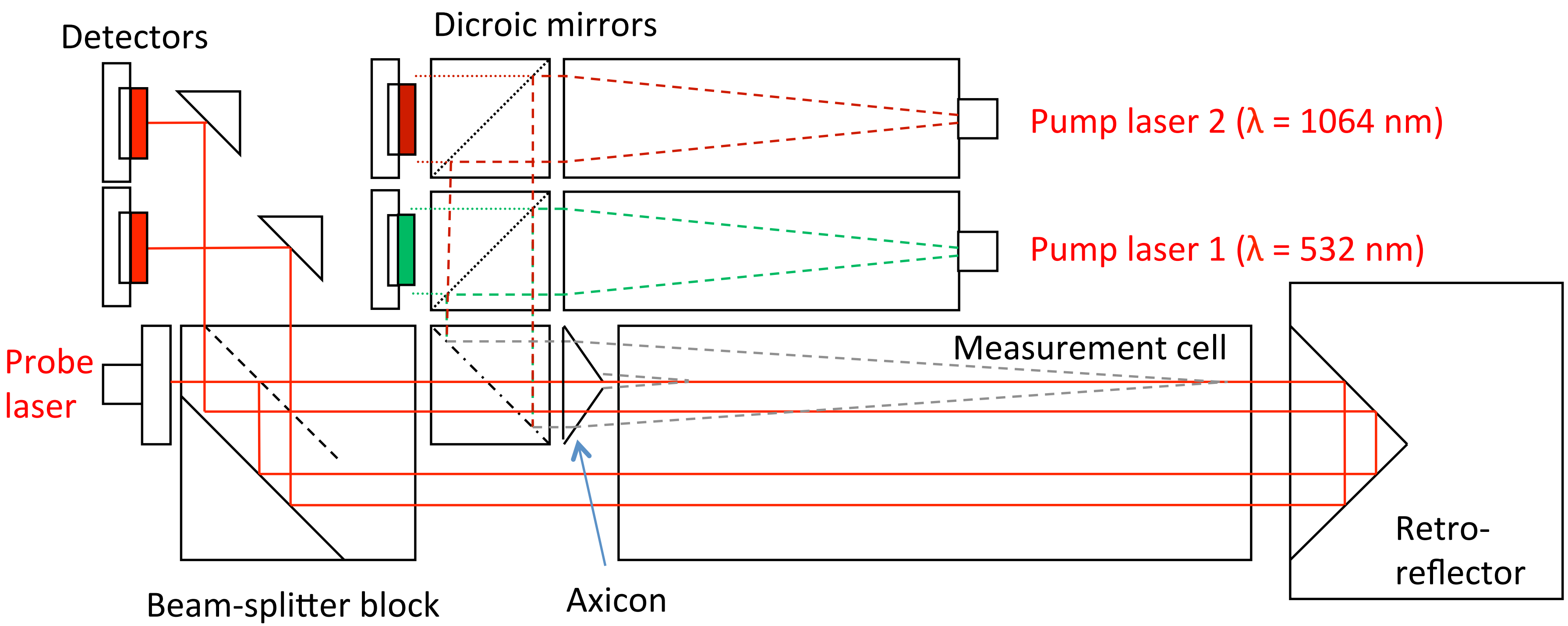
Dual wavelength Photo-Thermal Aerosol Absorption monitor (PTAAM-2λ)

HAZE INSTRUMENTS

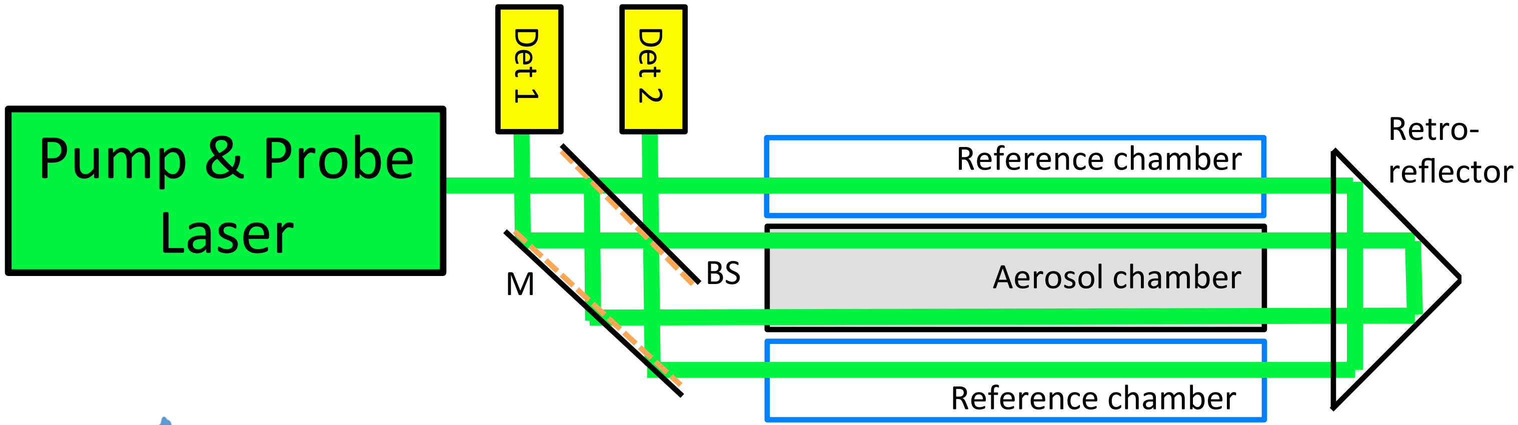
https://haze.si/

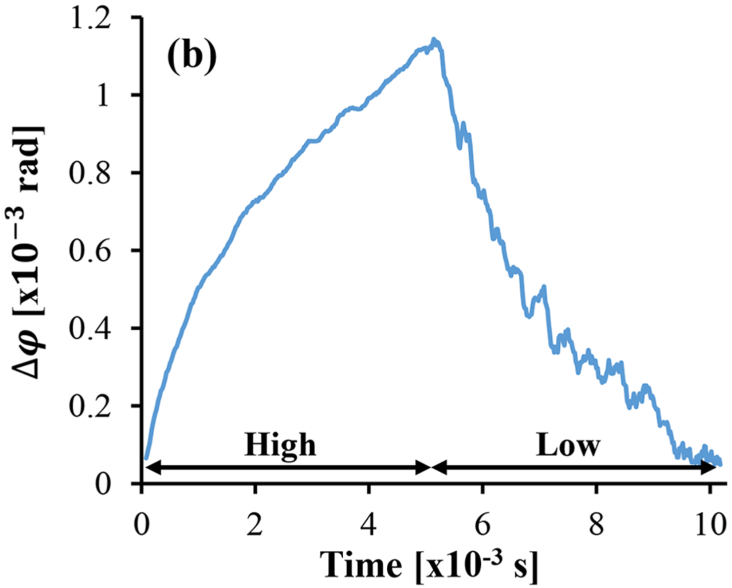
- Commercially available 3 beam PTI, design based on Moosmuller, Arnott, Sedlacek and Visser
- **Axicon** (conical lens) is used to focus pump beams on the axis of interferometer probe beam
- Measurements performed at **532 and 1064 nm**





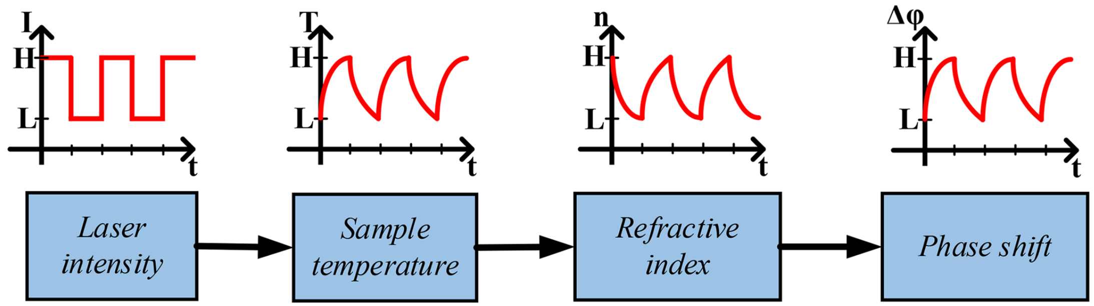
Our fundamentally new approach:
Single-beam PTI (modulated Interferometer)





The measurement of the light absorption coefficient b_{abs} is based in 1st principles:

$$\Delta\varphi/\Delta t = 2\pi(n-1)/\lambda \cdot T \cdot \rho \cdot c_p \cdot l \cdot P/A \cdot b_{abs}$$



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Atmos. Meas. Tech., 13, 7097–7111, 2020
https://doi.org/10.5194/amt-13-7097-2020

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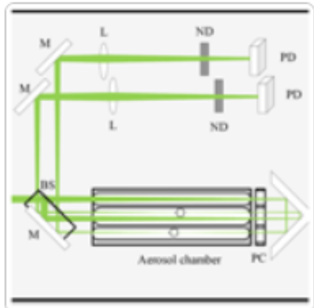
Research article

23 Dec 2020

A single-beam photothermal interferometer for in situ measurements of aerosol light absorption



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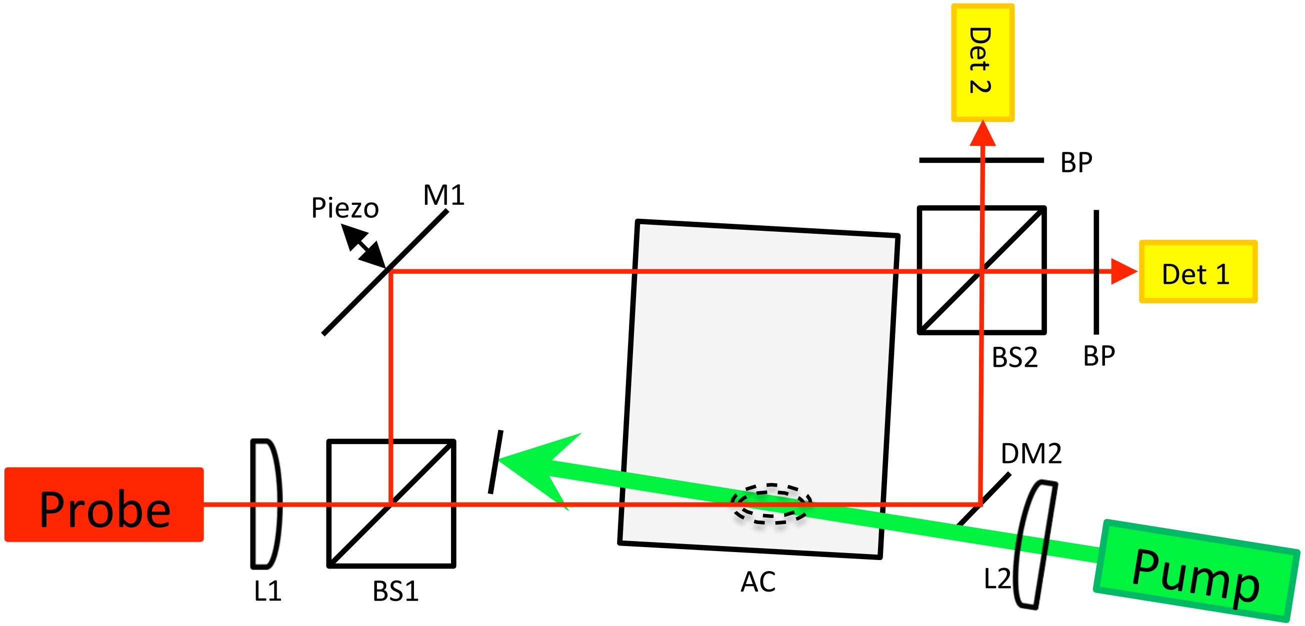
Standard PTI setup:
Pump laser in glancing configuration



$$\Delta\varphi = 2\pi(n-1)/\lambda \cdot T \cdot \rho \cdot c_p \cdot l \cdot P/A \cdot b_{abs} \Delta t$$

P: Power [W]

A: common cross section

l: interaction length

Standard PTI setup:
Pump laser in glancing configuration

$$\Delta\varphi = 2\pi (n-1)/\lambda T \rho c_p \cdot l P/A \cdot b_{abs} \Delta t$$

P: Laser Power [W]

Common cross-sectional area and length of Pump and interferometer laser: A, l

Specific heat capacity of air: c_p

Air density ant temperature: ρ, T

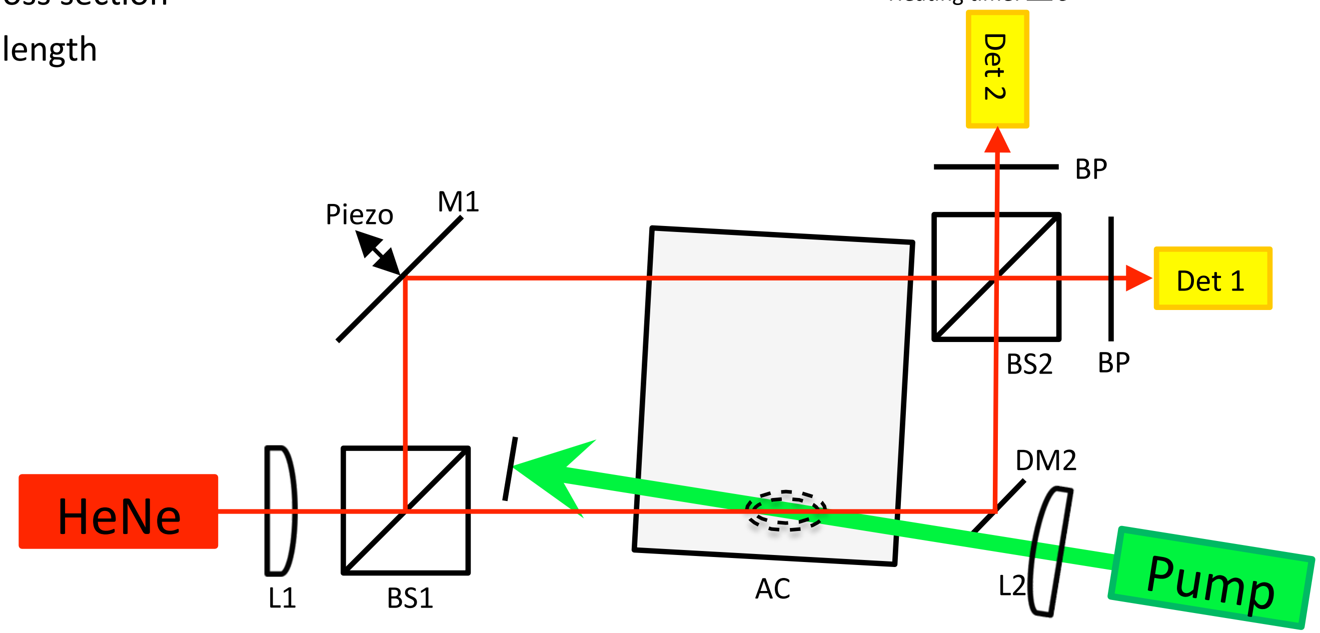
Heating time: Δt

Efficiency $= l \cdot P/A \cong 10\ \text{mm} \cdot 500\ \text{mW} / 0.1\ \text{mm}^2 \cong 500\ \text{kW/m}$

P: Power [W]

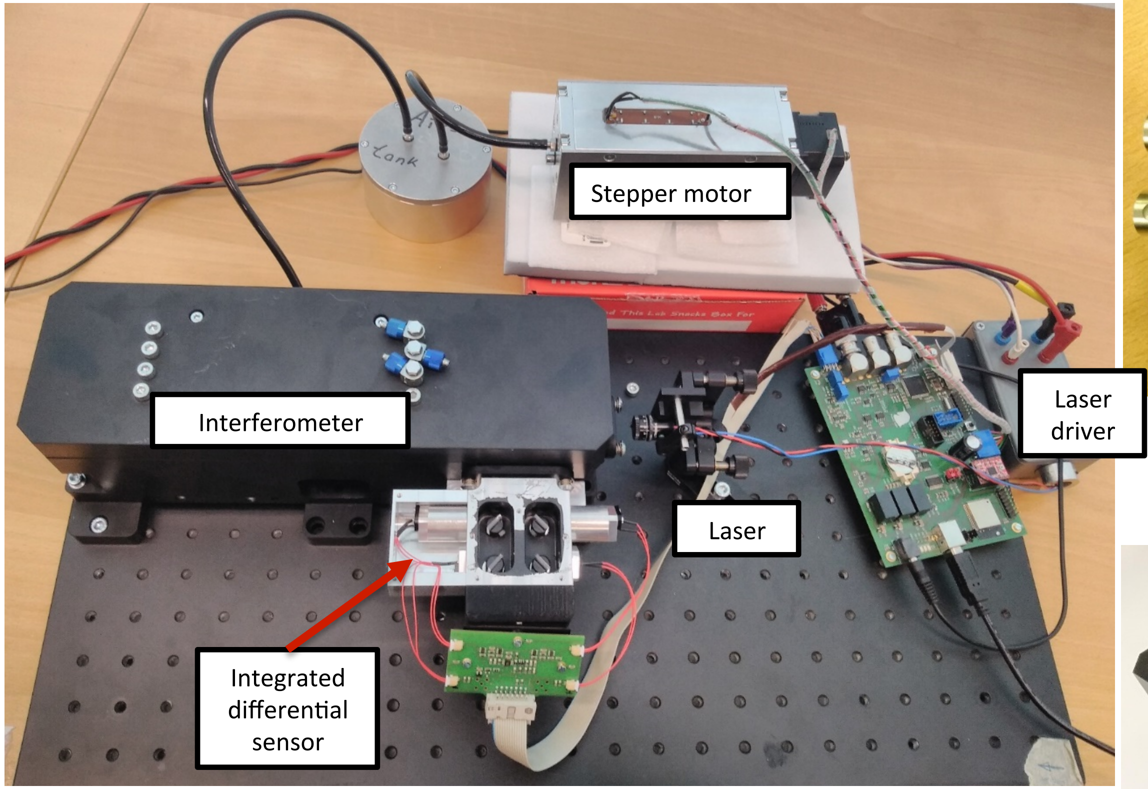
A: common cross section

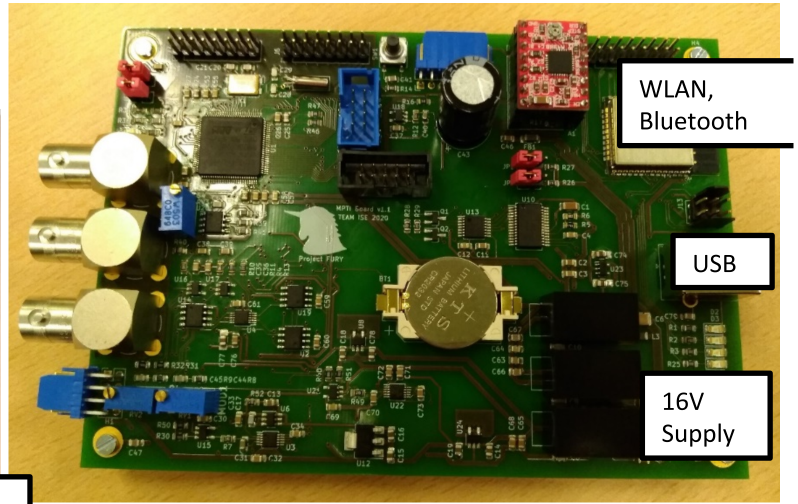
l : interaction length

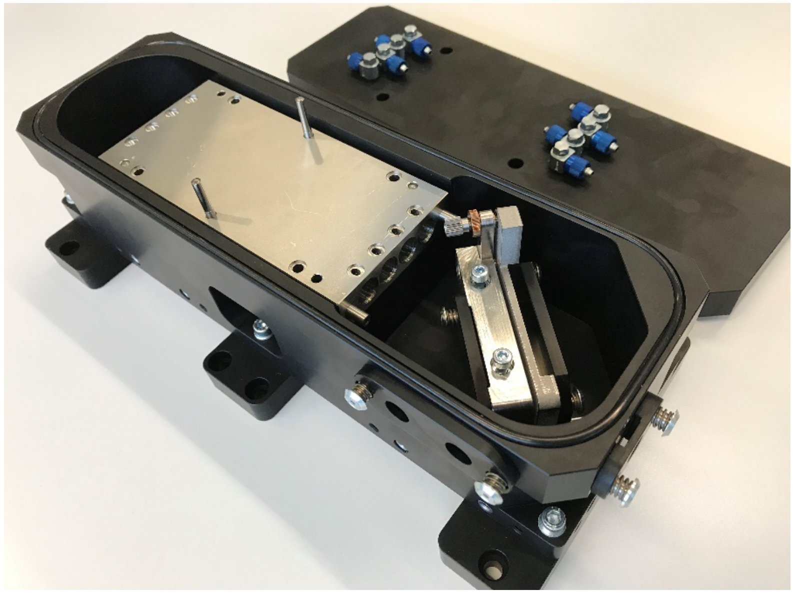


The setup used an aerosol chamber (AC), lenses (L), beam splitters (BS), a piezo controlled mirror (M), dielectric mirrors (DM) and band pass filters (BP). The Piezo is used to keep the instrument in quadrature (i.e. at highest sensitivity).

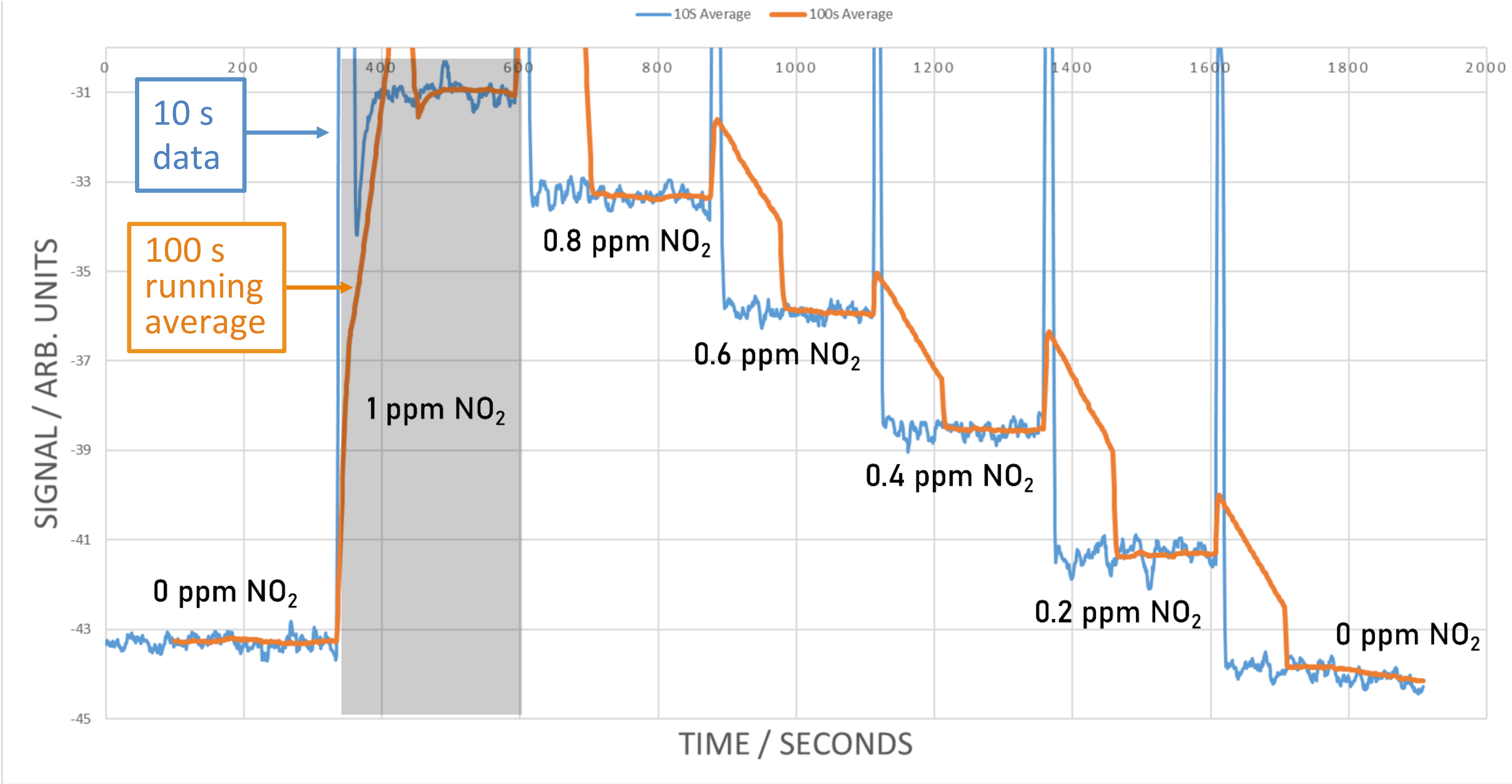
Our new compact PTI with embedded DAQ





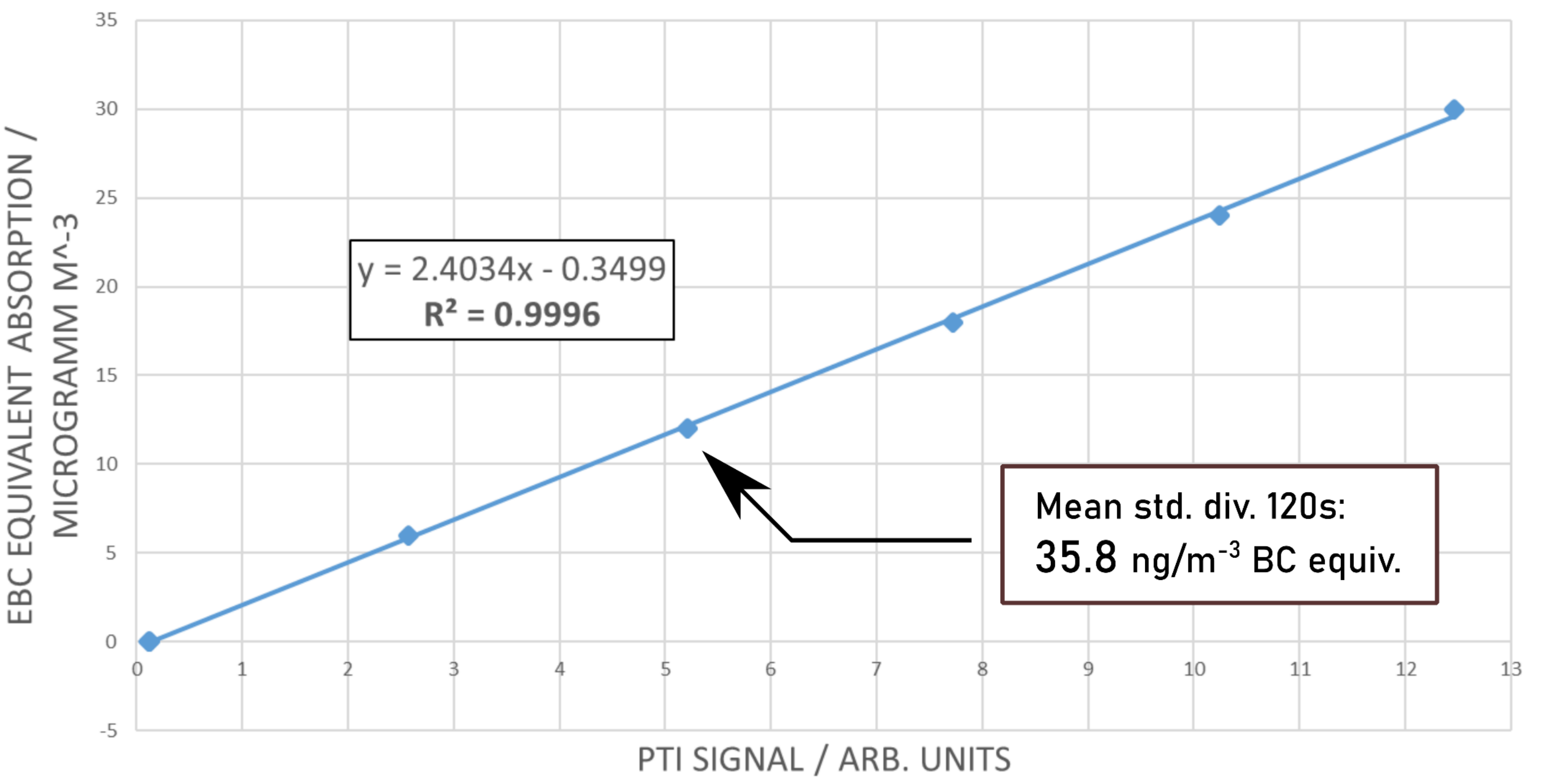


Current PTI performance



Concentration series with NO_2 shows the fast time resolution of our instrument, 1 ppm NO_2 ≅ 30 μg/m³ BC (λ = 532 nm, MAC = 10 m²/g)

Linear response and detection limit



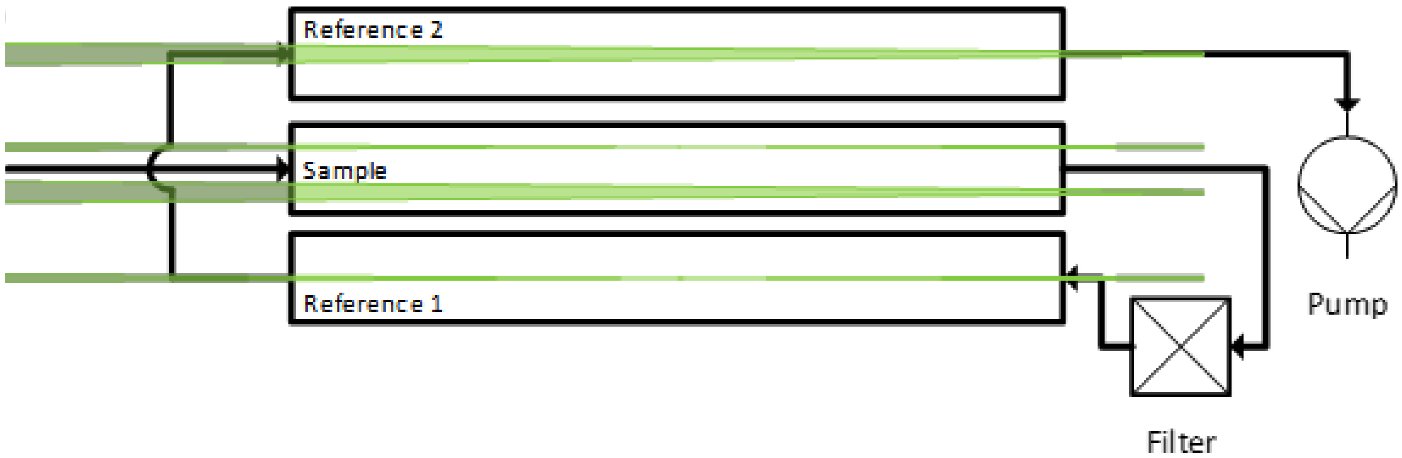
Current detection limit (1σ, 120 s):

35 ng/m^3 eBC or 0.35 Mm^{-1}

Gas flow system for the single-beam PTI

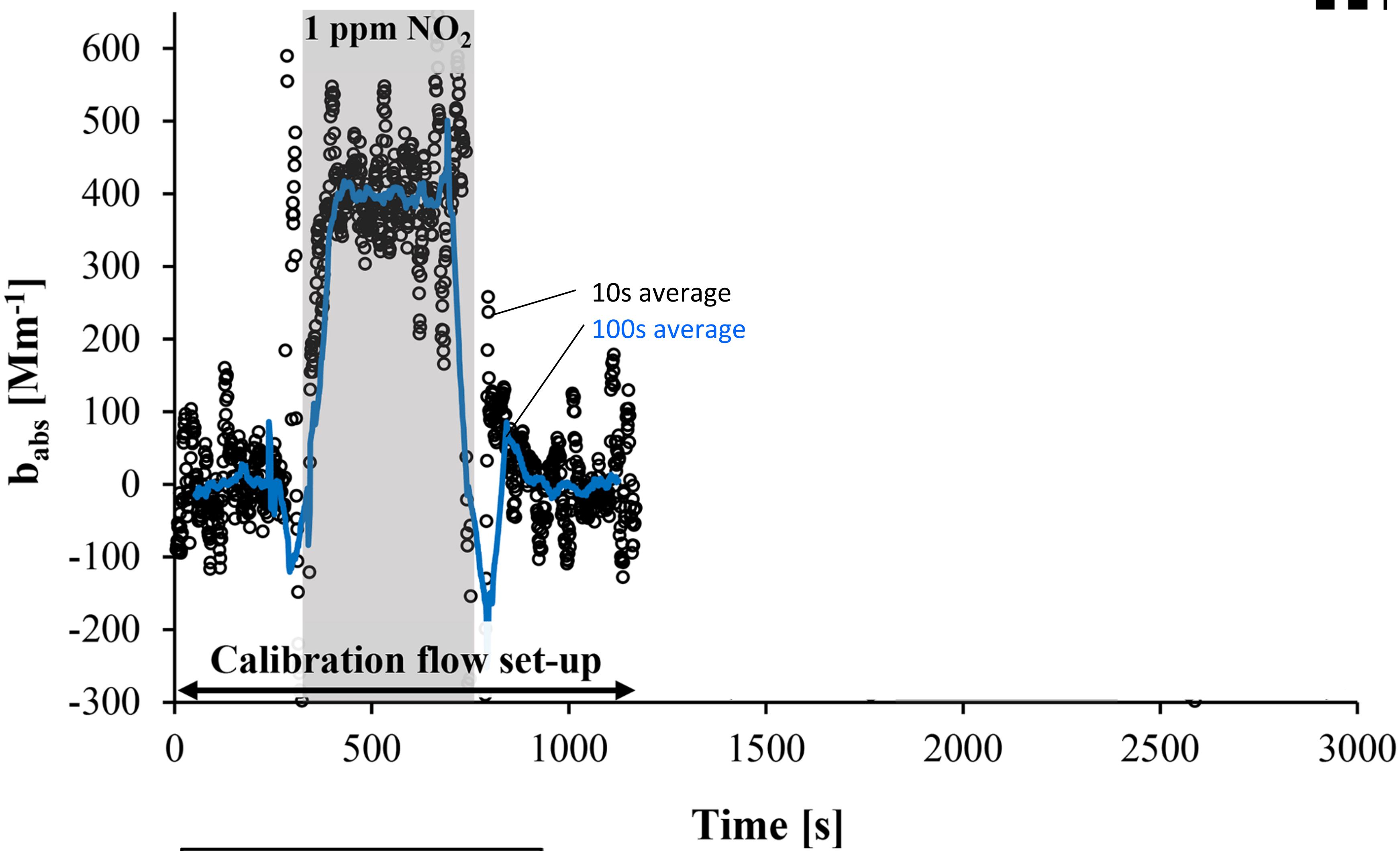
Calibration measurements are performed by filling the sample cell with the calibration gas and the reference cells with synthetic air.

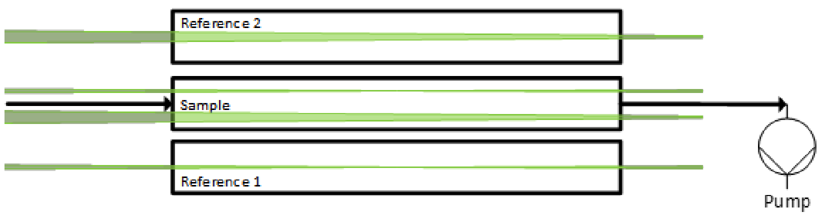
Standard BC measurements are done by connecting all three cells with the filtered sample flowing through both reference chambers in sequence.



Visser et al., AMT, 2020

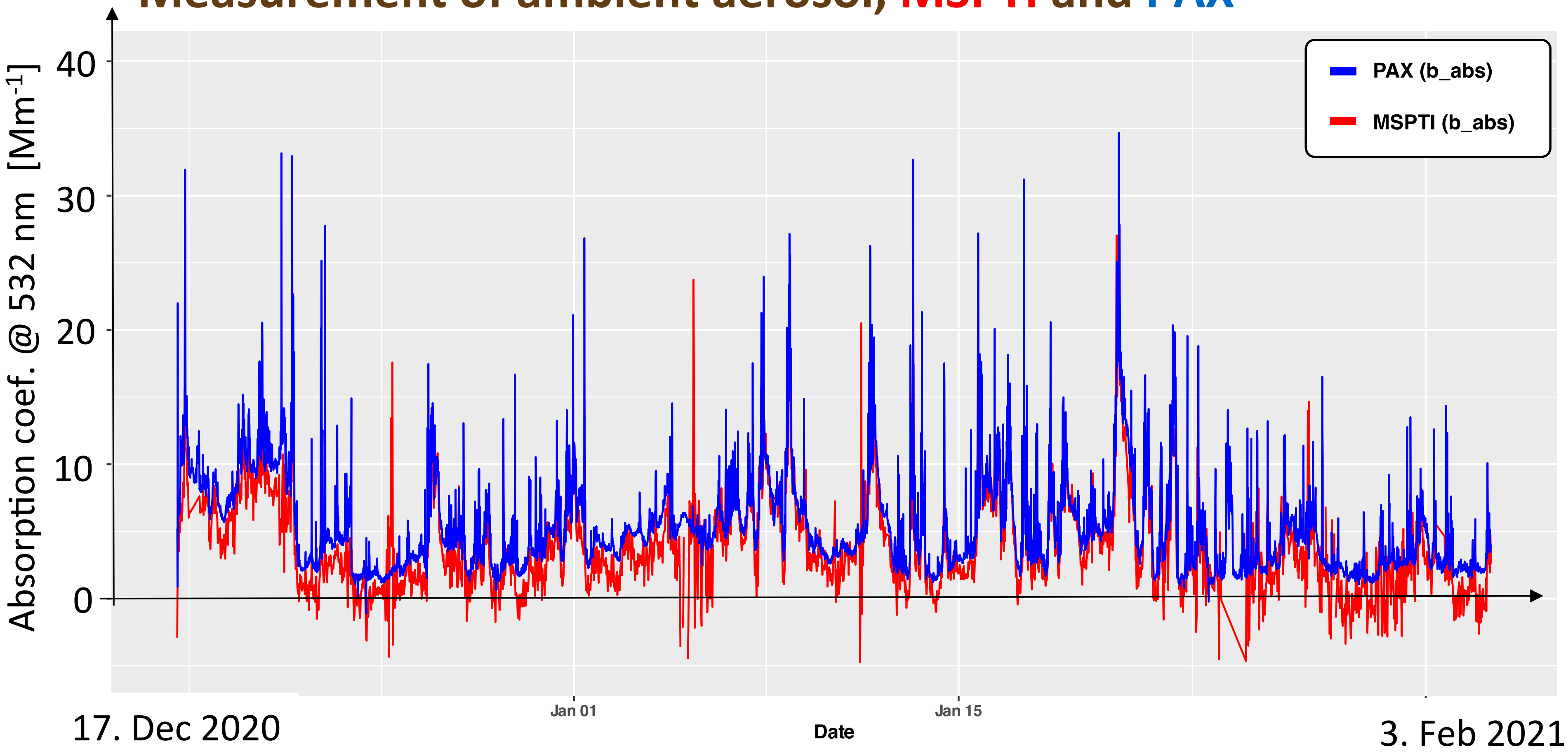
NO_2 test measurement





1st “mainly unattended” deployment:

Measurement of ambient aerosol, MSPTI and PAX



- 10 $Mm^{-1} \cong 1$ µg/m^3 BC (MAC = 10 m^2/g)
- Continuous measurement of ambient air at Windisch from 17.12.2020 to 3.2.2021.
  MSPTI is compared with a commercially available photoacoustic sensor (PAX).
- Good agreement in the wavelength corrected data (to 532 nm, Angström exponent 1) over this 1.5 month period.
- The largest deviations occur at very low concentrations of absorbing aerosol, when the PAX measurement never approaches 0 despite the prevailing meteorological conditions. This offset of the PAX is currently being investigated.

Conclusions

- Photo-thermal interferometry
  - in-situ measurement method for $b↓abs$
  - direct measurement of absorption
  - based on 1st principles

- We have developed a **new PTI instrument,** which has the ability to be calibrated and can be operated to measure eBC with no cross-sensitivity to absorbing gases

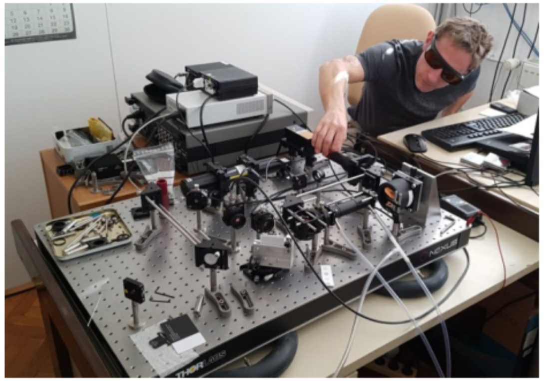
- Light absorbing gases (e.g. NO_x,O_3,H_2O) can lead to measurement artefacts in the determination of equivalent BC mass, but also present an opportunity for the calibration of in-situ instruments

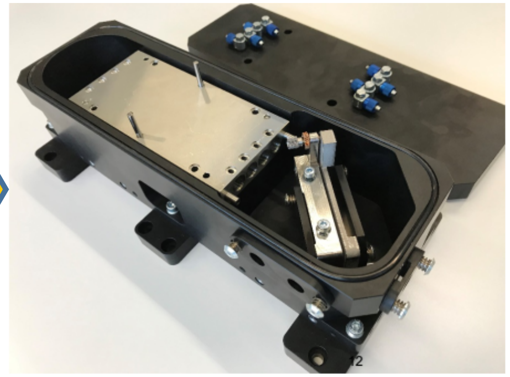
- Our PTI is sensitive (DL = 35 ng/m^3 eBC), accurate and fairly "simple"

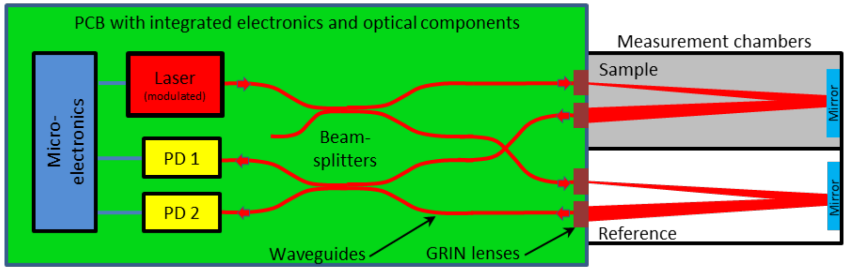
Roadmap for a miniaturized "Photothermal Black Carbon Sensing Module"

Our new custom-built **Photothermal Interferometer** is based on a new approach
https://doi.org/10.5194/amt-13-7097-2020

- It has no cross-sensitivity to absorbing gases
- Low detection limit: 35 ng/m^3 BC (0.35 Mm^{-1})





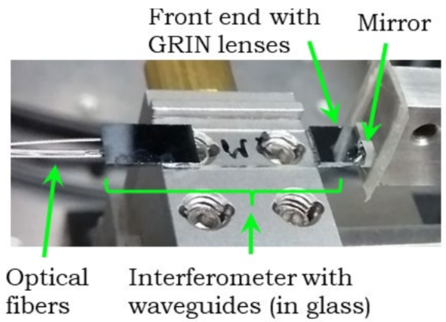


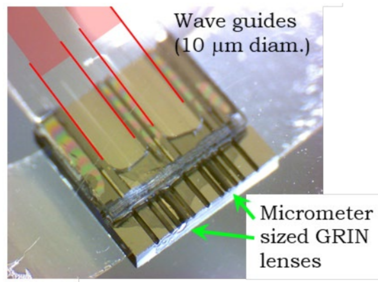
We are currently working on

- A significant miniaturization
- Develop small BC sensor based on Vario-optics polymer waveguide technology
- Electronics: Data acquisition, processing (e.g. Lock-in amplifier)

Expected benefits of a miniaturization:

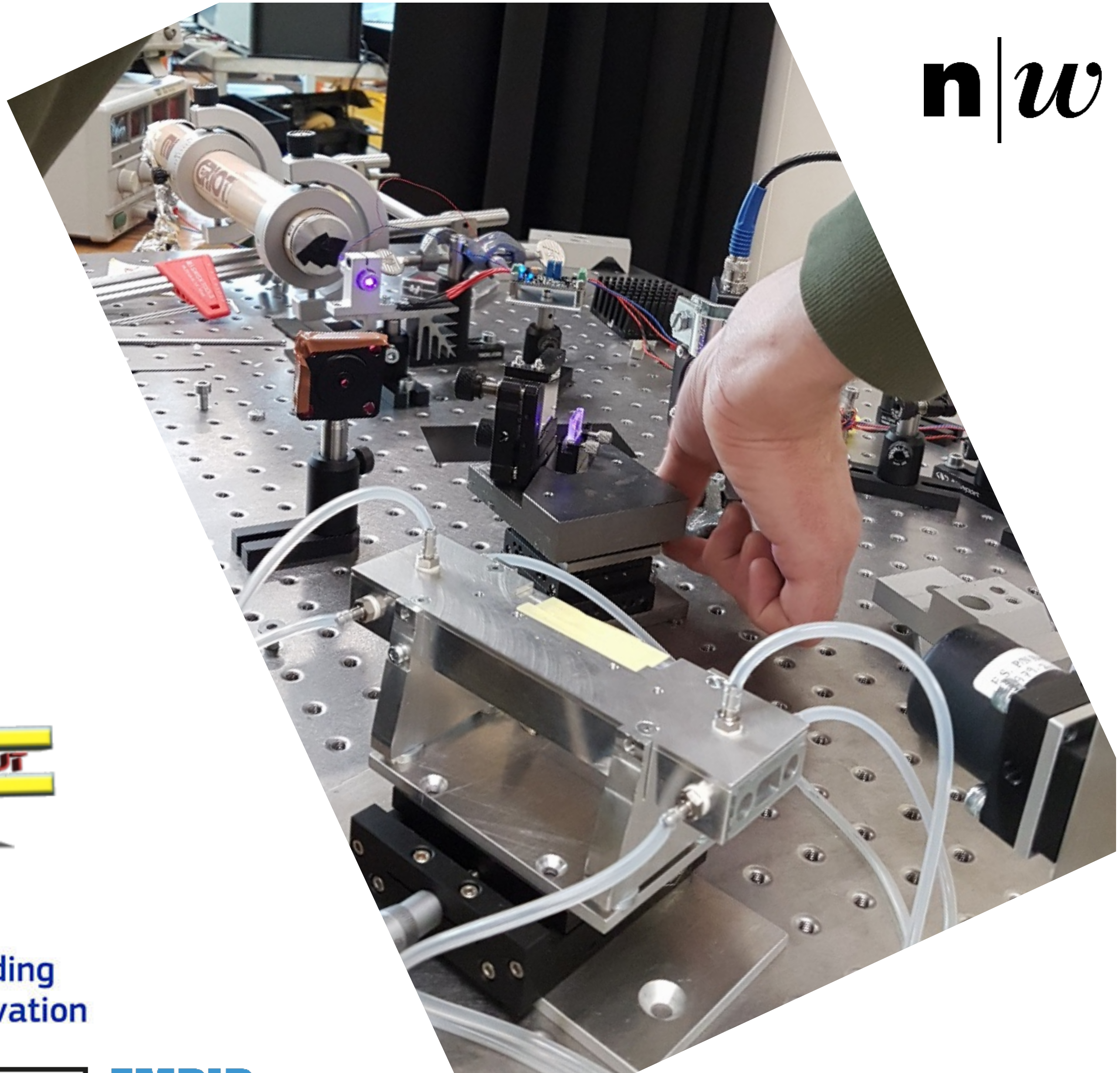
- Lower costs → better spatio-temporal coverage
- Portable devices → better source identification
- less susceptible to external vibrations and misalignments → better S/N ratio





Thank you !

n|w



Our PTI Funding:

PASSEPARTOUT

Horizon 2020
European Union Funding
for Research & Innovation

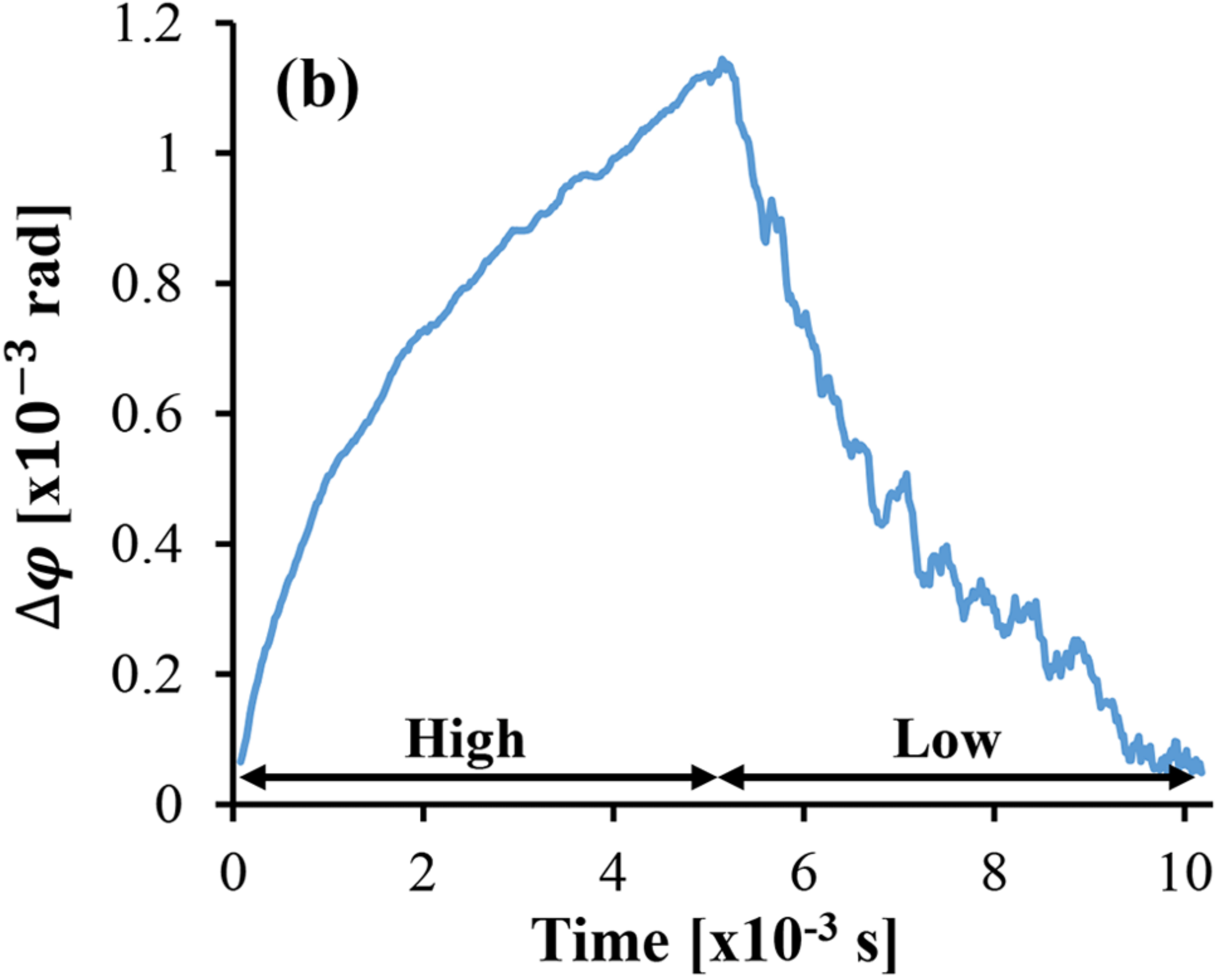
FNSNF

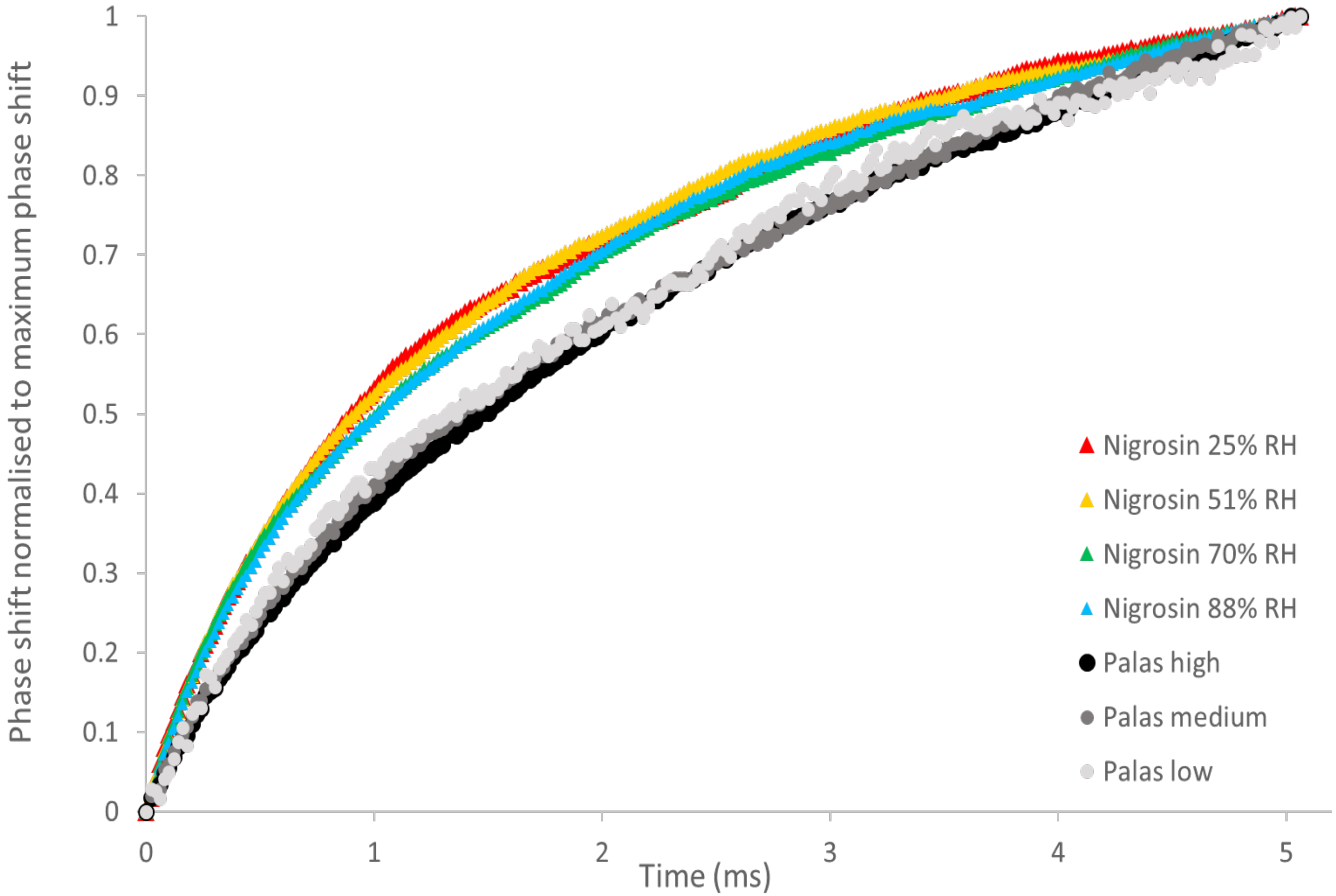
EMPIR BLACK CARBON

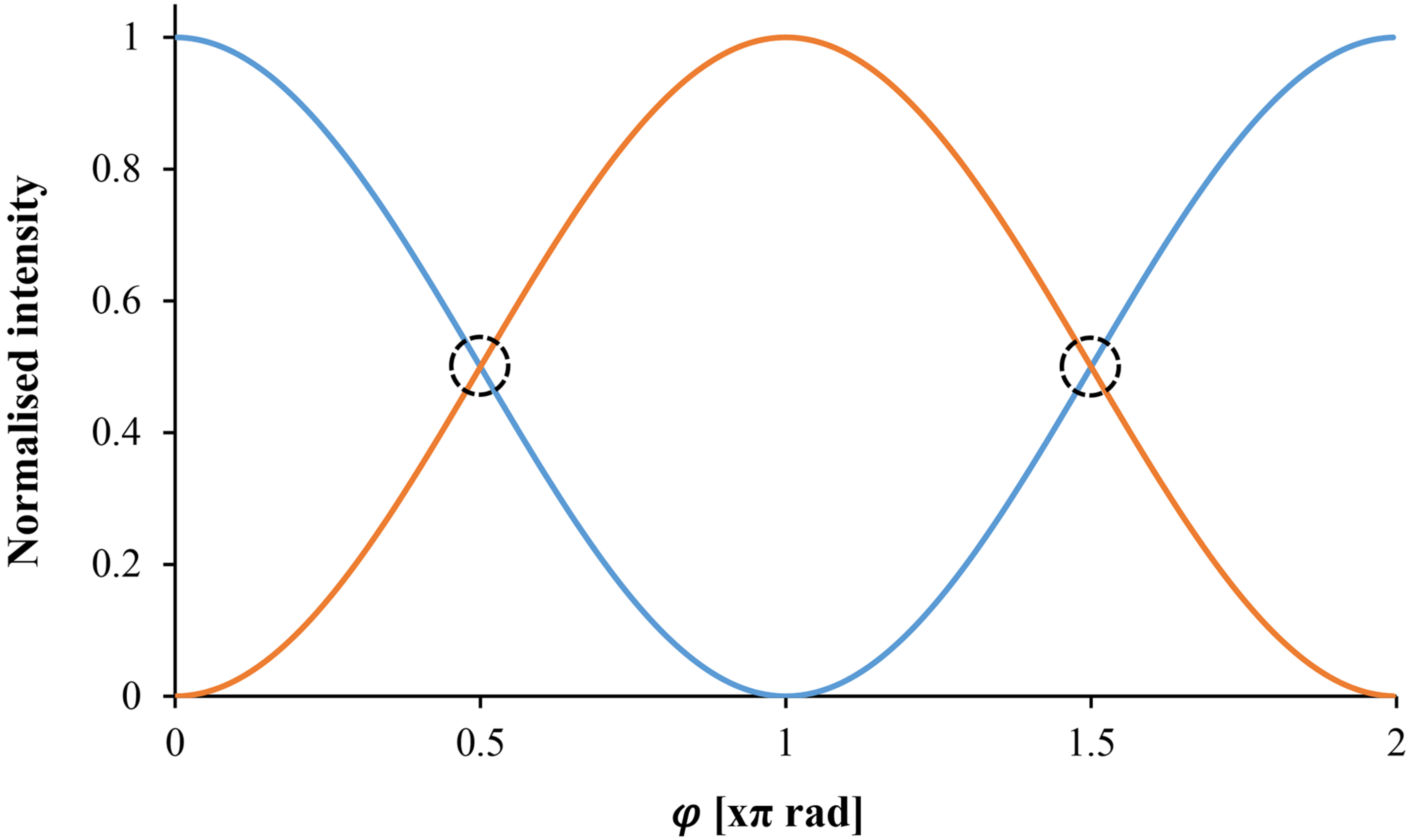
eurostars™

Innosuisse

BONUS Slides


(b)
High
Low
Δφ [x10⁻³ rad]
Time [x10⁻³ s]
0
0.2
0.4
0.6
0.8
1
1.2
0
2
4
6
8
10


Phase shift normalised to maximum phase shift
Time (ms)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
1
2
3
4
5
Nigrosin 25% RH
Nigrosin 51% RH
Nigrosin 70% RH
Nigrosin 88% RH
Palas high
Palas medium
Palas low

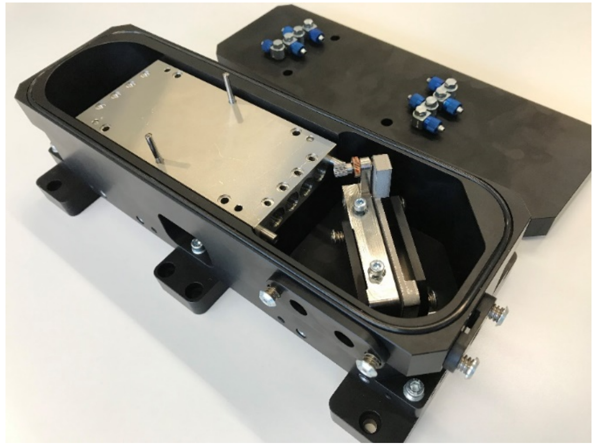


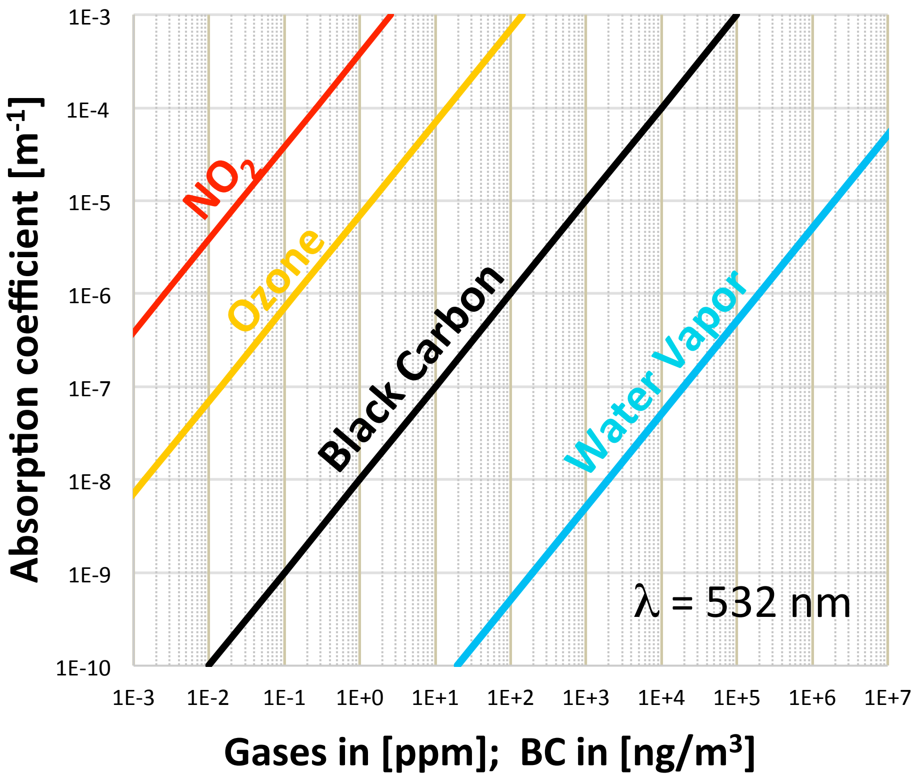
1
0.8
0.6
0.4
0.2
0
Normalised intensity
0
0.5
1
1.5
2
φ [xπ rad]

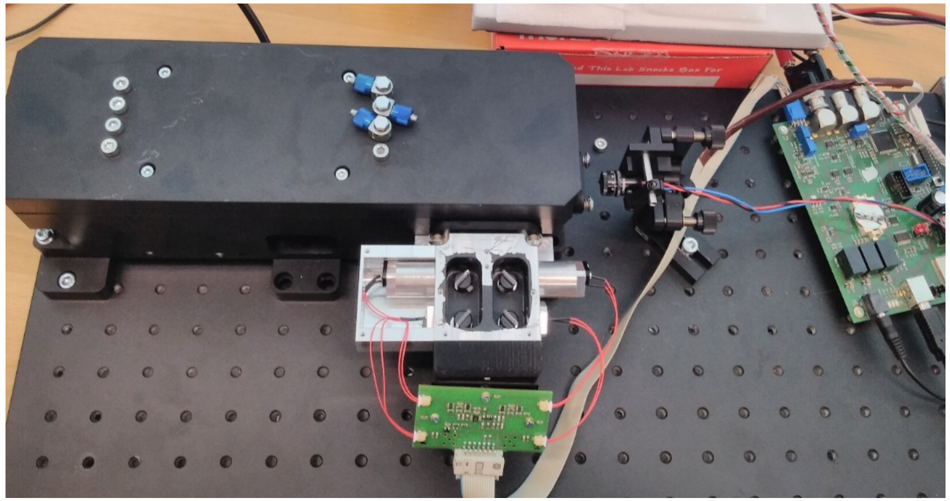
In-situ measurement of aerosol light absorption:

- Light absorbing gases are friend and foe
- Our new custom-built **Photothermal Interferometer** is based on a new approach

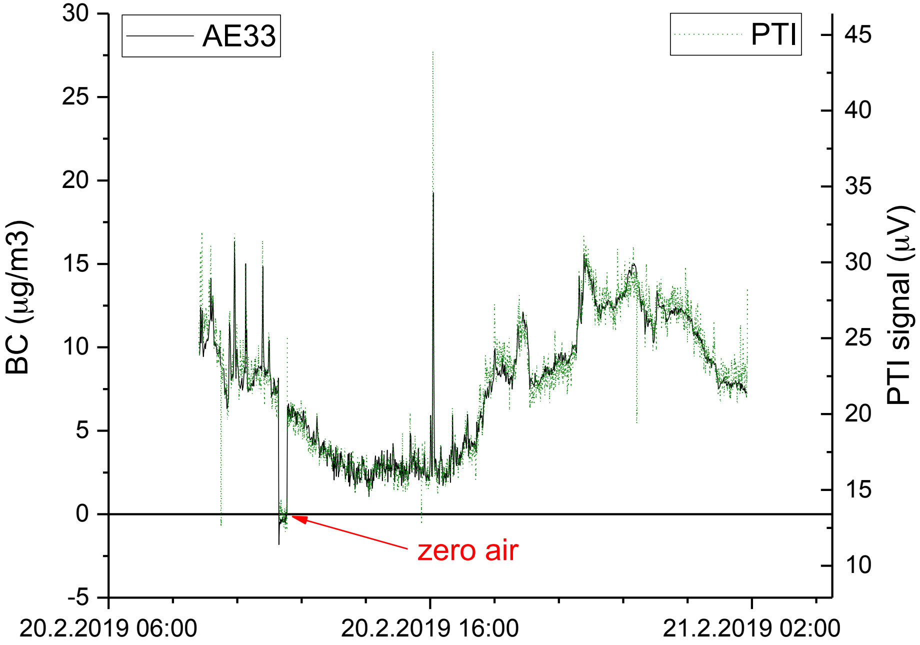
  - It has no cross-sensitivity to absorbing gases
  - Low detection limit: 35 ng/m^3 eBC (0.35 Mm^{-1})



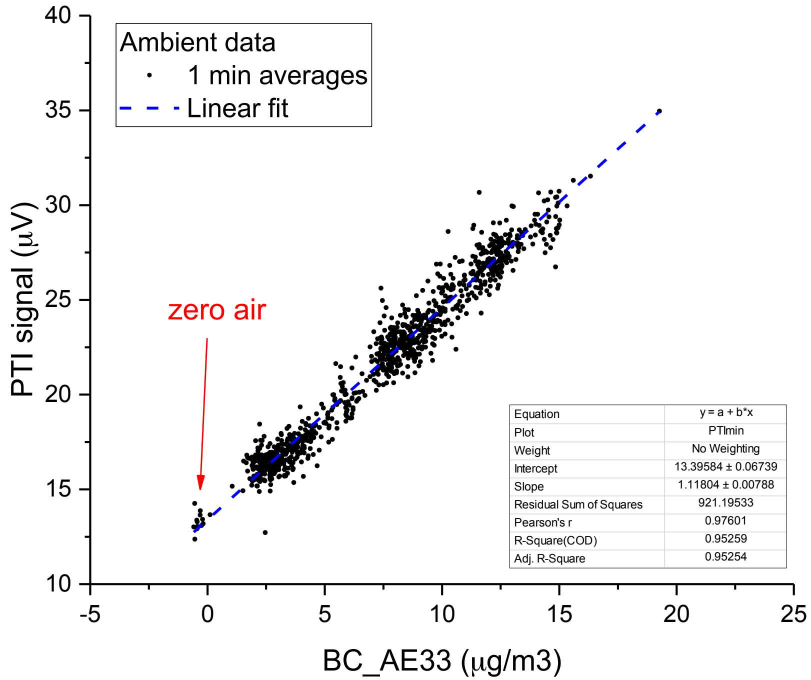




Recent PTI data (1064 nm) from Wintersmog in Ljubljana



The time series of ambient eBC measured by the Aethalometer AE33 and the PTI instrument.



Equation	y = a + b*x
Plot	PTImin
Weight	No Weighting
Intercept	13.39584 ± 0.06739
Slope	1.11804 ± 0.00788
Residual Sum of Squares	921.19533
Pearson's r	0.97601
R-Square(COD)	0.95259
Adj. R-Square	0.95254

The regression between the PTI and the Aethalometer measurements.

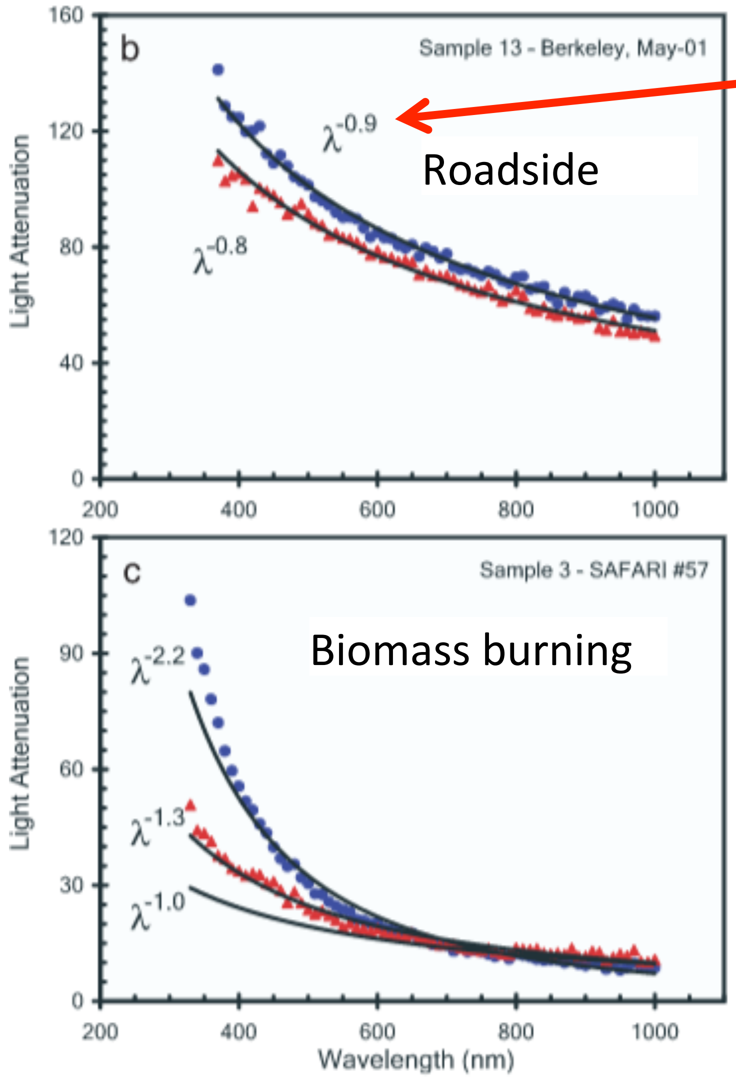
G. Močnik, B. Visser, P. Steigmeier, E. Weingartner, L. Drinovec

Interferometric measurements of the aerosol optical absorption coefficient – a new instrument and its characteristics

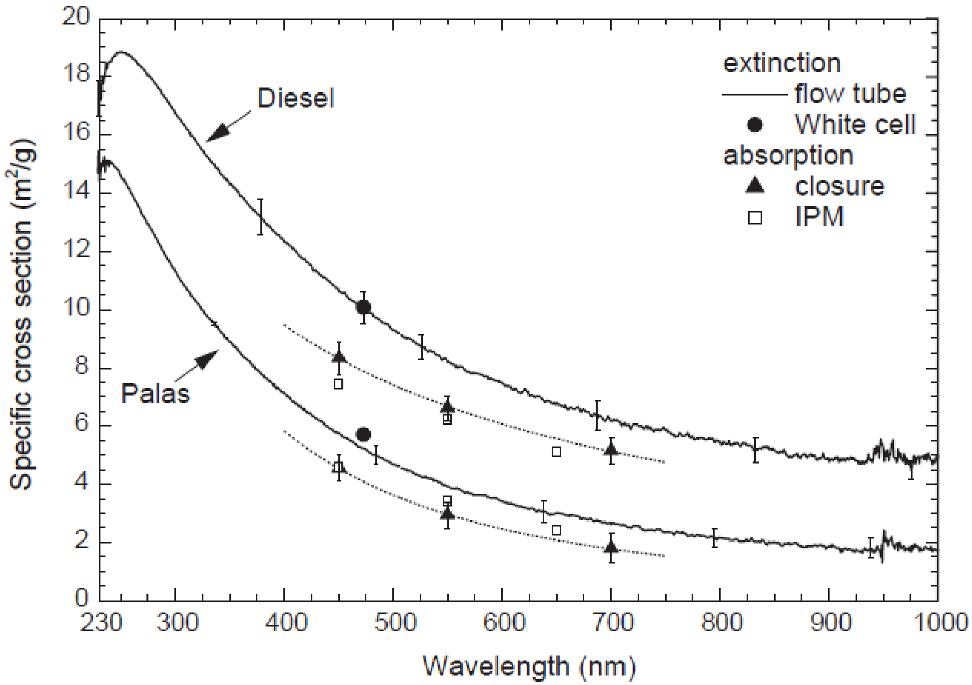
Conference Abstract, EAC Gothenburg, 2019

Use well defined aerosols for the transfer of a primary calibration to other wavelength…

Absorption Ångström exponent AAE

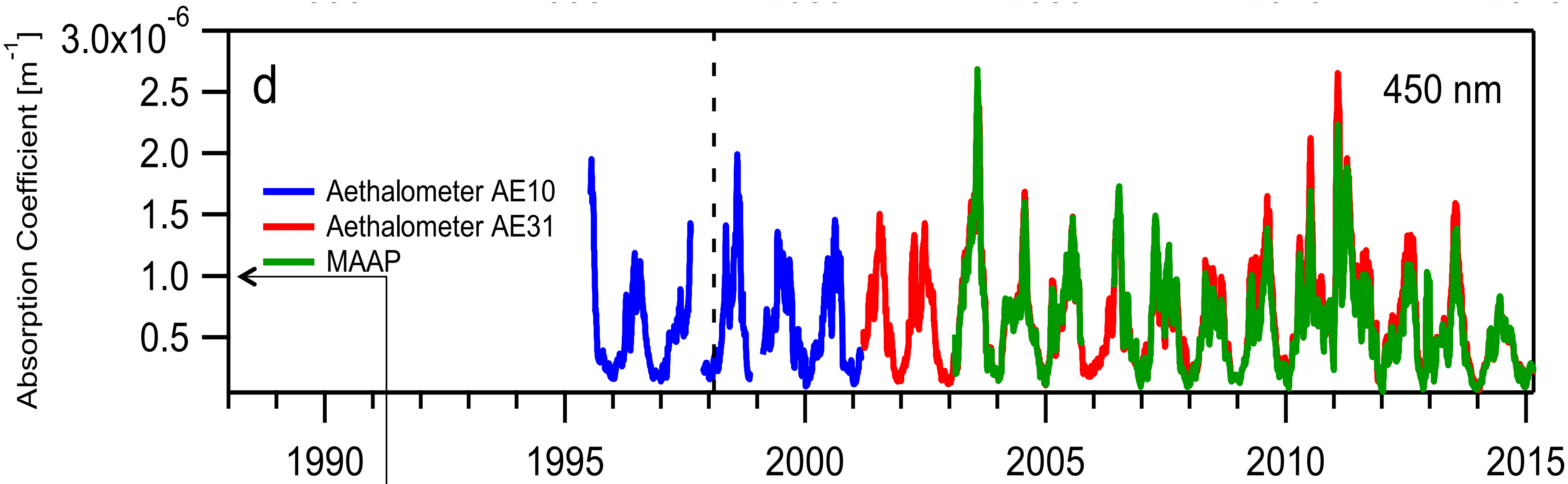


Kirchstetter et al., *J. Geophys. Res.*, 109(D21), D21208, doi:10.1029/2004JD004999, 2004.



Schnaiter et al. J. Aerosol. Sci., 34, doi:10.1016/S0021-8502(03)00361-6, 2003.

b_{abs} Data from Jungfraujoch



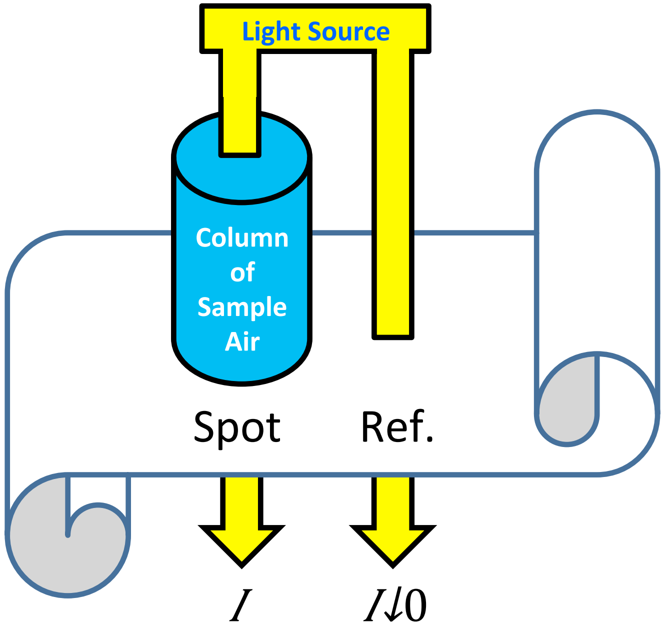
b_{abs} = 10^{-6} m^{-1} = ~ 100 ng m^{-3} BC

Correct C-values are important for interpreting long term data correctly !

Bukowiecki et al., AAQR, 2015

The Aethalometer

- The Aethalometer principle was developed in the 1950s
- It measures the attenuation (ATN) of a specific wavelength of light through a quartz fiber filter as it loads with particles over time.
- Latest instrument operate at defined monochromatic wavelength (λ=370-950 nm) and can correct for loading artefacts - but not for the unknown C-value.



$$\text{Attenuation} = \text{ATN} = \ln(I_0/I)$$

$$b_{ATN} = \frac{Spot\ Area}{Flow\ Rate} \cdot \frac{\Delta \text{ATN}}{\Delta t}$$

Aethalometer Retrieval

Reported quantity	*Measured quantity*	*Retrieved quantities*	
BC mass conc. BC $[\mathrm{ng/m^3}]$	absorption coef. of the <u>filtered particles</u> b_{ATN} $[1/\mathrm{m}]$	“true” absorption coef. b_{abs} $[1/\mathrm{m}]$	equivalent BC concentration eBC $[\mathrm{ng/m^3}]$

$$\mathrm{BC} = \frac{1}{\mathrm{MAC}_{ATN}} \cdot b_{ATN} = \frac{\lambda}{14625\ nm\ m^2/g} \cdot \frac{A}{Q} \frac{\Delta \mathrm{ATN}}{\Delta t}$$

$$b_{ATN} = C \cdot R(\mathrm{ATN}) \cdot b_{abs}$$

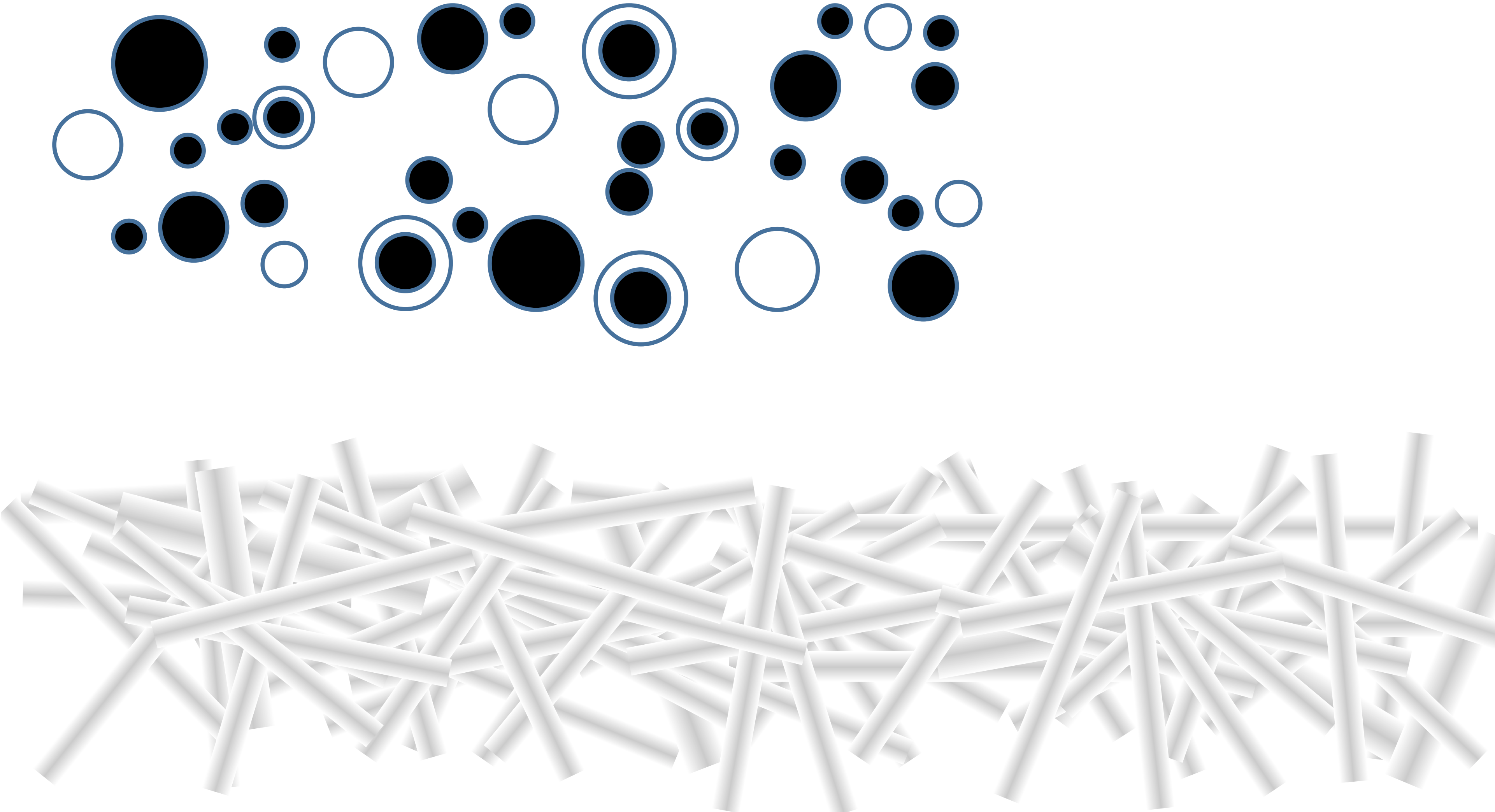
$$b_{abs} = \mathrm{MAC}(\lambda) \cdot \mathrm{eBC}$$

$\boldsymbol{R = 0.3 - 1}$,
depends on filter loading (ATN) and particle size (penetration depth)

$\boldsymbol{C = 2 - 5}$,
accounts for enhanced light scattering within the filter matrix

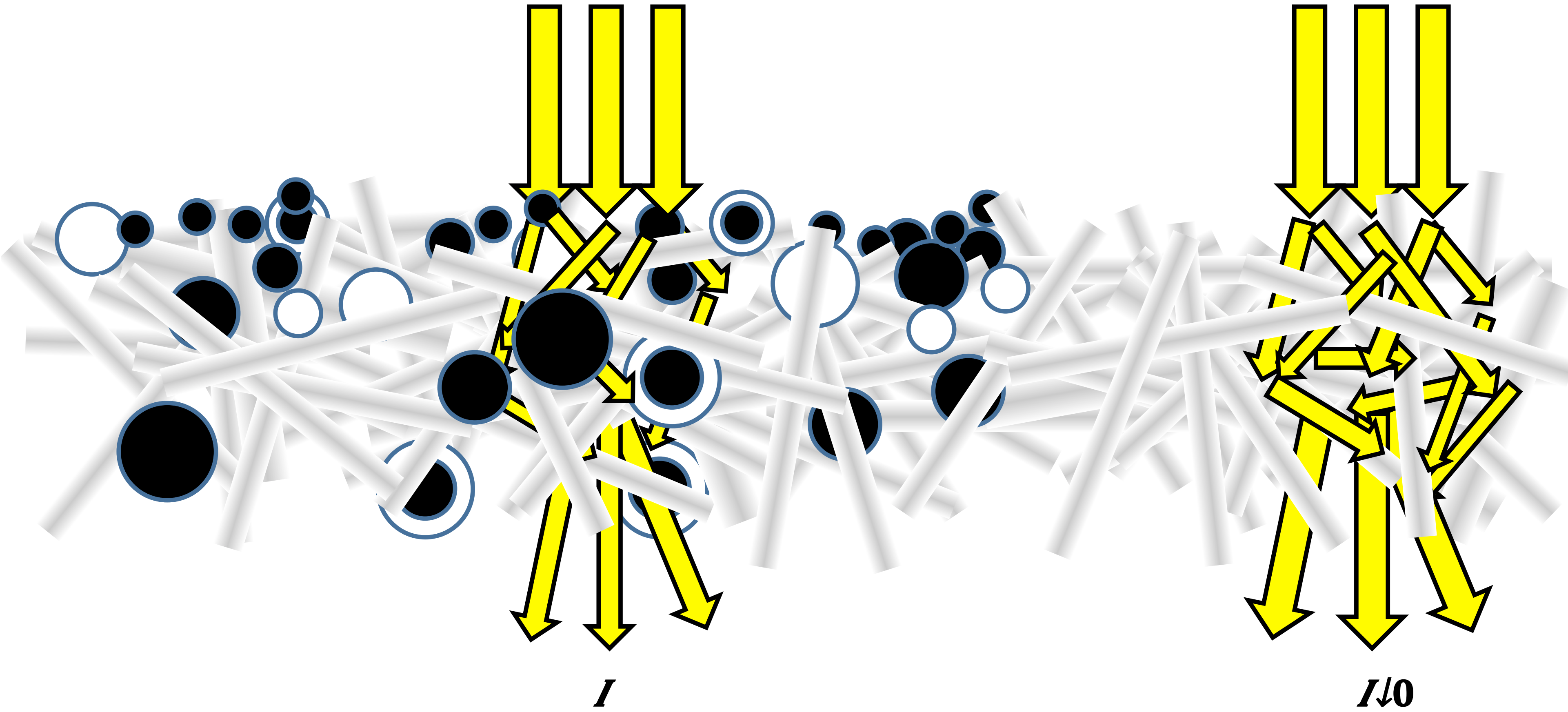
MAC($\boldsymbol{\lambda}$) $\boldsymbol{= 5 - 20\ m^2/g}$

Filter Artefacts



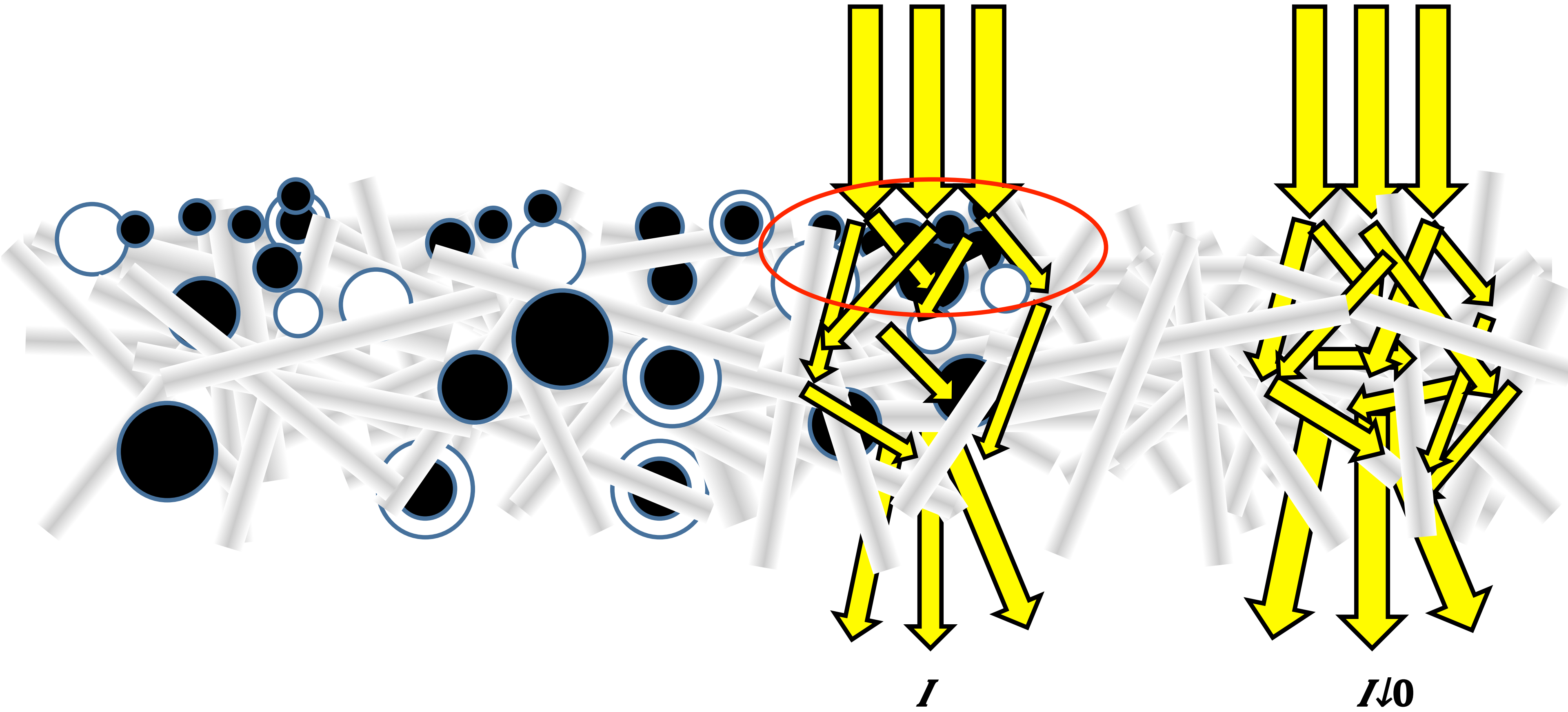
Multi-Scattering Correction (C-Value)

- correcting for enhanced light absorption within the filter
- the apparent absorption is higher than the true value



Loading Correction (R-Value)

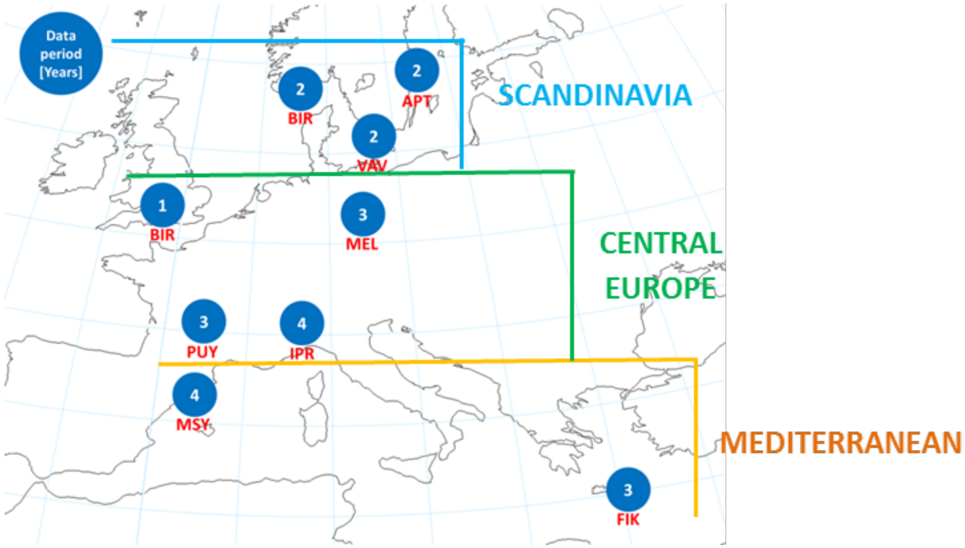
- correcting for “shadowing effects” within the filter
- reduces the apparent absorption

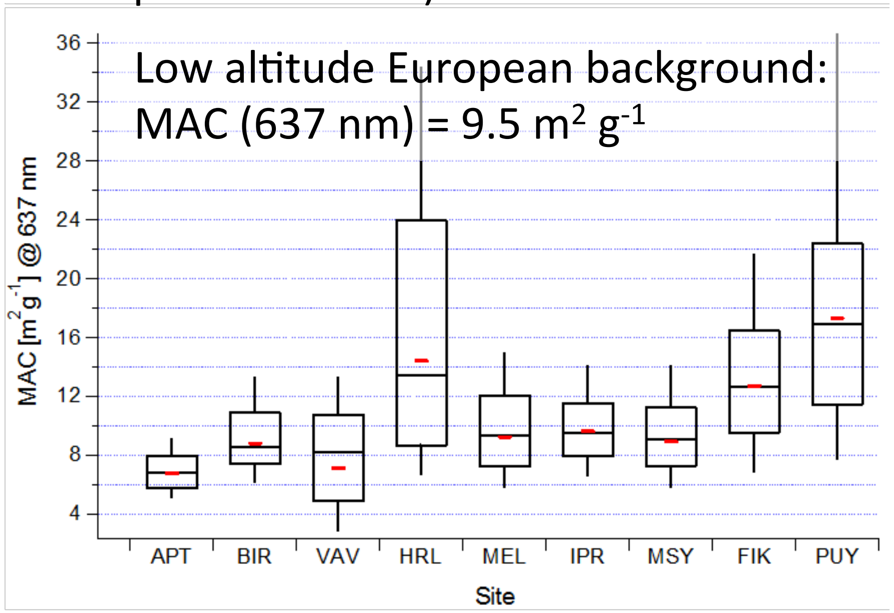


M. Zanata et al.
https://doi.org/10.1016/j.atmosenv.2016.09.035

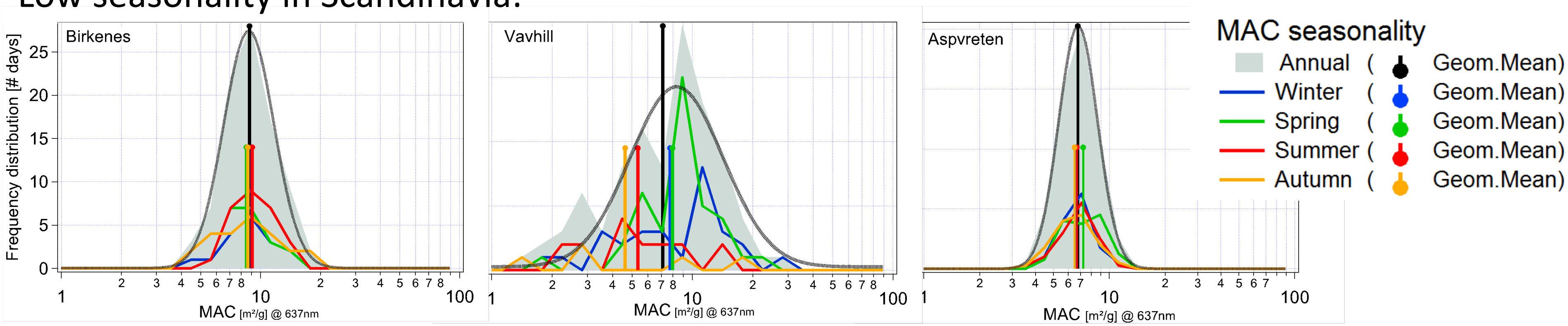
AC Value: eBC=$b\downarrow abs$ /MAC(λ)

Comparison of long-term measurements of $b\downarrow abs$ (from Aethalometer, PSAP and MAAP) with EC mass concentrations (from thermo-optical methods).





Low seasonality in Scandinavia:

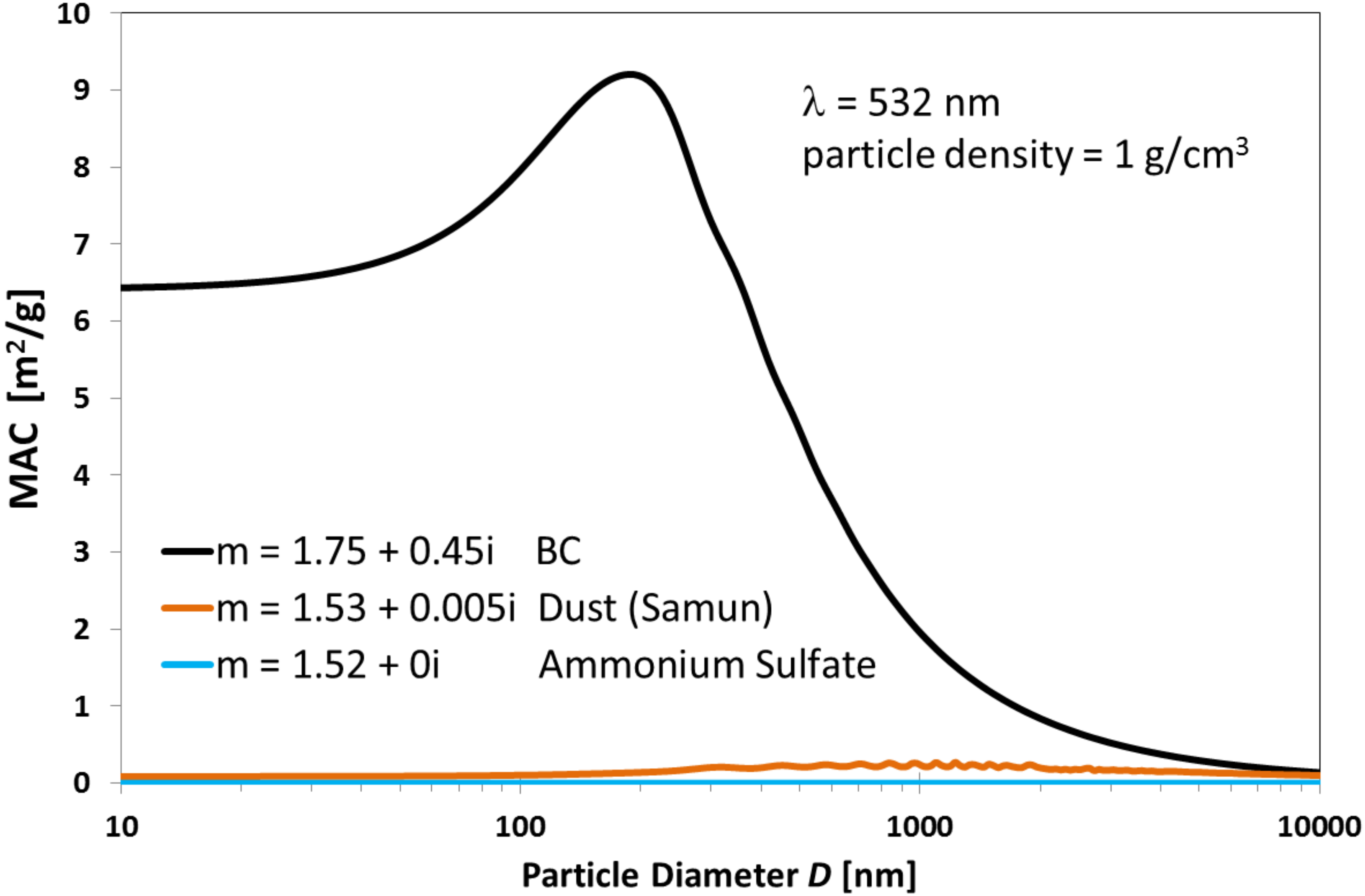


Which Aerosol Types Absorb Light?

n|w

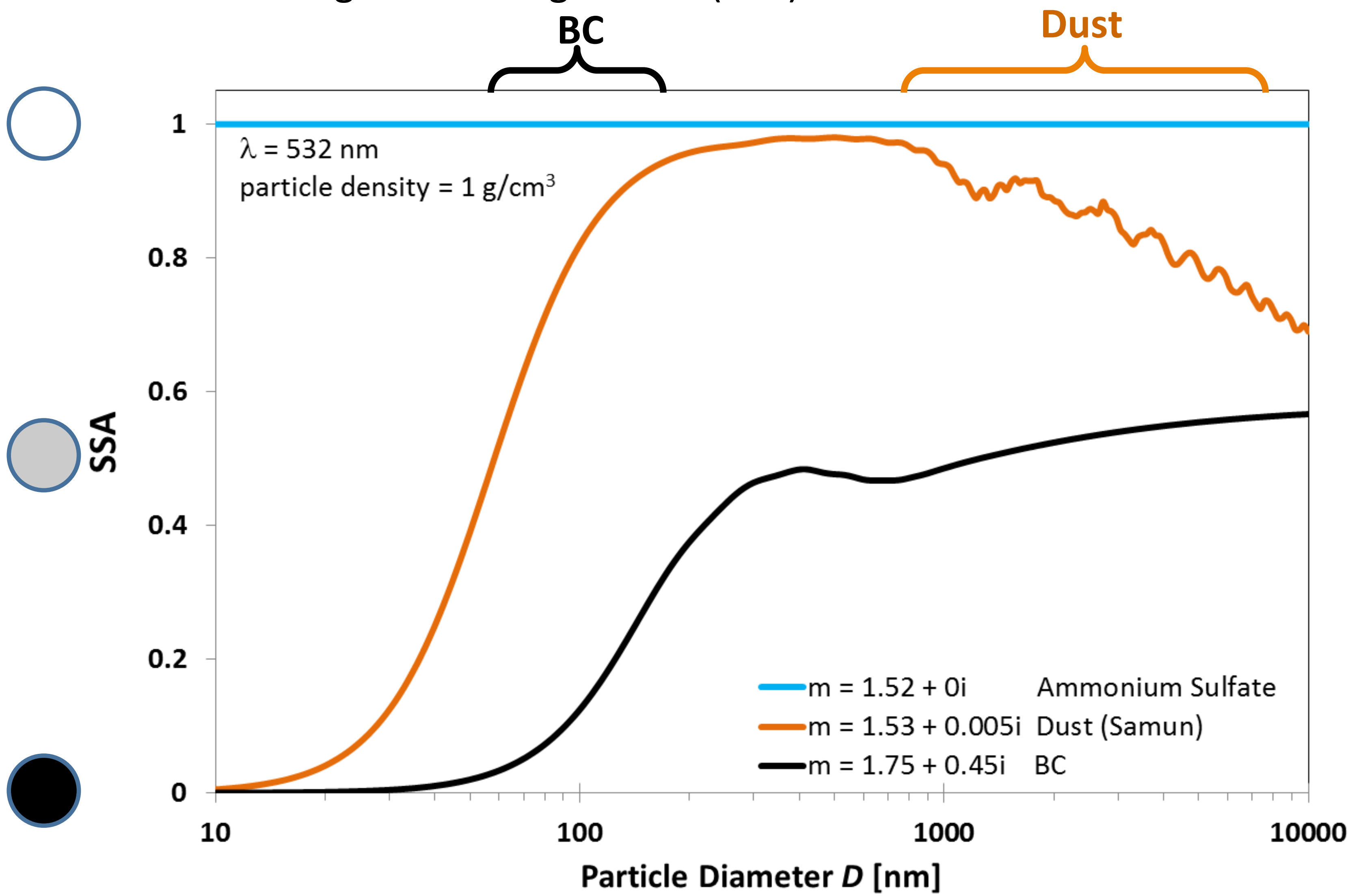
Mass absorption coefficients (MAC) $[m^2/g]$

b_{abs} = **MAC(*D*, *λ*)** · BC Mass



Blackness of the Aerosol: $SSA = b_s / b_e = b_s / (b_s + b_{abs})$

Direct radiative effects of aerosols
are sensitive to the single scattering albedo (SSA)



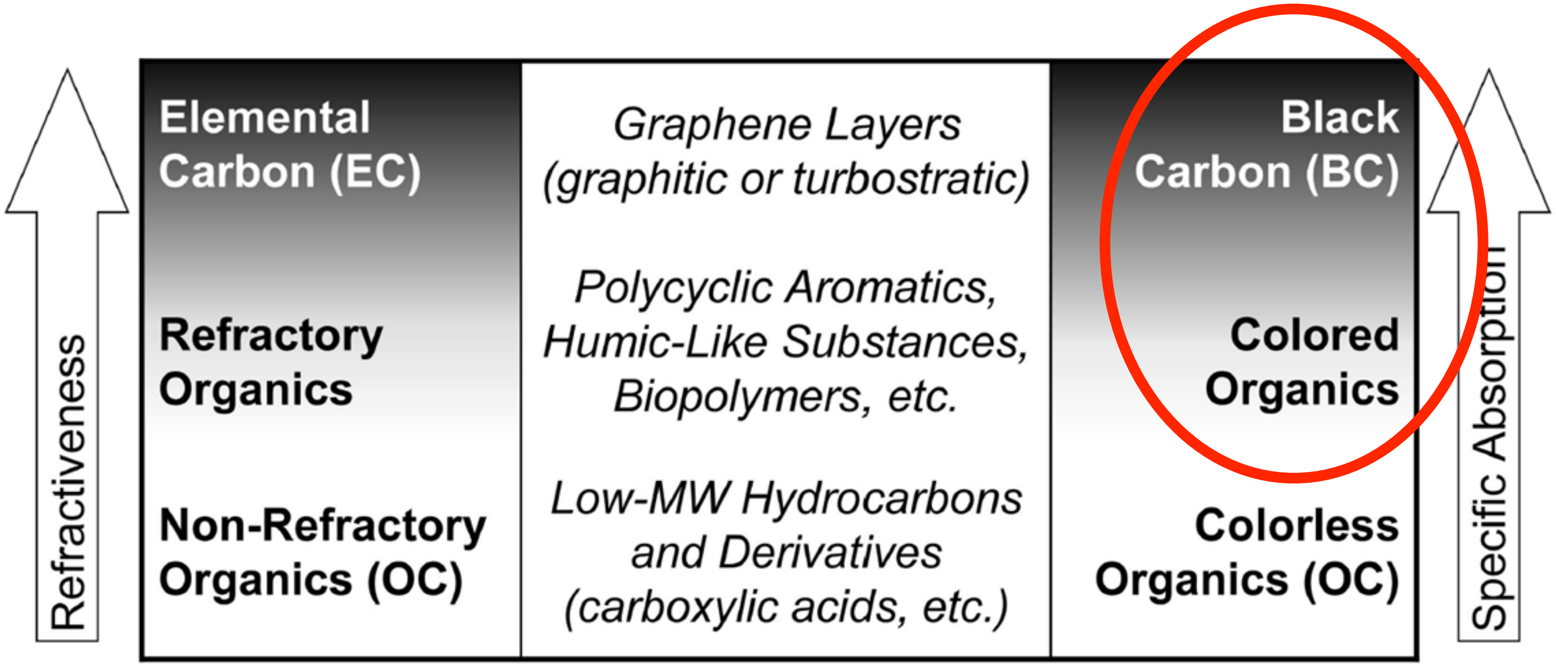
What is Black Carbon (BC)?

Black carbon (BC) is the most strongly light-absorbing component of particulate matter, and is formed by the incomplete combustion of fossil fuels, biofuels, and biomass.

Organic carbon (OC) denotes the total carbon associated with the organic compounds

Organic mass (OM) refers to the mass of the entire carbonaceous material, including hydrogen and oxygen.

Elemental carbon (EC) denote the non- organic, refractory portion of the total carbon and is an indicator for BC.

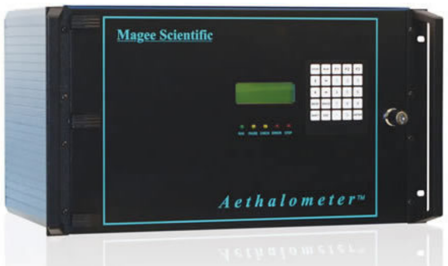


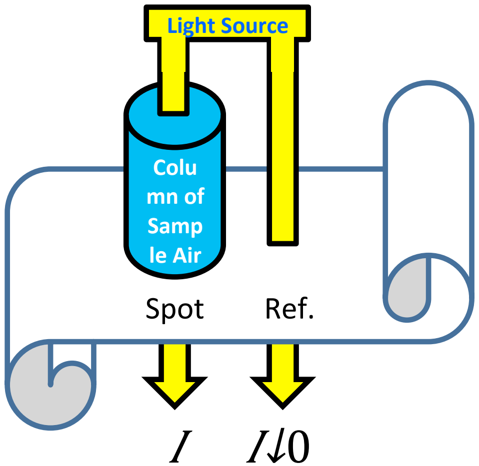
(Pöschl, Anal Bioanal Chem., 2003)

Filter Based Instruments for Measuring b_{abs}

Aethalometer

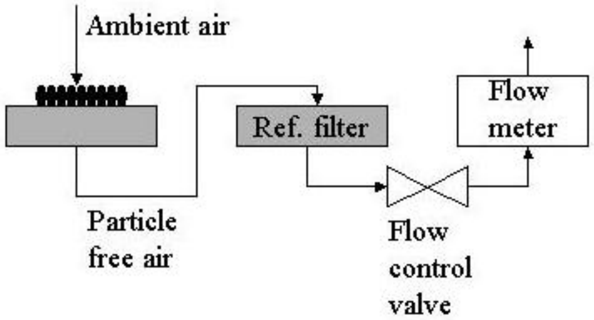
Hansen et al.
(1984), Sci. Tot. Env.





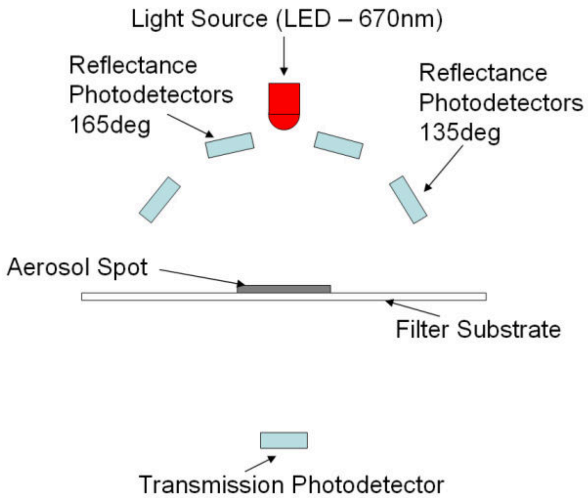
PSAP

Bond et al.
(1999), AS&T



MAAP

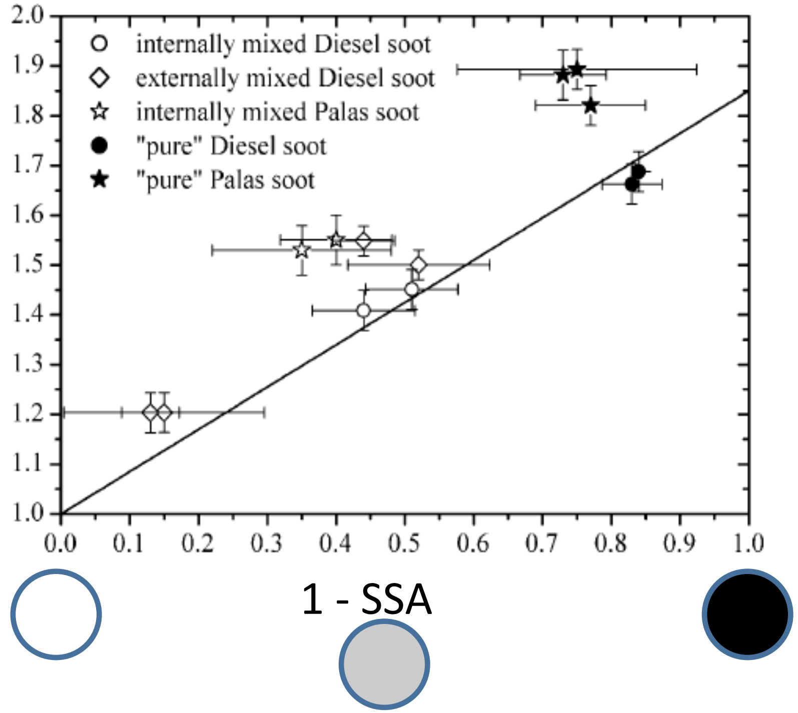
Petzold and Schönlinner
(2004), J. Aerosol Sci.



Loading Correction (R-Value)

Scattering of transparent aerosol embedded in the filter reduce the loading effect:

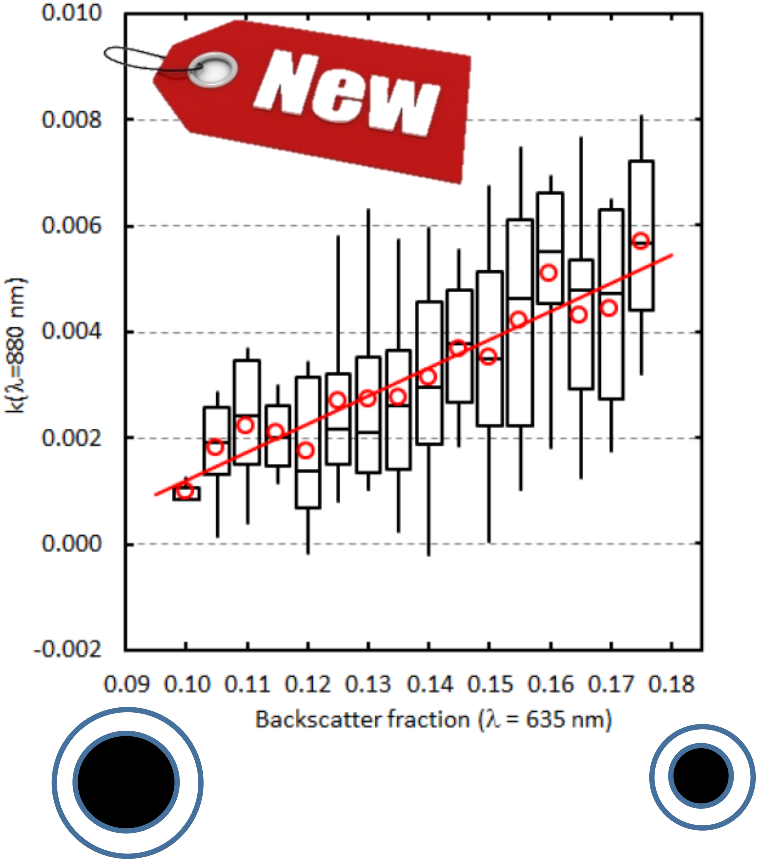
Magnitude of the loading effect



Weingartner et al. (2003), JAS

Evidence that loading effect mainly depends on soot particle size (via penetration depth in the filter):

Magnitude of the loading effect



Virkkula et al. (2015), AMTD