A 2-λ Photo-Thermal Aerosol Absorption Monitor:
design, calibration and measurements of absorption enhancement due to coating

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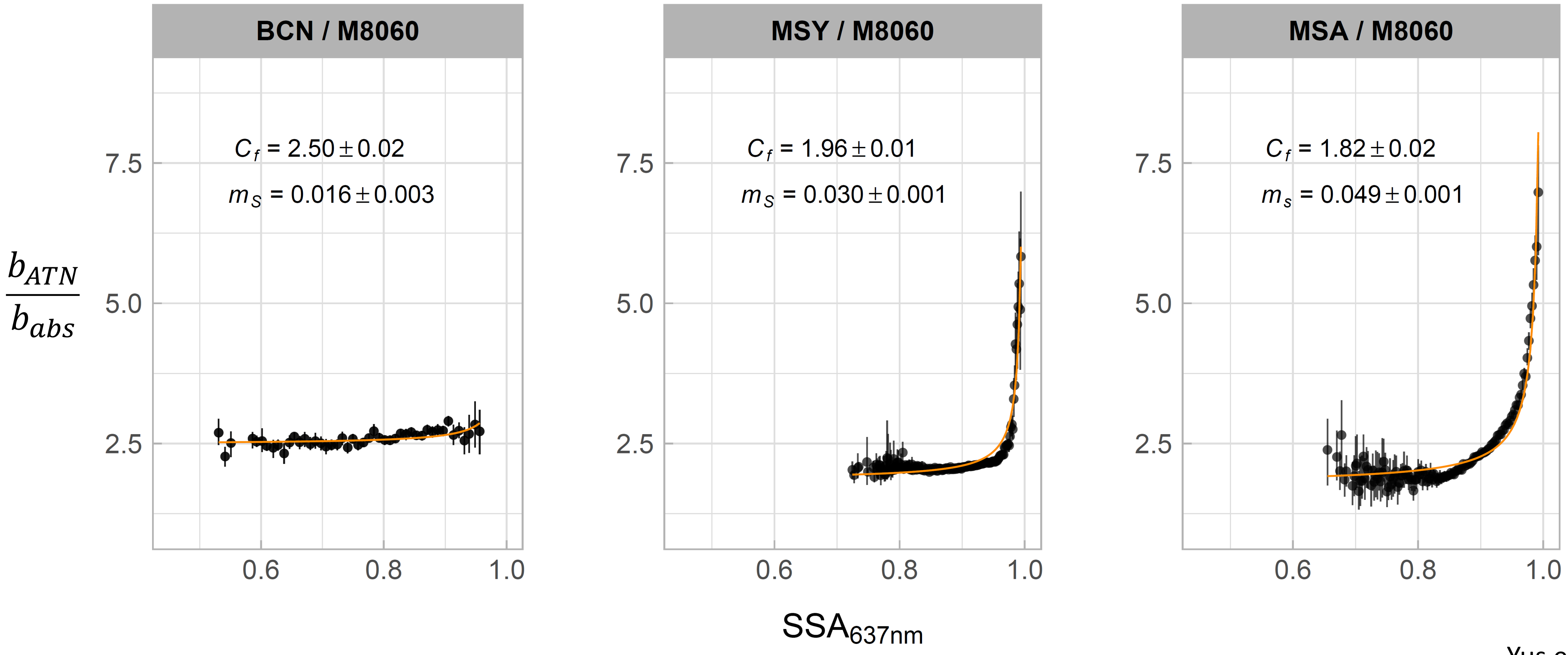
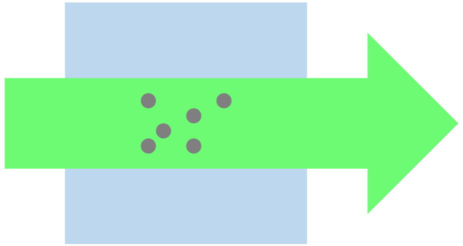
Filter photometer biases



Yus et al., 2021

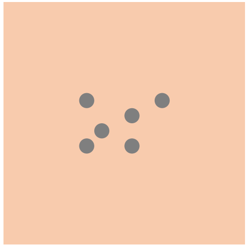
Photo-thermal interferometry

Particle absorb light



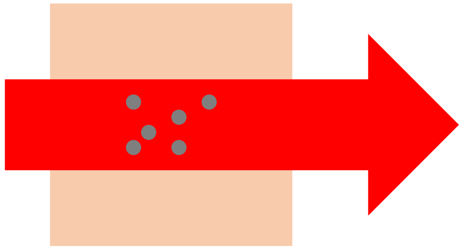
Pump beam intensity: $I=1\ W/mm^2$
Particle temperature: $\Delta T=3.3\ K$

Heat transfered to gas



Particle number: $2500\ cm^{-3}$
Air temperature: $\Delta T=42\ \mu K$
Refractive index: $\Delta n=47*10^{-12}$

Measurement of interferometer phase change



Light path length: $\Delta s=47*10^{-15}\ m$
Interferometer phase: $\Delta\phi=0.15\ \mu Rad$

Phase change is proportional to absorption!!

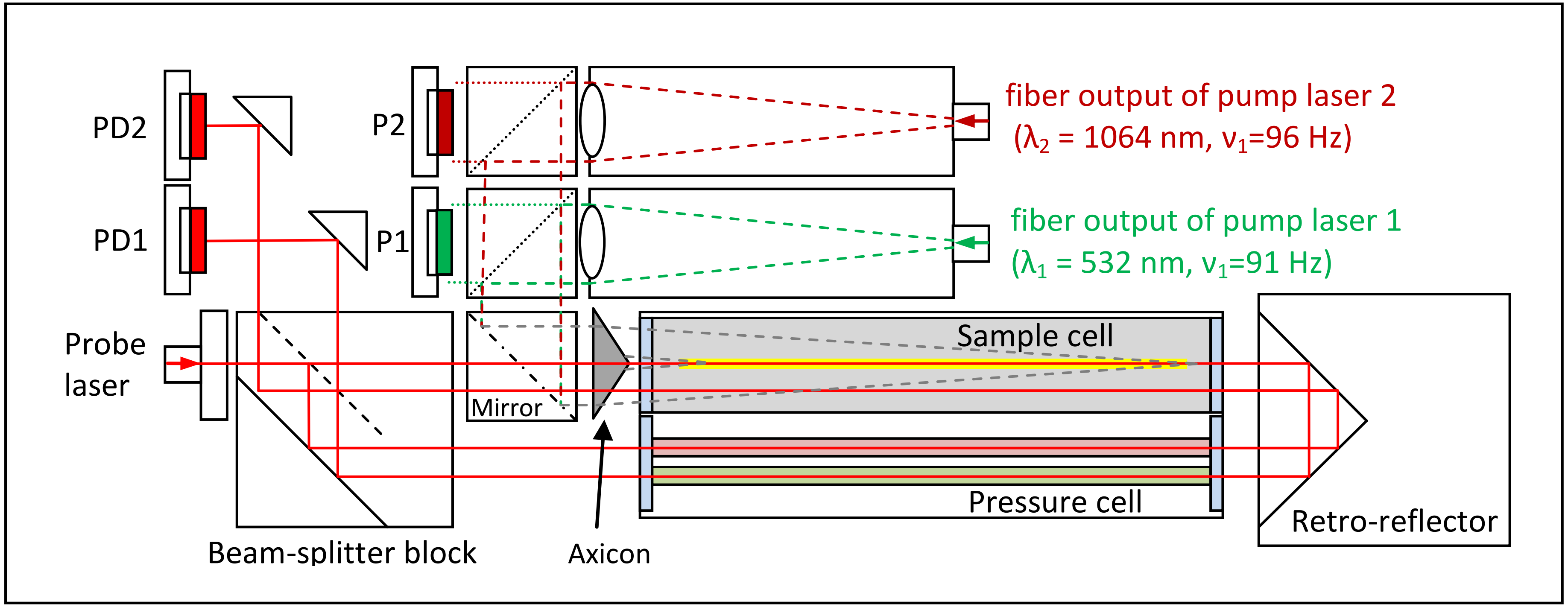
Moosmüller and Arnott, 1996; Sedlacek, 2006; Sedlacek and Lee, 2007; Lee and Moosmüller, 2020; Visser et al., 2020; Drinovec et al., 2022

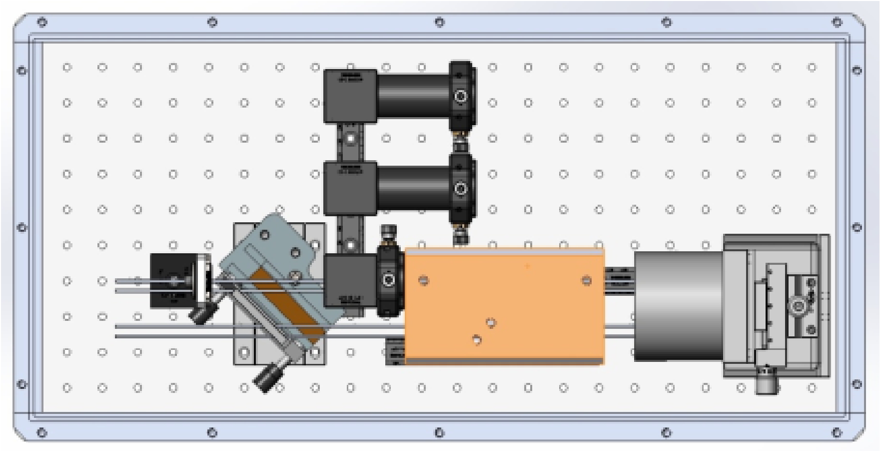
Instrument: PTAAM-2λ

•Moosmüller, H. & Arnott, W. (1996). *Opt. Lett.*, 21, 438-440.
•Sedlacek, A.J. (2006). *Rev. Sci. Instrum.*, 77, 064903, 1-8.
•Visser et al. (2020). *Atmos. Meas. Tech.* 13, 7097–7111.
•Drinovec et al. (2022), *Atmos. Meas. Tech. Discuss.*, amt-2021-21

Europäisches Patentamt
European Patent Office
Office européen des brevets

- **P**hoto-**T**hermal **A**erosol **A**bsorption **M**onitor
- Mach-Zender interferometer, similar to Moosmuller, Arnott, Sedlacek and Visser
- Pump beam focused by **axicon** (patent EP 3492905)
- Simultaneous measurements at **532 and 1064 nm**





$pump$:532 nm & 1064 nm

Article

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Atmospheric Measurement Techniques

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Abstract | Discussion | Metrics

22 Feb 2022

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A dual-wavelength photothermal aerosol absorption monitor: design, calibration and performance

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Photo-Thermal Aerosol Absorption Monitor
PTAAM 2 λ

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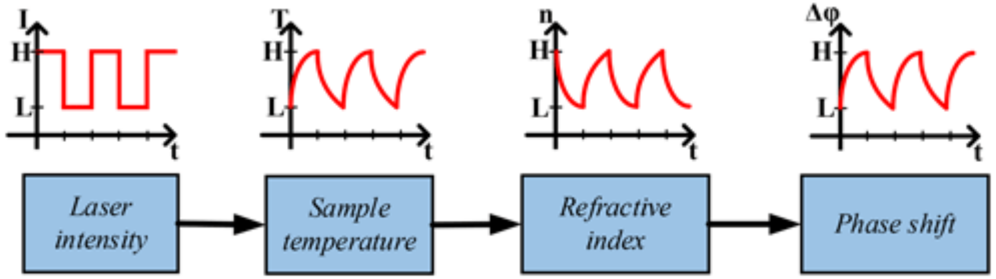
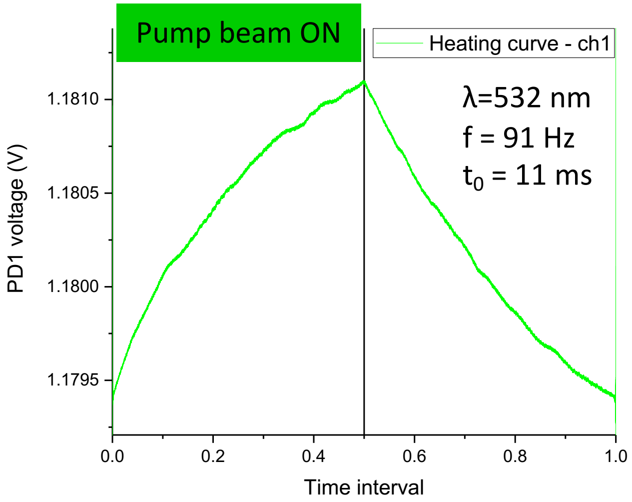
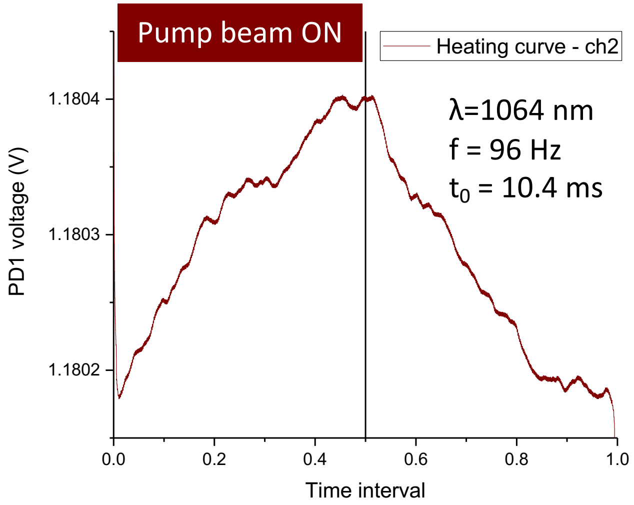
Photo-thermal signal







- Signal shape defined by the pump geometry
- Signal amplitude proportional to the absorption coefficient – lock-in amplifier

532 nm channel calibration

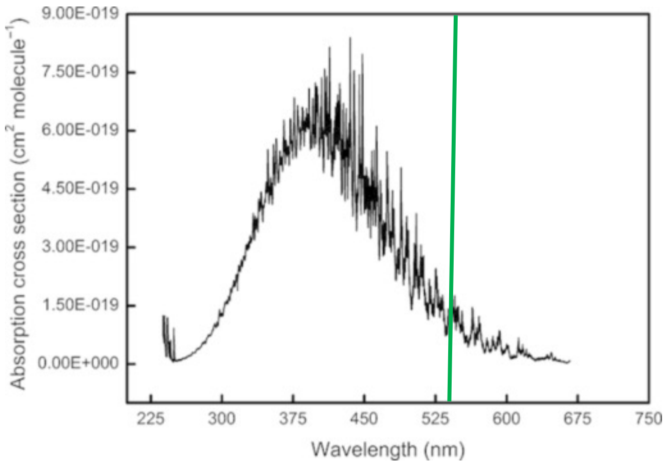
Instrument response denpends on:

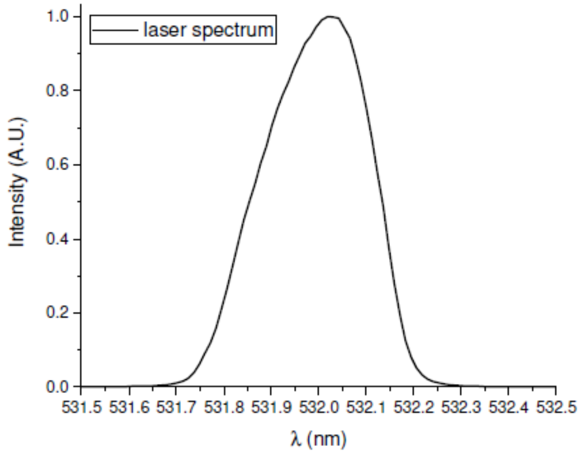
- Pump beam intensity
- Overlap between pump and probe beams

-> instrument must be **calibrated**.

532 nm channel calibration:

- Using absorbing gas: $\mathbf{NO_2}$
- Absorption cross-section = $1.47*10^{-19}$ cm^2
- High uncertainty of NO_2 concentration < sub ppm range



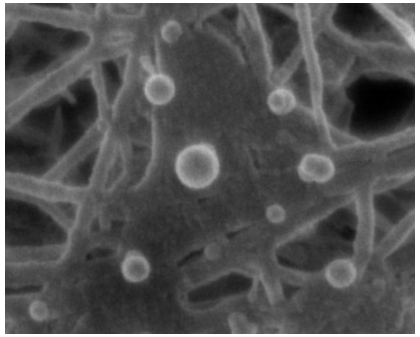


Calibration gas cylinder

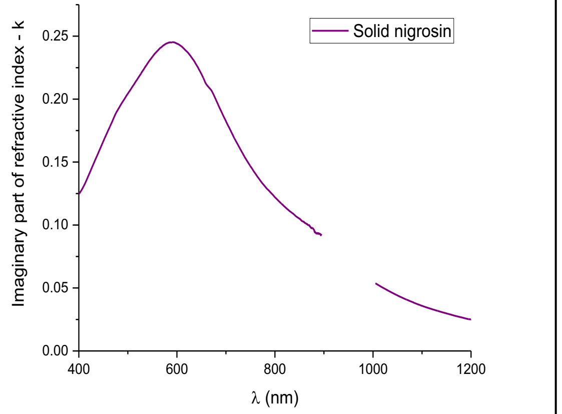
Permeation NO_2 generator

1064 nm channel calibration

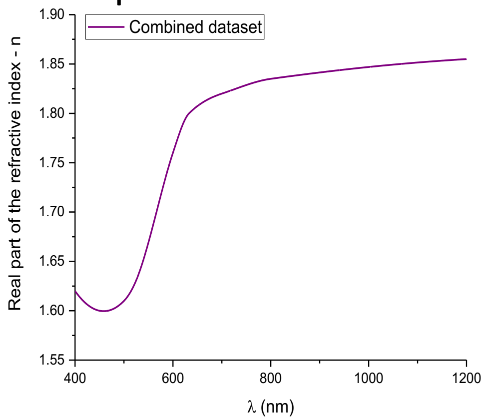
- lack of absorbing gasses in near-IR region
- calibration with **nigrosin** particles
  - absorbtion in VIS and IR
  - water soluble pigment -> forms nice **spherical** particles



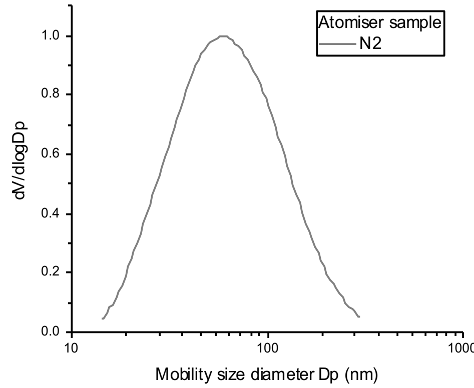
Imaginary part of refractive index



Real part of refractive index



Aerosol size spectra



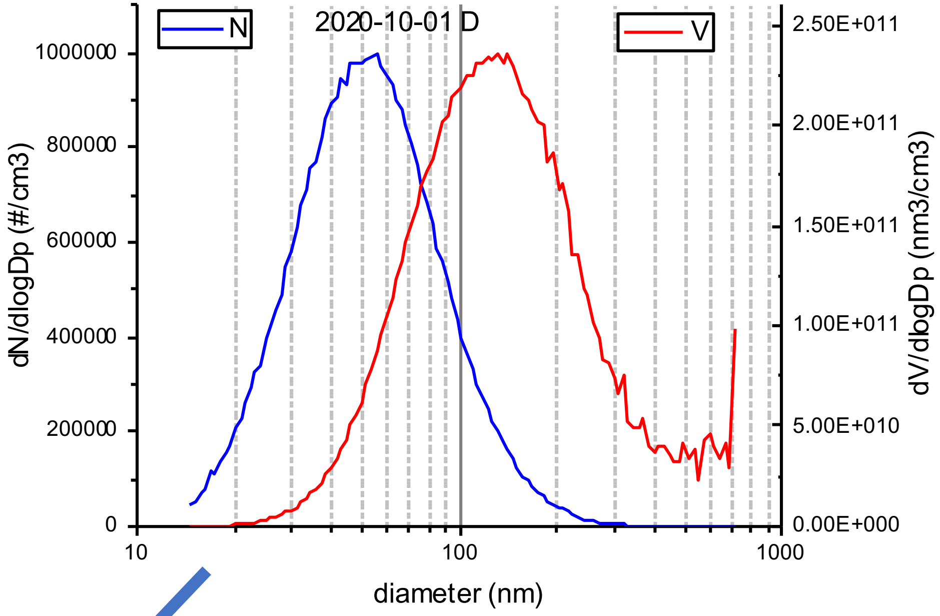
Mie theory

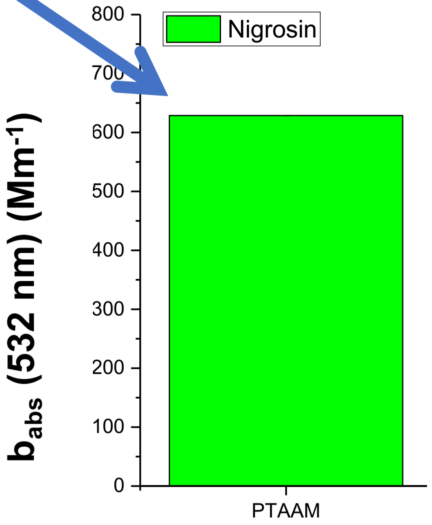
Absorption coefficient

babs(1064 nm)/babs(532 nm) ≈ 0.075

Validation – AeroTox and MORE-RAINI campaigns

Size distribution of aerosolized nigrosin



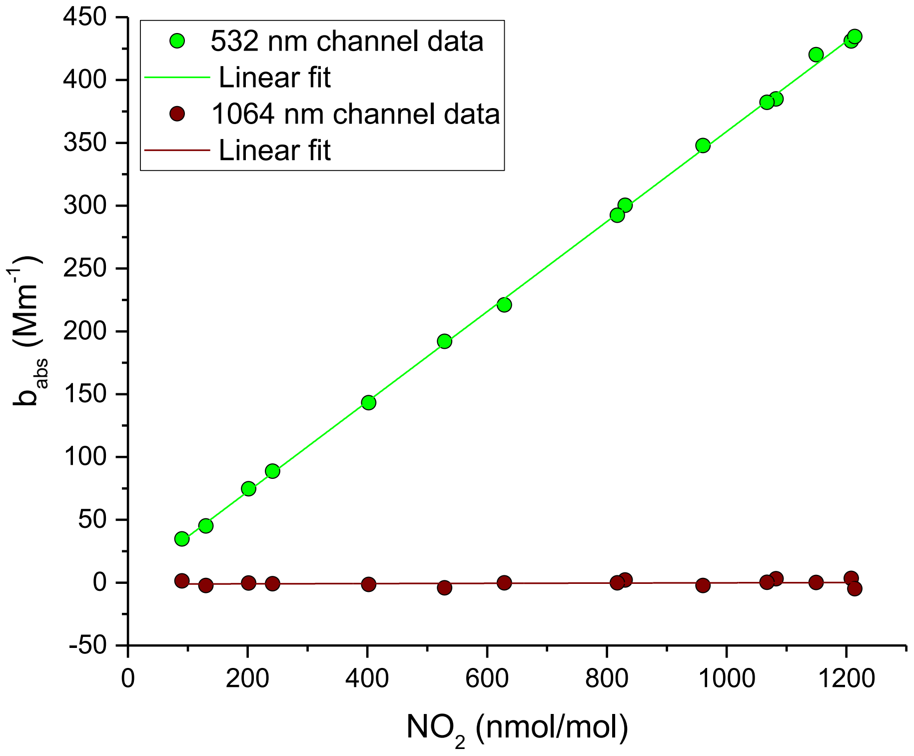


5-6% difference

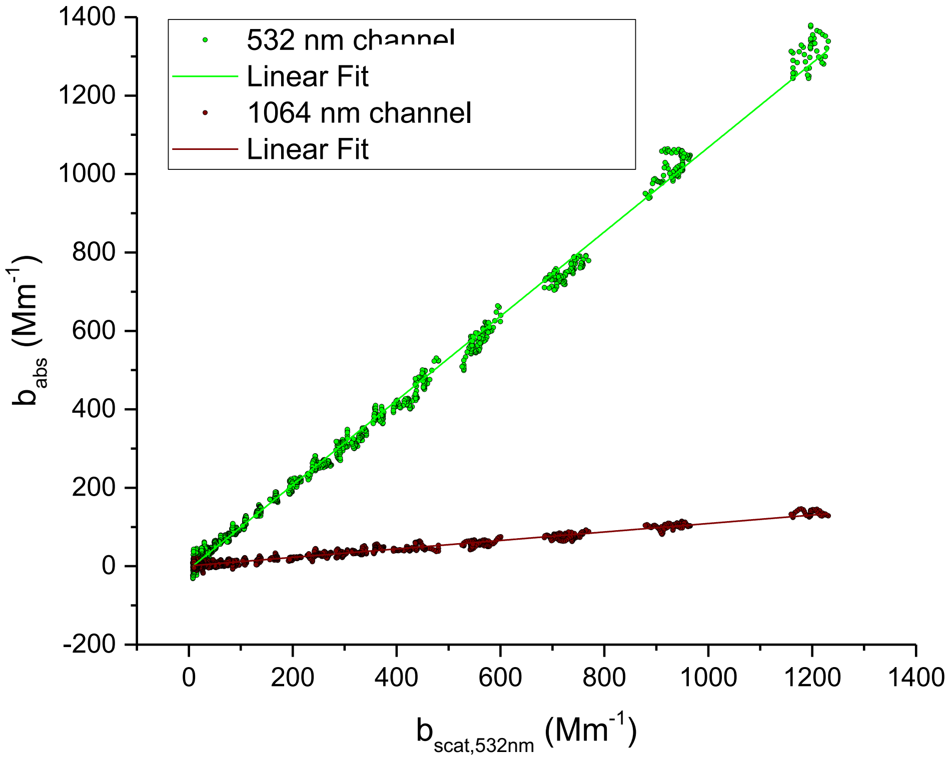
in absorption coeff. between measurement and Mie model

Results – linearity of response

NO_2



Nigrosin



Measurement uncertainty

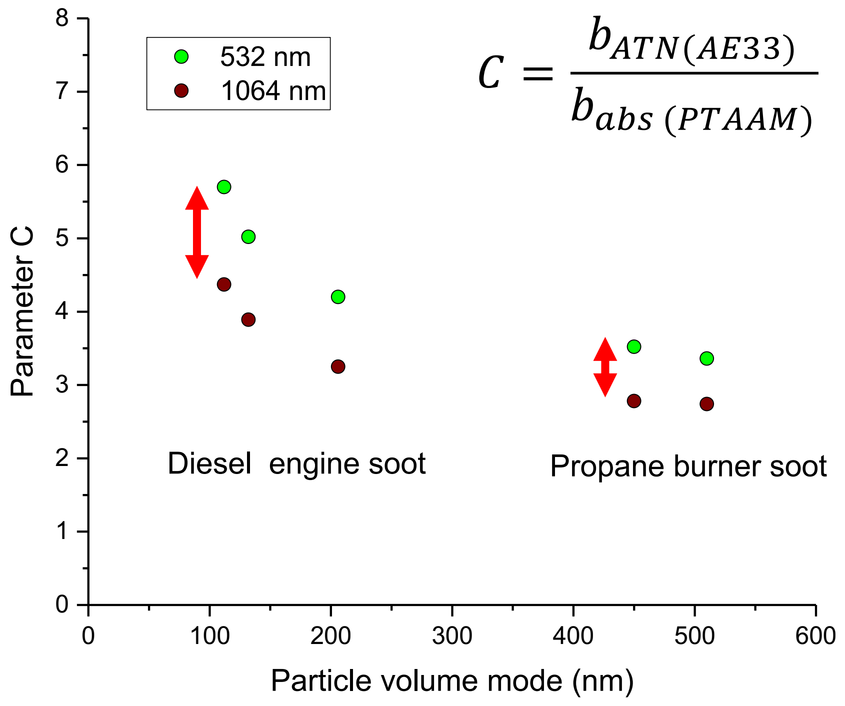
	Sources of uncertainty	Uncertainty	Components
A	NO_2 amount fraction	2%	
B	Nigrosin refractive index	2%	
C	Mie calculation of $b_{abs,1064\ nm}/b_{abs,532\ nm}$	4%	
D	Scattering & absorbing gases	1%	
E	Stability of instrument	3%	
	Combined uncertainties		
	$b_{abs,532nm}$	4%	A, D, E
	$b_{abs,1064nm}$	6%	A, B, C, D, E
	AAE	9%	B, C, D, E, ln

Low measurement uncertainty -> **reference method** for aerosol absorption measurements.

Lab soot – calibration of filter photometers

Campaign	Sample	Volume mode (nm)	Angstrom exp PTAAM (532 nm/1064 nm)	Angstrom exp AE33 (470 nm/950 nm)
Ljubljana	Diesel soot	130	**1.05**	1.31
AEROTOX	CAST soot	160	**0.87**	1.20
Ljubljana	Propane soot	400	**0.86**	1.03

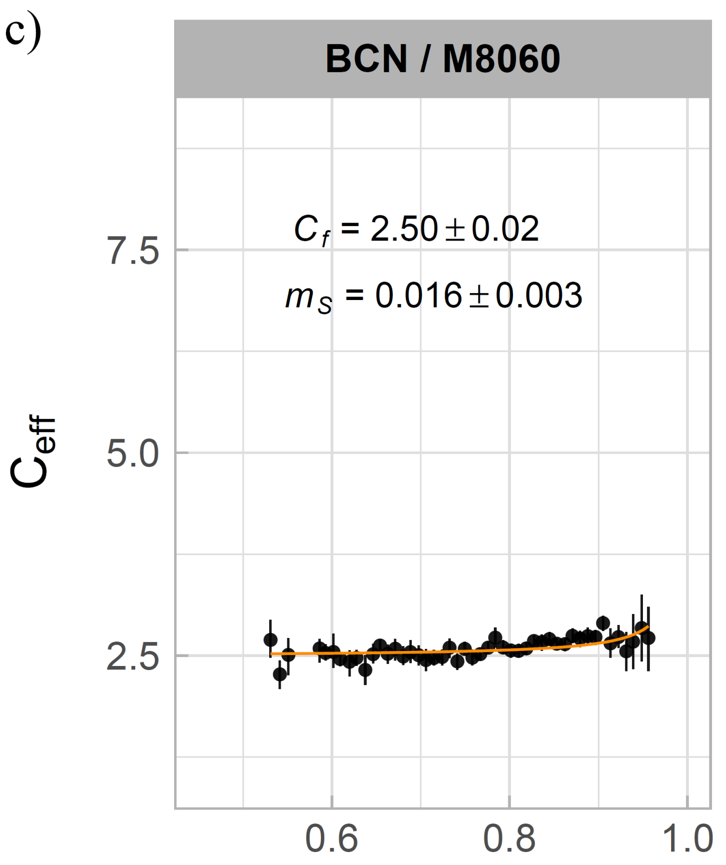
as expected from Mie theory for particles of this size

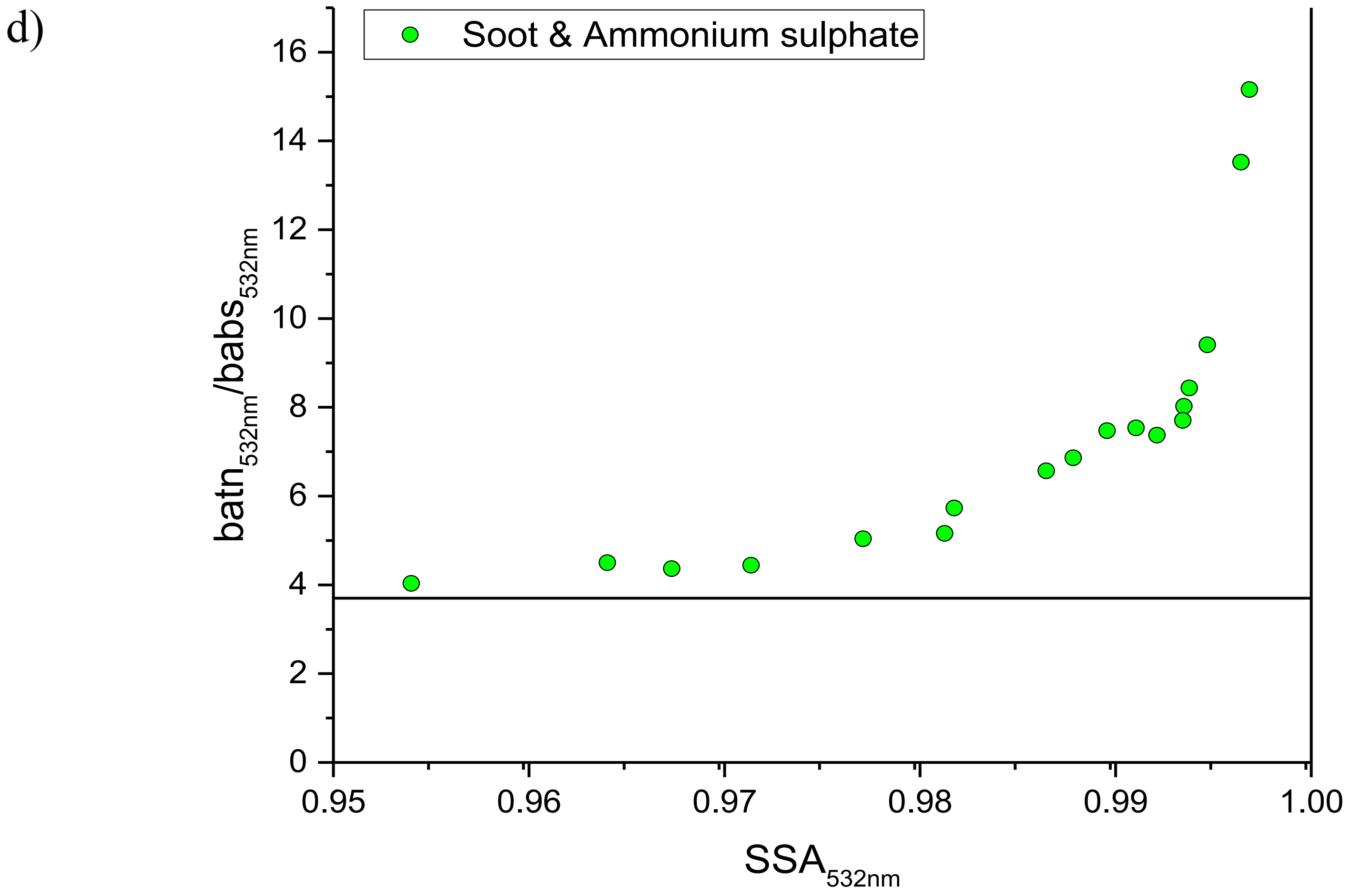


$$C = \frac{b_{ATN(AE33)}}{b_{abs\ (PTAAM)}}$$

- *C* depends on the particle size
- higher *C* at 532 nm compared to 1064 nm
  → higher apparent Angstrom exp. in AE33

Filter photometers – SSA dependence



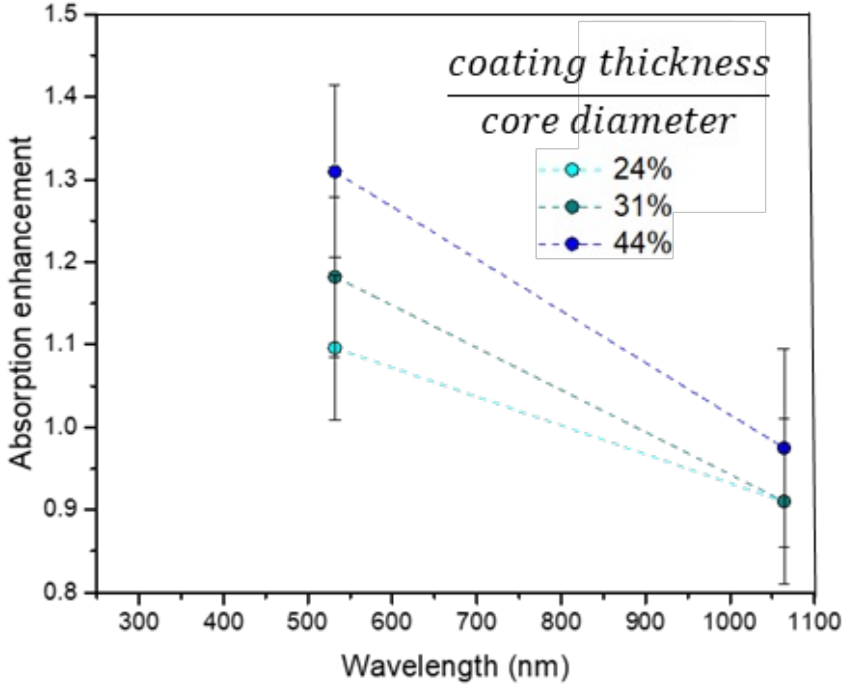


Yus et al., 2021

Drinovec et al., 2022

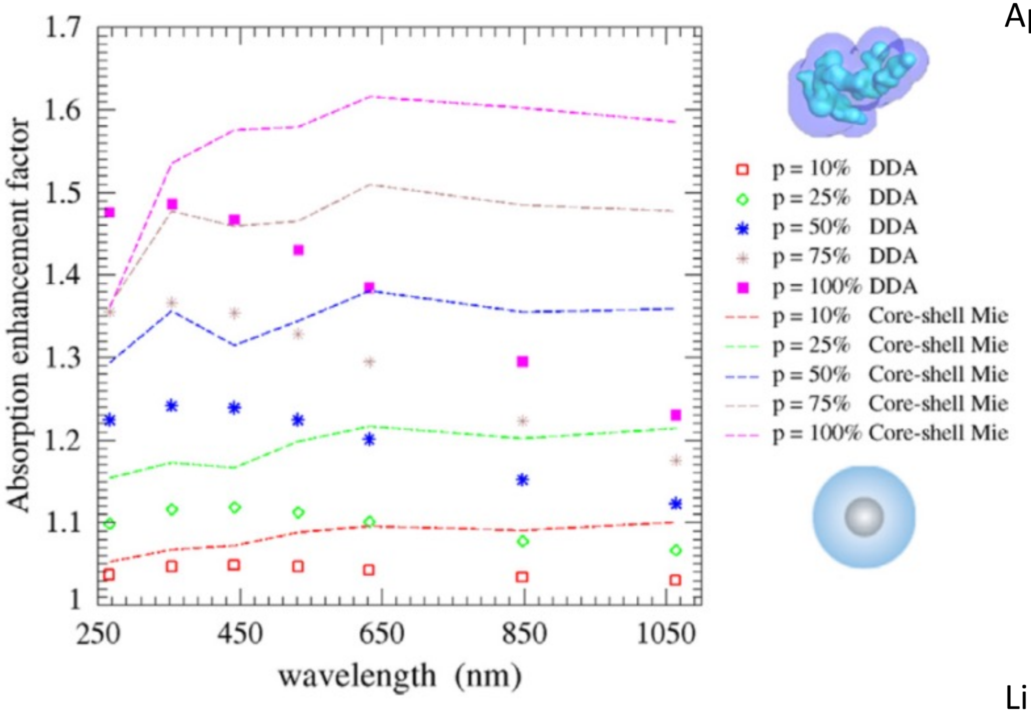
Absorption enhancement by coating

BC particles coated with α-pinene



Kalbermater et al., 2022

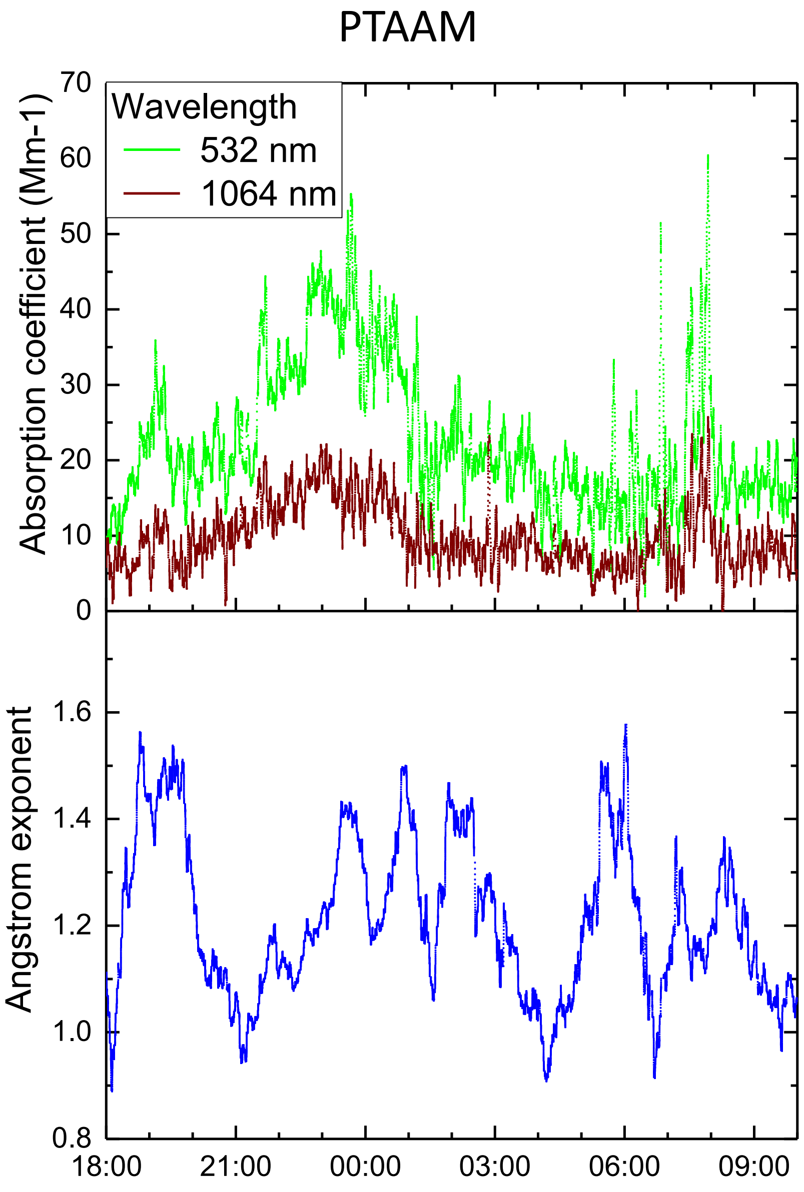
Discrete
Dipole
Approximation

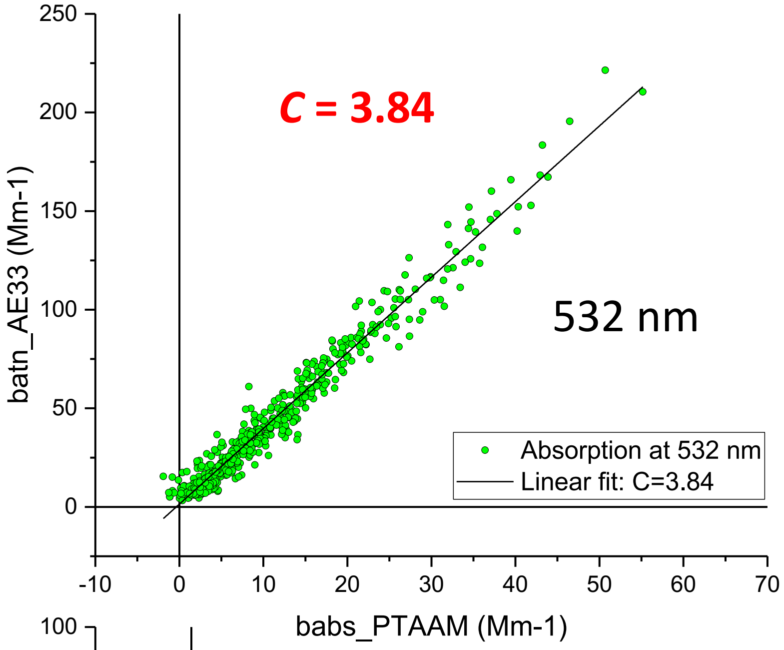


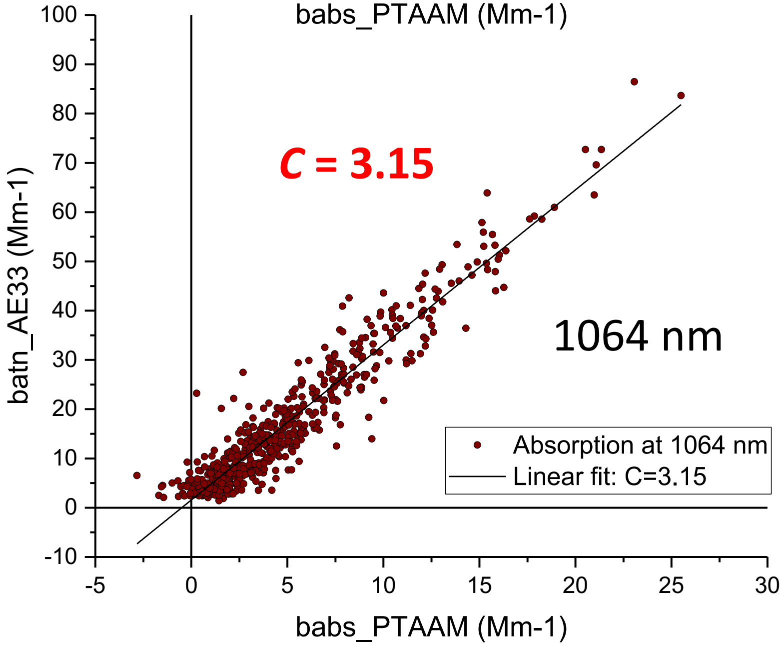
Liu et al., 2016

Models are not adequate for description of absorption enhancement!

Ambient calibration of filter photometers







Conclusions

- **new** photo-thermal aerosol absorption monitor
- **calibrated** to **primary standards**
- **absorption** coefficient at **532 nm** & **1064 nm**
- **linear** response & **no artefacts**
- **low** measurement **uncertainty** -> **reference** instrument for absorption

Thank you!

Questions?

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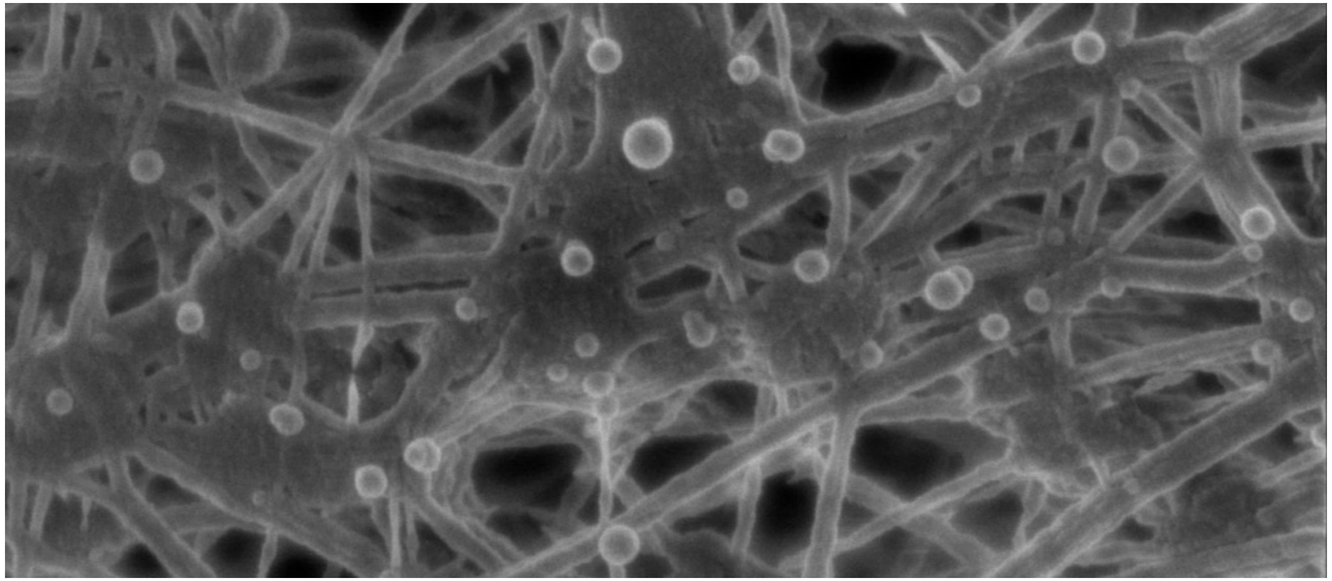

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A note on the **terminology**

- **Black Carbon mass** concentration BC **µgm^{-3}**
  - Optical meas. **equivalent** to mass **eBC** (filter photometers)

  …

- **Aerosol absorption coefficient** b_{abs} **Mm^{-1}**
  - Optical measurements, in-situ, (in)direct

$$\boldsymbol{b_{abs} = BC \cdot MAC}$$

C…c…c…calibration to determine $C \leftrightarrow MAC$!

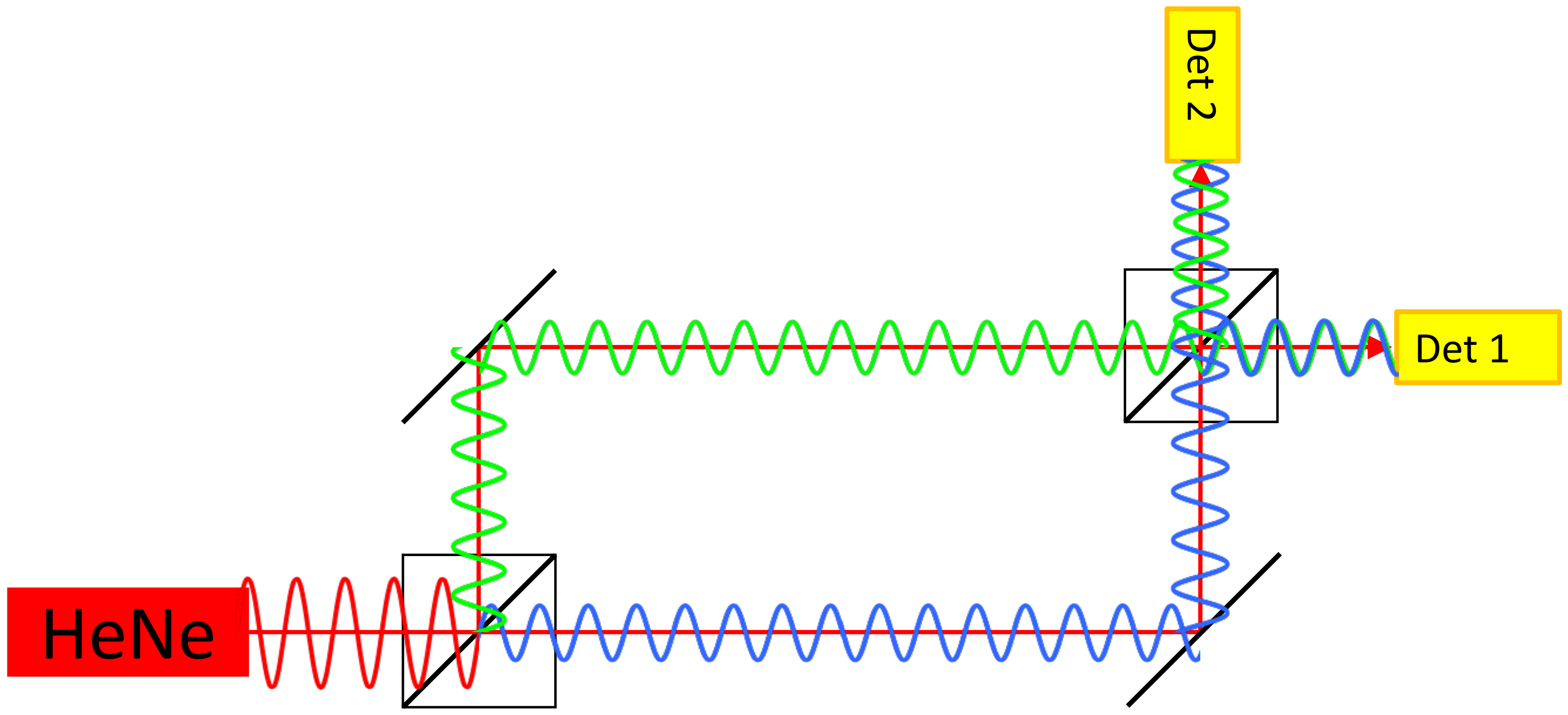
Field: comparison w/ other filter photometers

Aerosol absorption coefficient b_{abs} **Mm**$^{-1}$

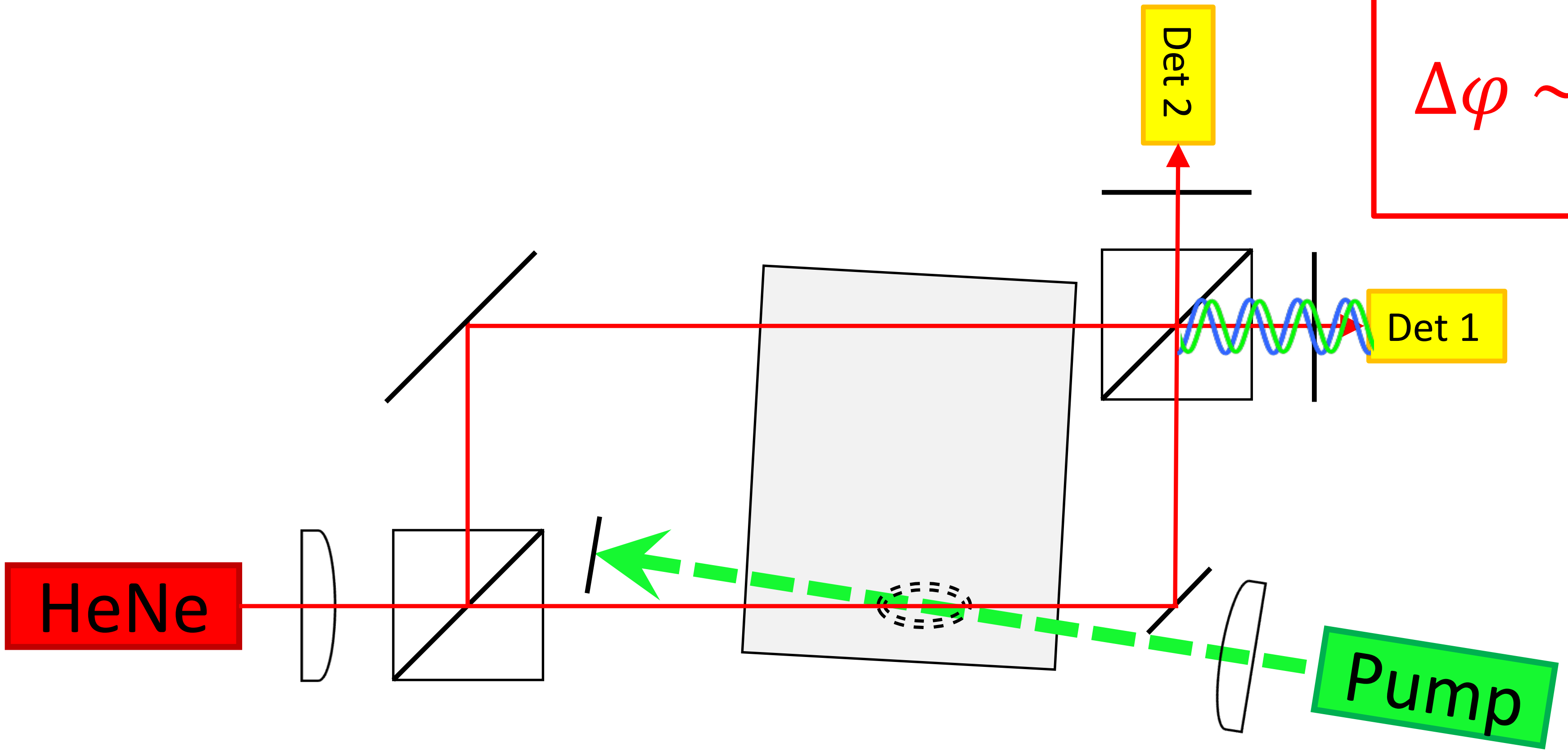
- need reference sample
- need **reference method to measure absorption**

- **Reference methods:**
  - extinction - scattering: low *SSA*
  - photoacoustics: non-coated particles, no VOCs or water
  - **photothermal interferometry**: sensitivity

Mach-Zehnder Interferometer



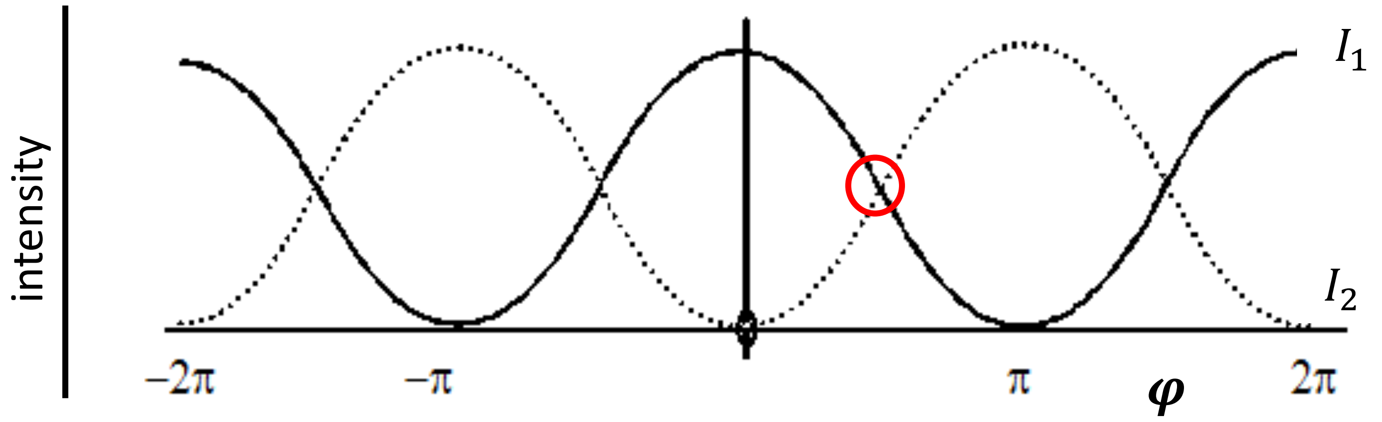
Mach-Zehnder Photothermal Interferometer



$\Delta\varphi \sim b_{abs}$

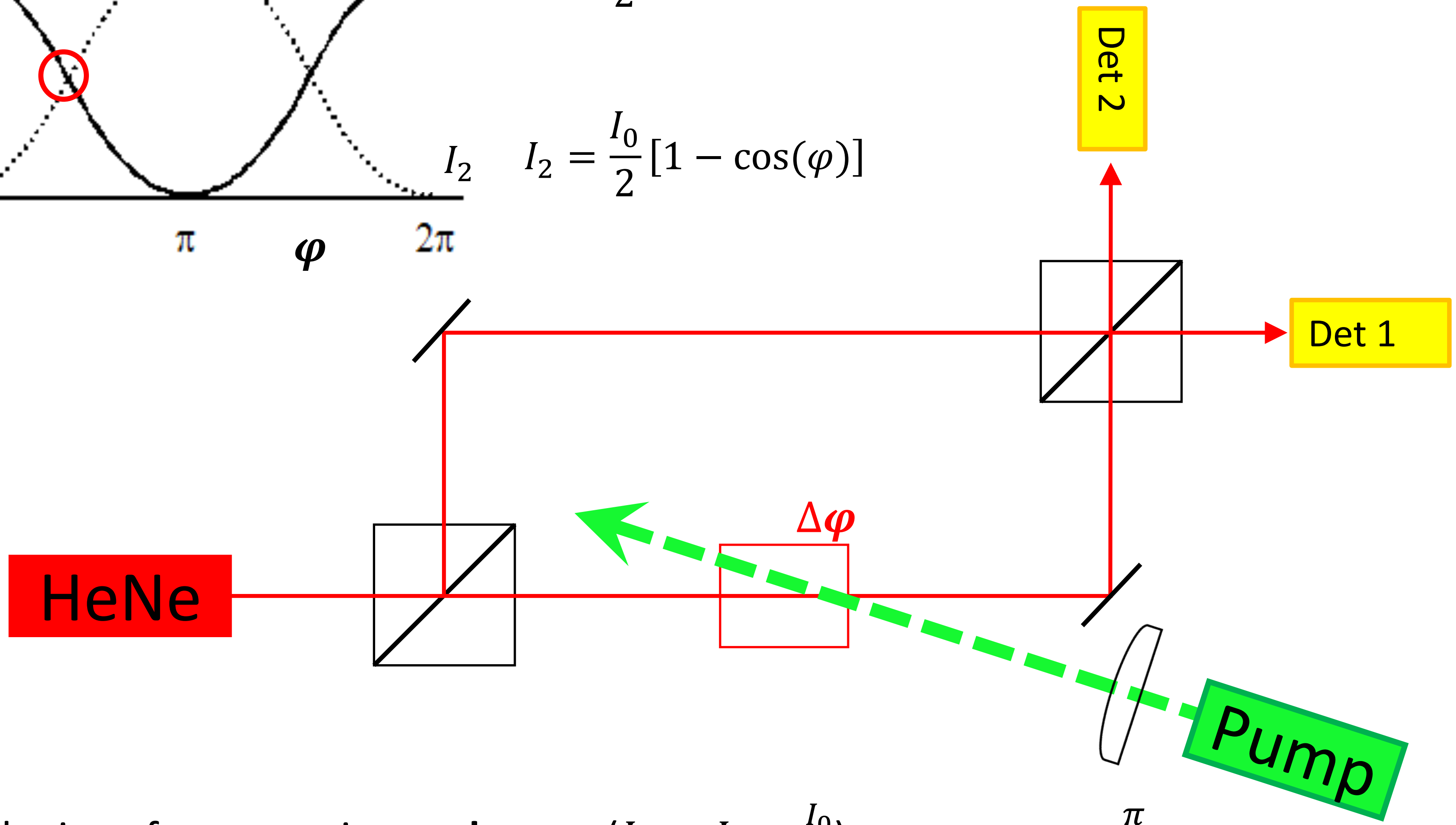
Courtesy of: E. Weingartner

Quadrature Point



$$I_1 = \frac{I_0}{2}[1 + \cos(\varphi)]$$

$$I_2 = \frac{I_0}{2}[1 - \cos(\varphi)]$$



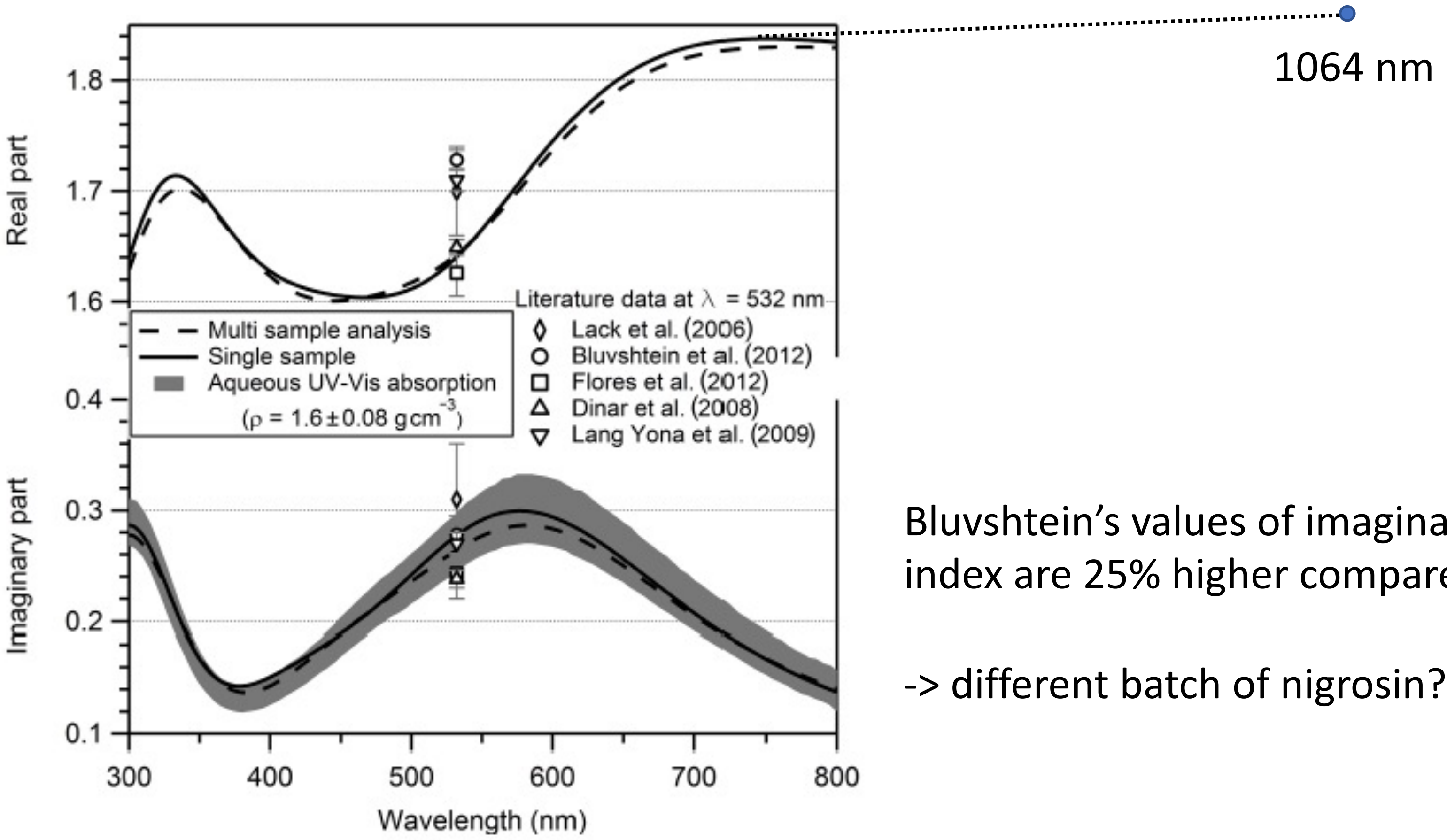
Highest **sensitivity** in φ change – the interferometer in **quadrature** ($I_1 = I_2 = \frac{I_0}{2}$), e.g. at $\varphi_o = \frac{\pi}{2}$.

$\rightarrow$ *φ change* $\Delta\varphi = \varphi - \varphi_o = \frac{\Delta I}{I_o} = \frac{I_1 - I_2}{I_1 + I_2}$

Real part of the refractive index

- Real part for the UV-VIS region is taken from Bluvshtein et al. (2017)
- Near infrared value was determined by Brewster angle measurement:

  n (1064 nm) = 1.848 ± 0.005



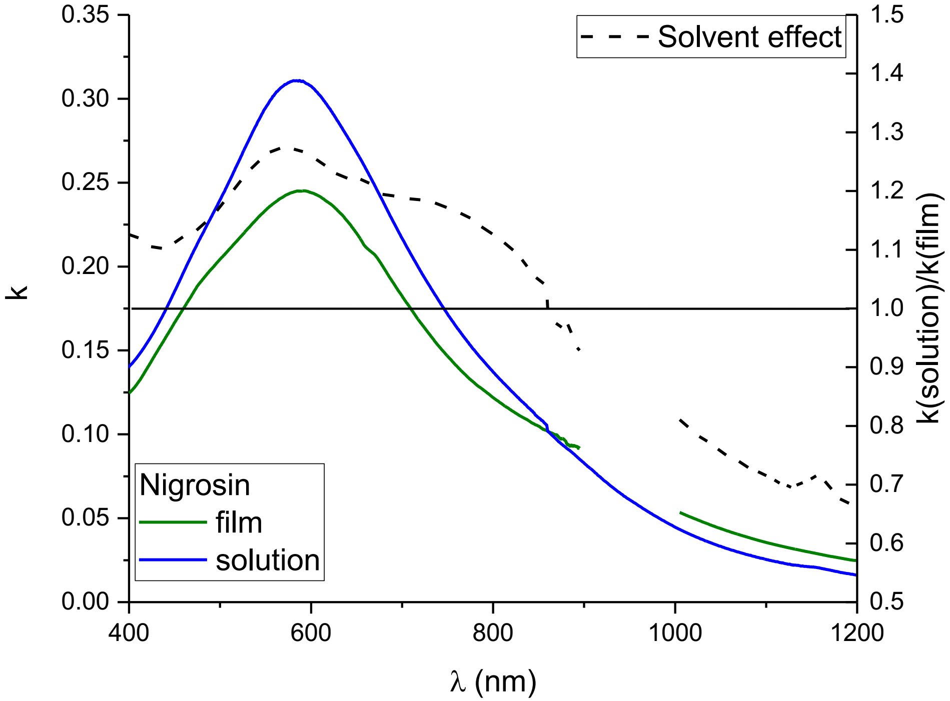
Bluvshtein's values of imaginary part of the refractive index are 25% higher compared to our data

-> different batch of nigrosin?

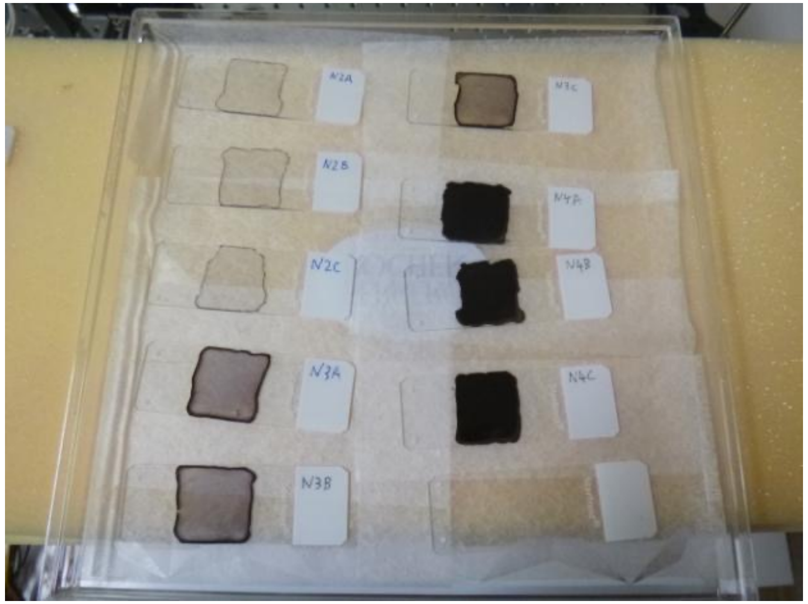
Nigrosin refractive index determination

Comparison of aquaous solution of nigrosin and thin film:

- solvent effect: +/-25%



Nigrosin film samples

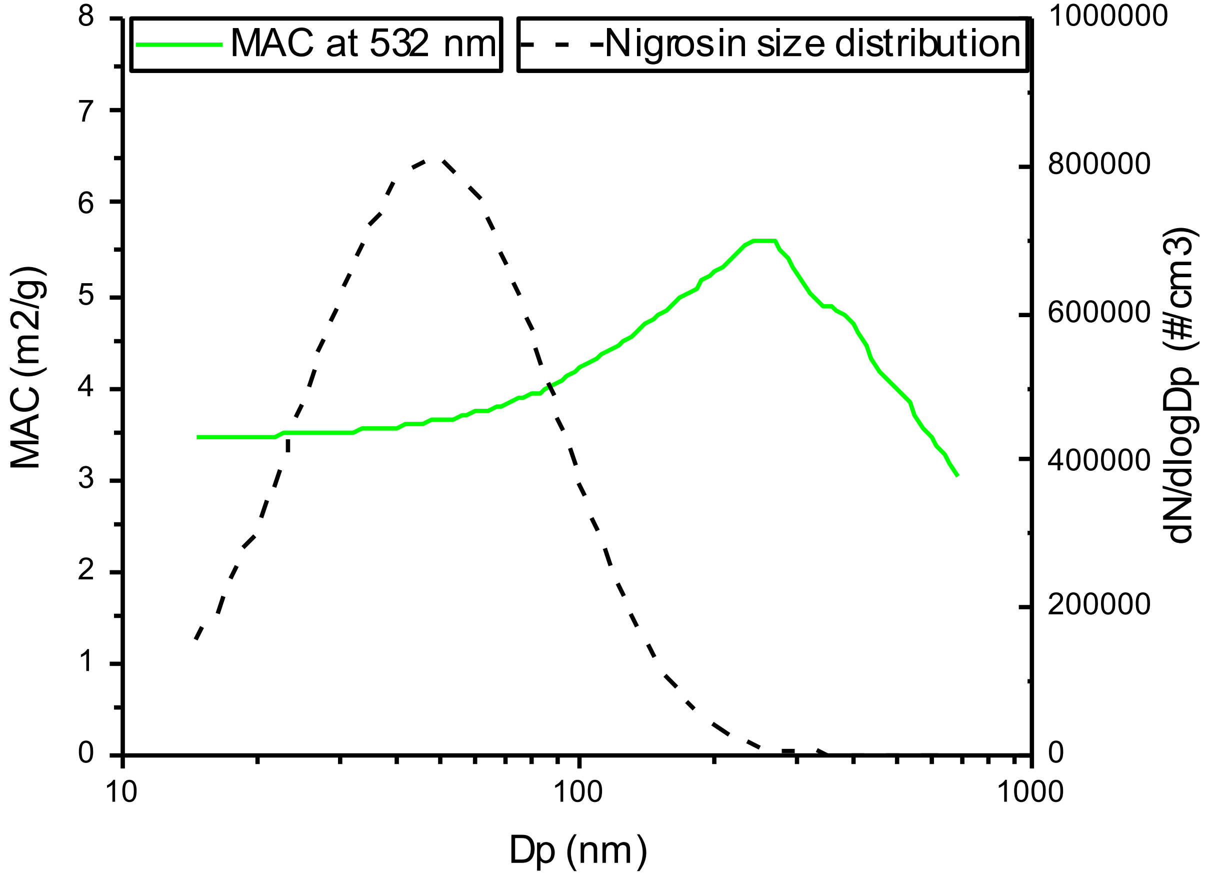


n(532 nm) = 1.62 + 0.223i

n(1064 nm) = 1.73 + 0.0419i

Mie calculation

- Nigrosin aerosolisation using Topas ATM 226
- Particle size spectra measurements with SMPS
- Calculation of absorption using Mie routines in Mathlab



MAC is stable for particles generated with 0.1 g/l nigrosin solution

babs(1064 nm)/babs(532 nm) ≈ 0.075