University of
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stanBC

Measurement of light absorption coefficient – reference methods, standardization and calibration

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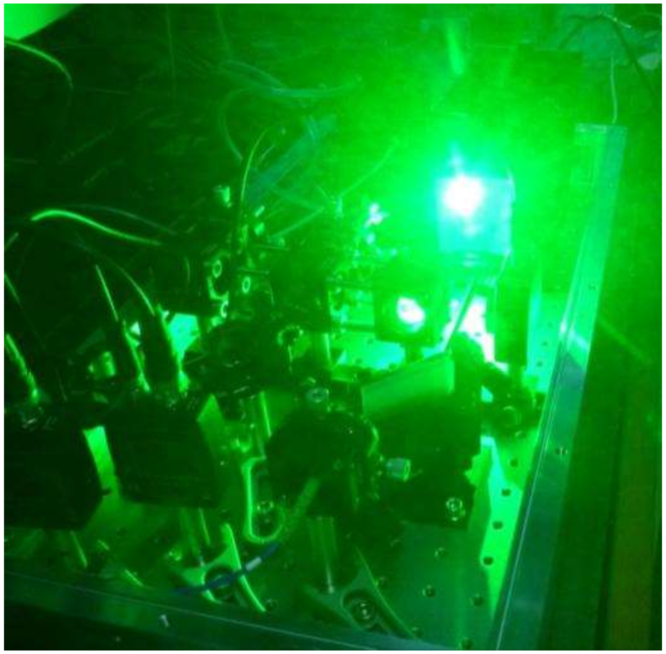
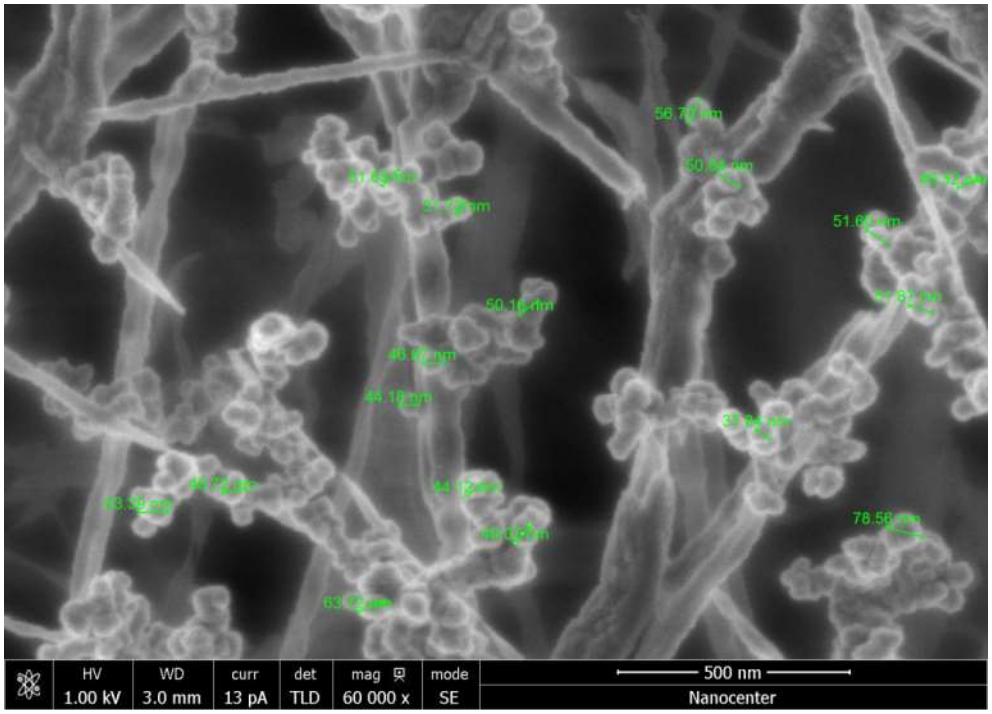


WeBaSOOP2004, Training School on Black and Brown carbon, 3 Apr 2024, online

Aerosol absorption measurements



Particles on filter:

- High particle concentration -> high sensitivity
- Filter-particle interaction -> artefacts

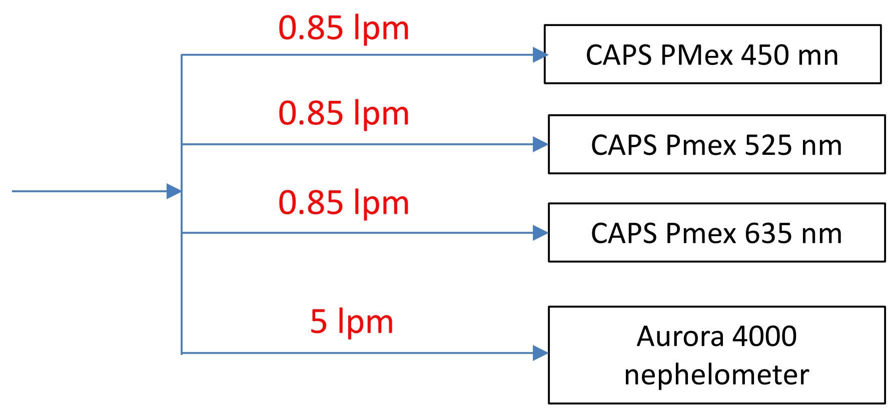
In-situ measurements -> low particle number

Example:

• BC=1 µg/m3 -> 2500 particles/cm3

In-situ methods: Extinction-minus-scattering (EMS)

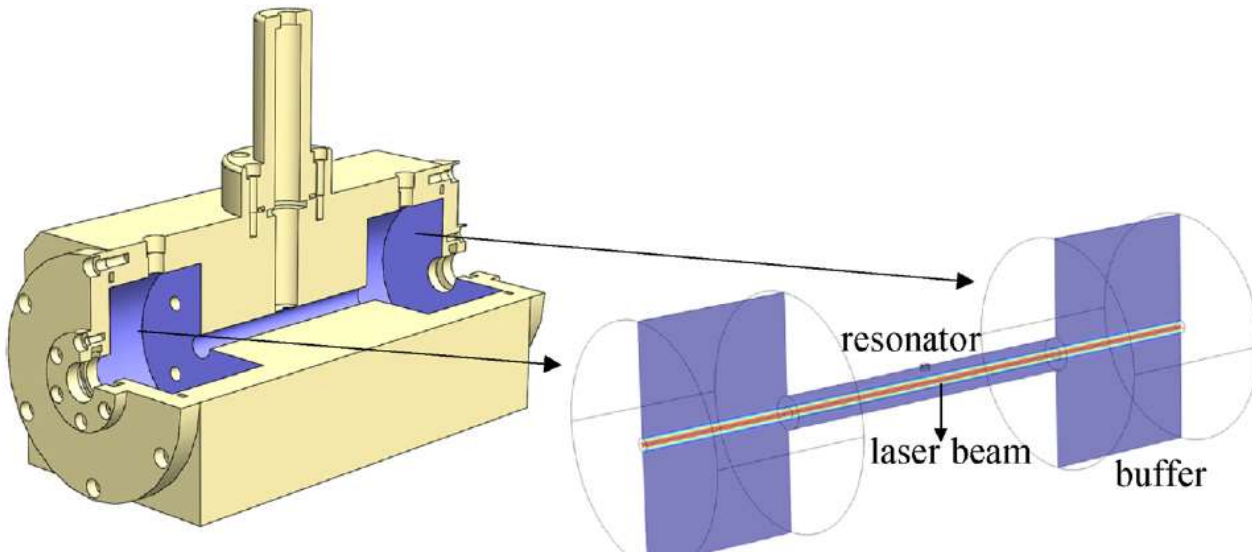
$b_{abs} = b_{ext} - b_{scat}$



Method

- Extinction – cavity ring-down spectroscopy
- Scattering - truncation correction needed
- High sample flow
- Uncertain at high single scattering albedo

Photo-acoustic spectroscopy



Measurement principle

-> light absorption on particles

-> change of air temperature

-> sound-wave formation

-> sound amplification in the acoustic resonantor

-> mikrophone

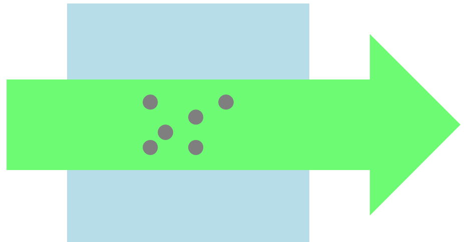
Properties

-> high sensitivity

-> sensitive to evaporation of VOC

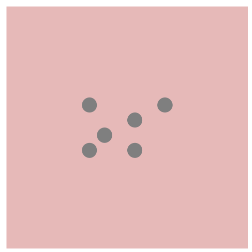
Photo-thermal interferometry

Particle absorb light



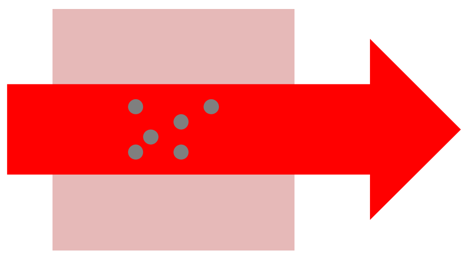
Pump beam intensity: I=1 W/mm^2
Particle temperature: ΔT=3.3 K

Heat transfered to gas



Particle number: 2500 cm^{-3}
Air temperature: $\Delta T=4.2*10^{-5}$ K
Refractive index: $\Delta n=4.7*10^{-11}$

Measurement of interferometer phase change



Light path length: $\Delta s=4.7*10^{-14}$ m
Interferometer phase: $d\phi$=0.15 µRad

Phase change is proportionl to absorption!!

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

Instrument: PTAAM-2λ

- **P**hoto-**T**hermal **A**erosol **A**bsorption **M**onitor
- Interferometer on work from Moosmuller, Arnott, Sedlacek and Visser
- Pump beam focused by **axicon** (patent EP 3492905)
- Simultaneous measurements at **532 and 1064 nm**

•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. Discuss., amt-2020-242

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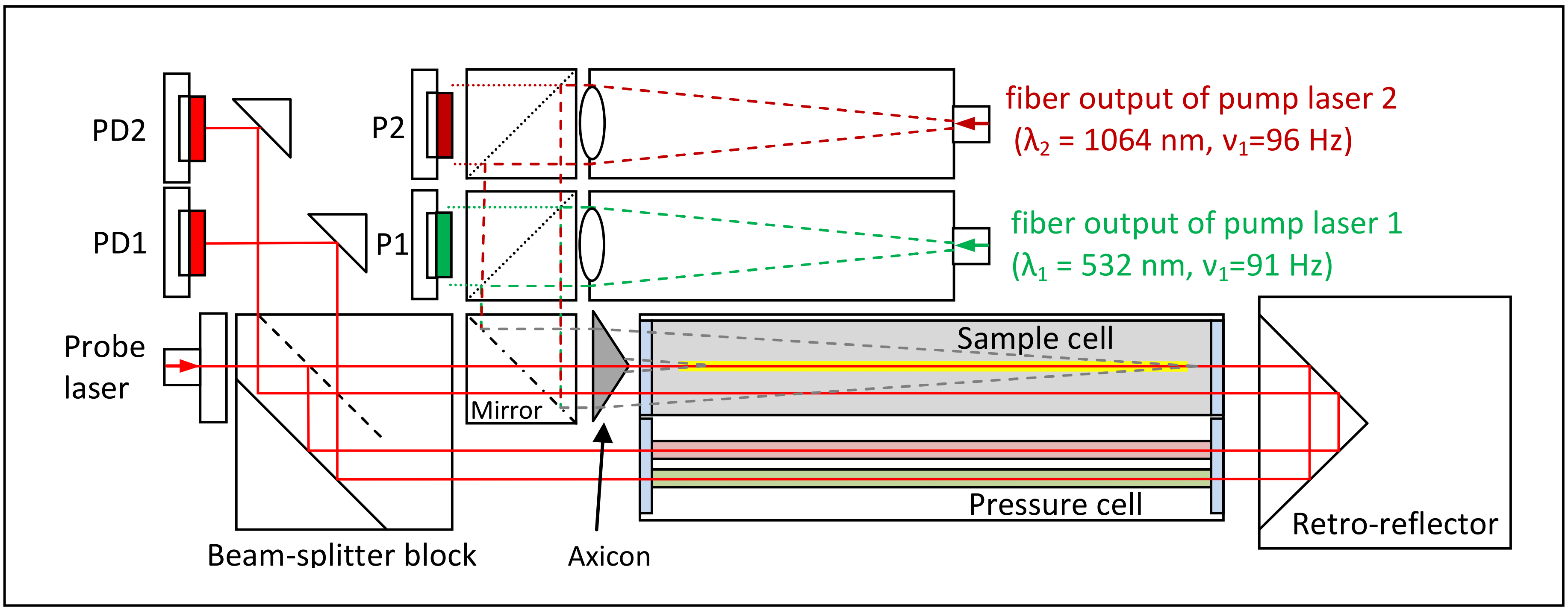

Article

Atmospheric Measurement Techniques

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Abstract | Discussion | Metrics

22 Feb 2022

Review status: this preprint is currently under review for the journal AMT.

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

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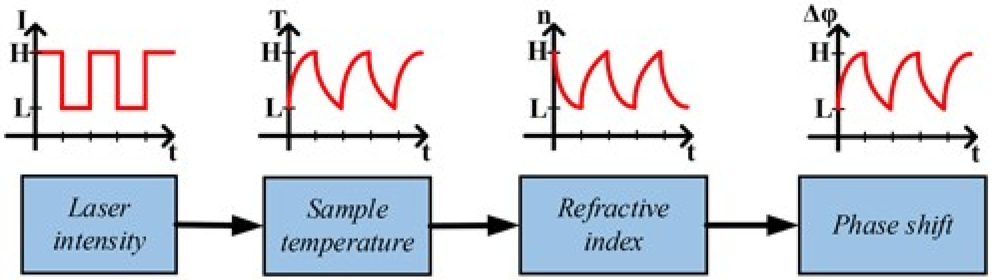
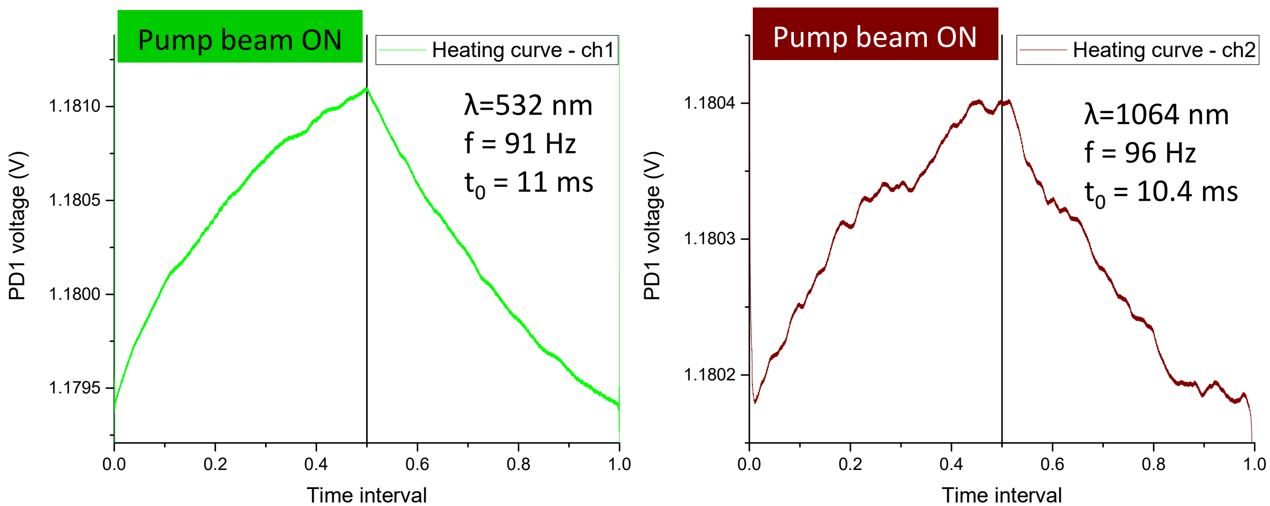
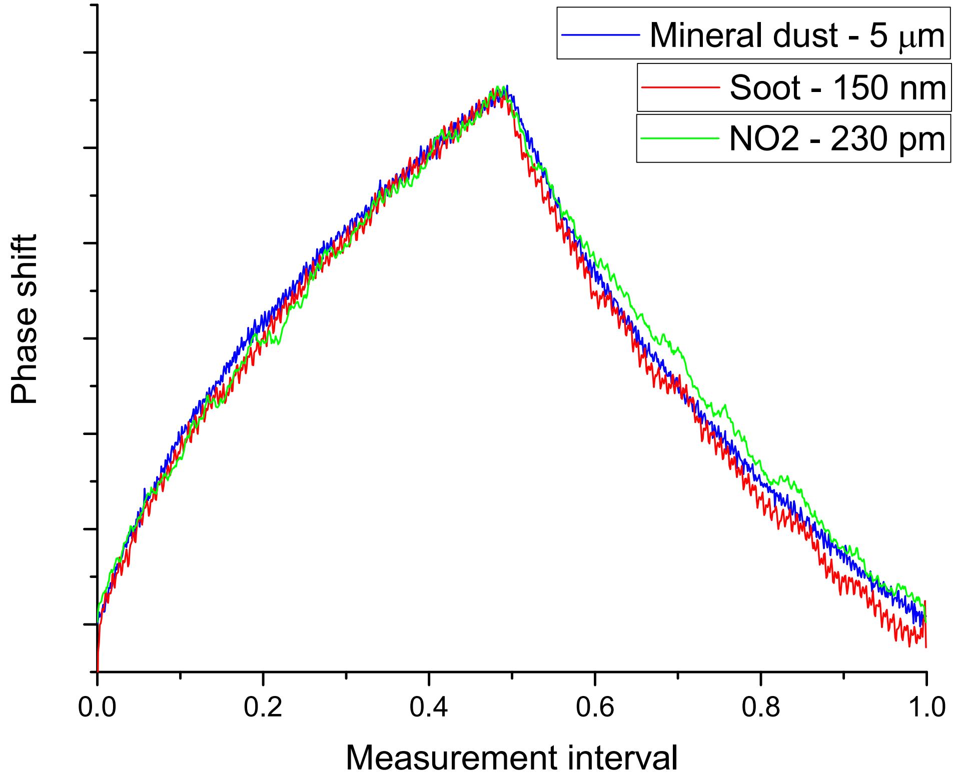
Photo-thermal signal





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

Photo-thermal signal – particle size independence



From molecules to stones - signal shape does not depend on particle size
-> NO2 can be used for calibration

532 nm channel calibration

Instrument response denpends on:

- Pump beam intensity
- Overlap between pump and probe beams

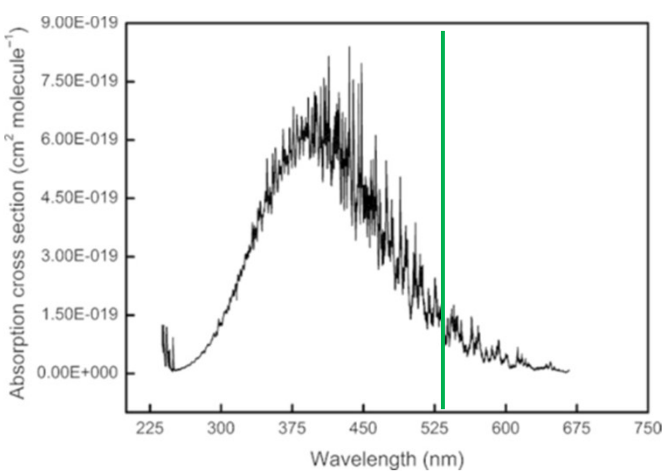
-> instrument must be calibrated

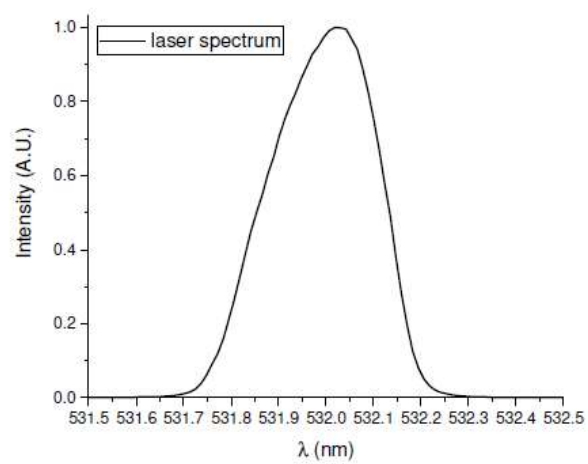
532 nm channel calibration:

- Using absorbing gasses: NO_2
- Absorption cross-section = 1.47*10E-19 cm^2
- High uncertainty of NO_2 concentration in cilinders with NO_2 in sub ppm range -> use permeator

Calibration gas cylinder

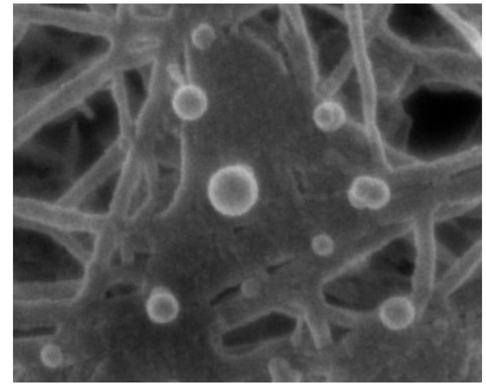
Permeation NO_2 generator



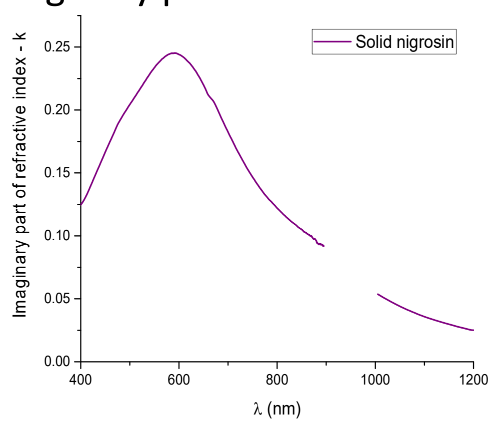


IR nm channel calibration

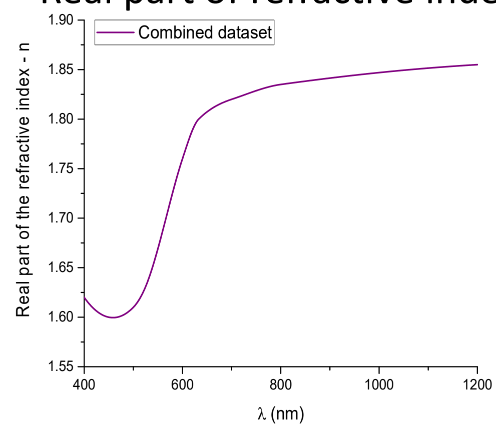
- lack of absorbing gasses in near-infra-red region
- calibration done with nigrosin particles
  - absorbtion in VIS and IR
  - water soluble pigment -> forms nice spherical particles



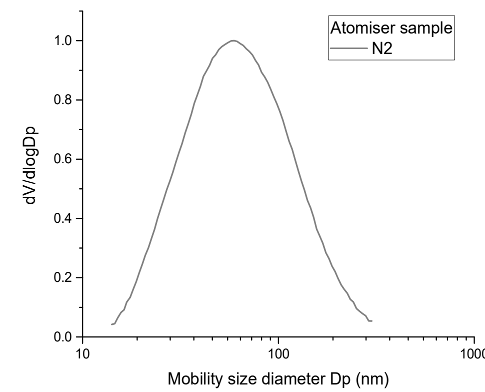
Imaginary part of refractive index



Real part of refractive index



Aerosol size spectra



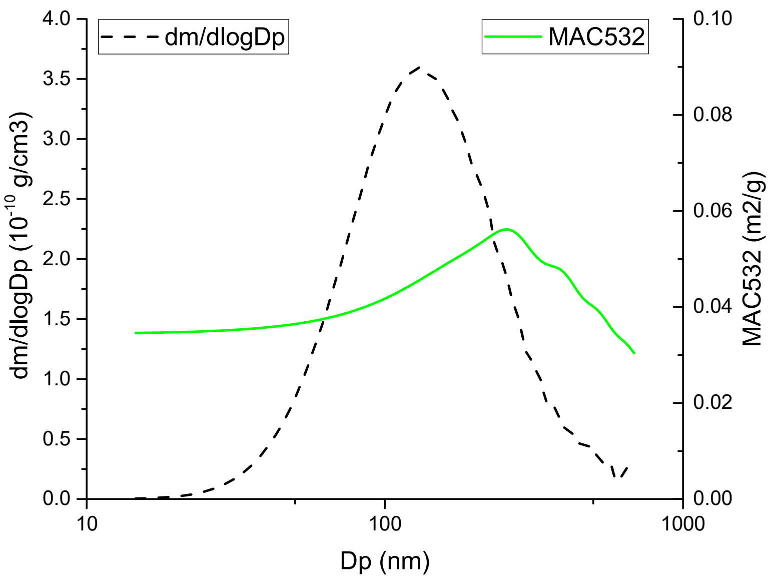
Mie theory

Absorption coefficient

Clculation of polydisperse nigrosin absorption

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

(Mätzler C., IAP RP No. 2002-08, 2002)



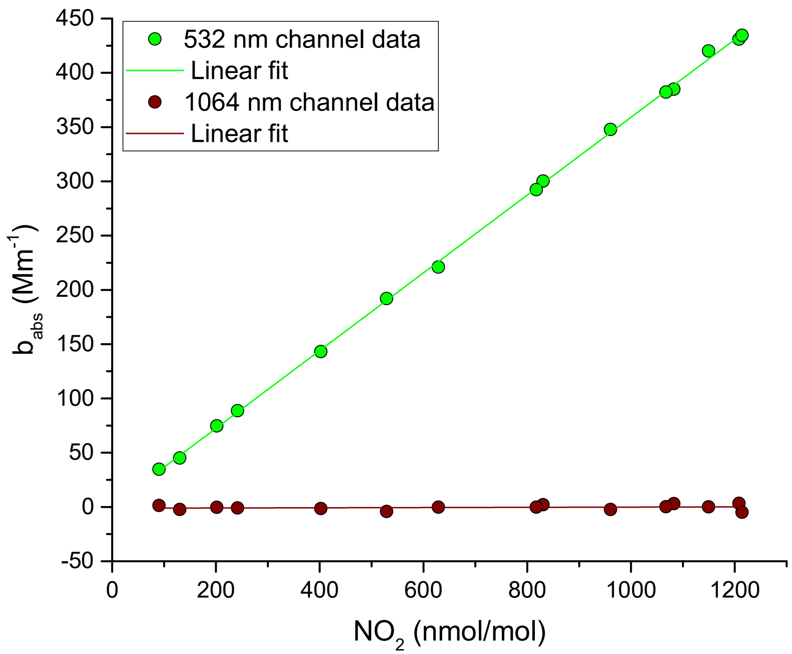
Absorption coefficient

babs(1064 nm)/babs(532 nm) ≈ 0.075

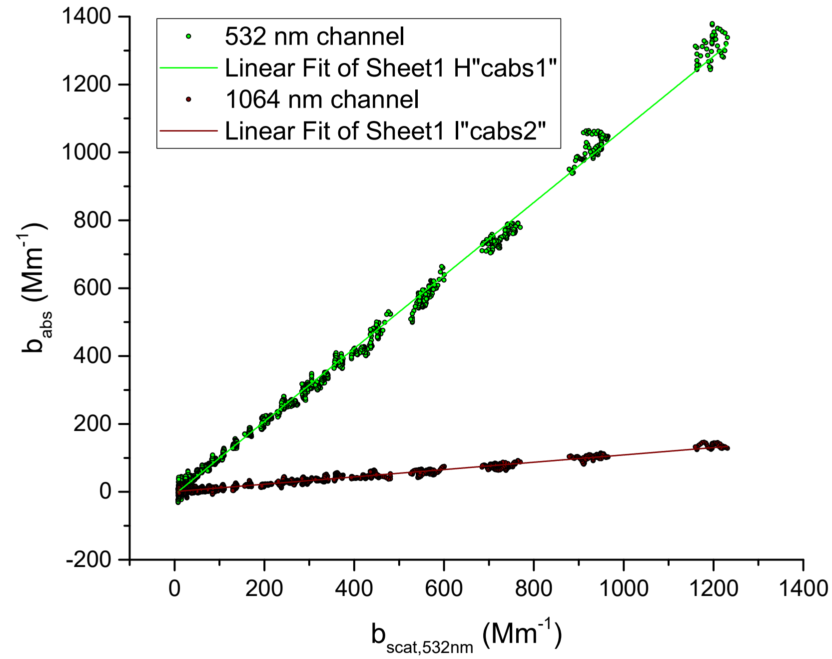
babs(808 nm)/babs(450 nm) ≈ 0.334

Results – linearity of response

NO_2



Nigrosin

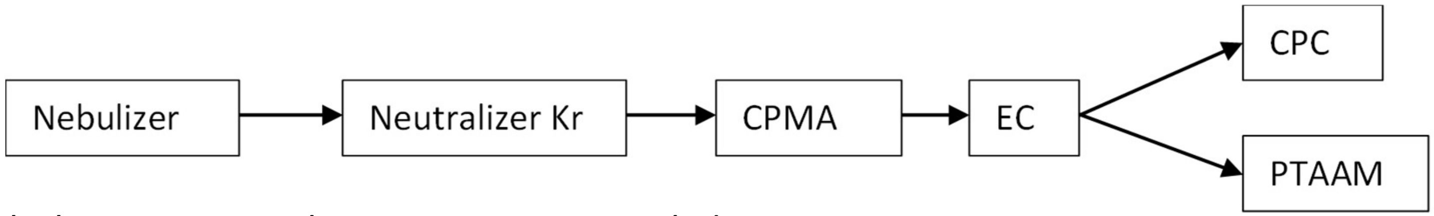


Measurement uncertainty

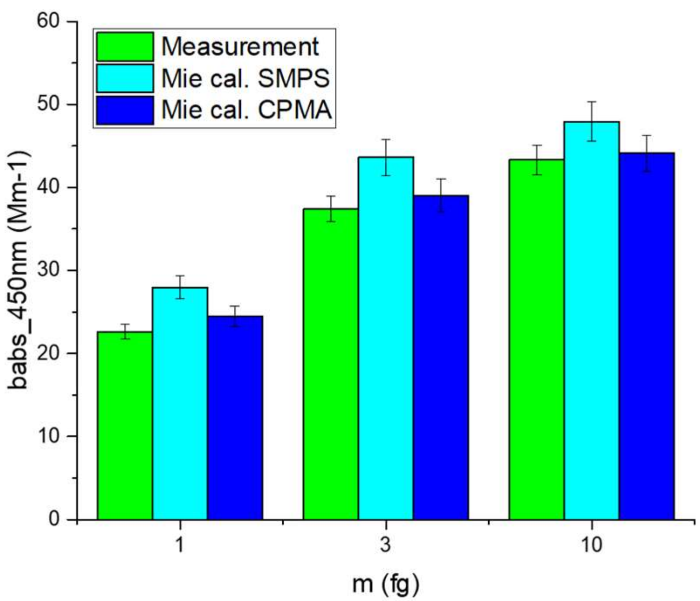
	Sources of uncertainty	Uncertainty	Components
A	NO_2 amount fraction	2%	
B	Nigrosin refractive index	3%	
C	Mie calculation of $b_{abs,1064\ nm}/b_{abs,532\ nm}$	4%	
D	Scattering & absorbing gases	1%	
E	Stability of instrument	3%	
	Combined uncertainties		
	$b_{abs,532nm}$	4%	A, D, E
	$b_{abs,1064nm}$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

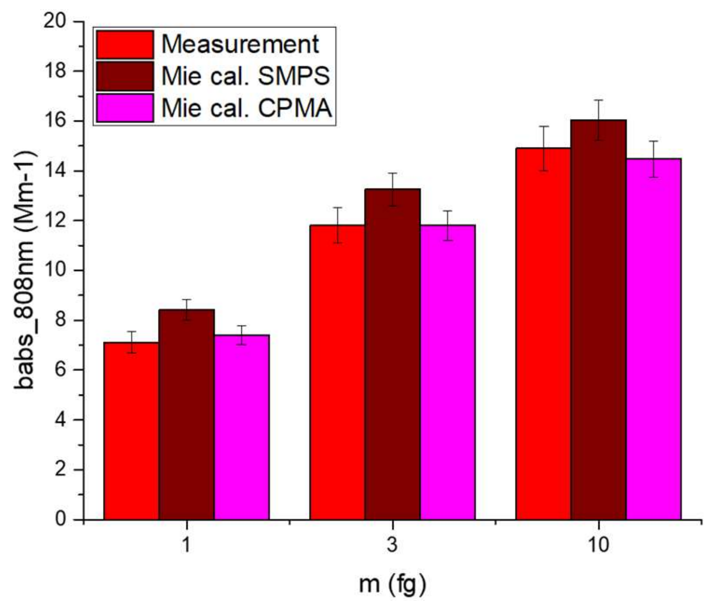
Low measurement uncertainty -> reference method for aerosol absorption measurements

Validation with monodisperse nigrosin



1. Nebulise nigrosin solution -> generate polydisperse nigrosin
2. Charge particles
3. Size select particles with CPMA (neutral & multiple charged particles present)
4. Remove unwanted particles with Electrostatic classifier (EC (or DMA))
5. Measure particle number and absorption coefficient
6. Calculate absorption using Mie theory – based on measured particle mass or diameter

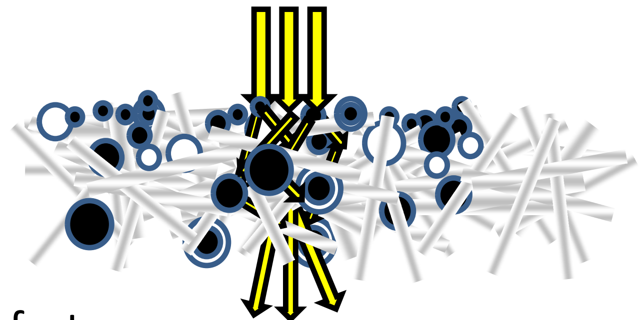




stanBC project – standardization of BC measurements using filter photometers

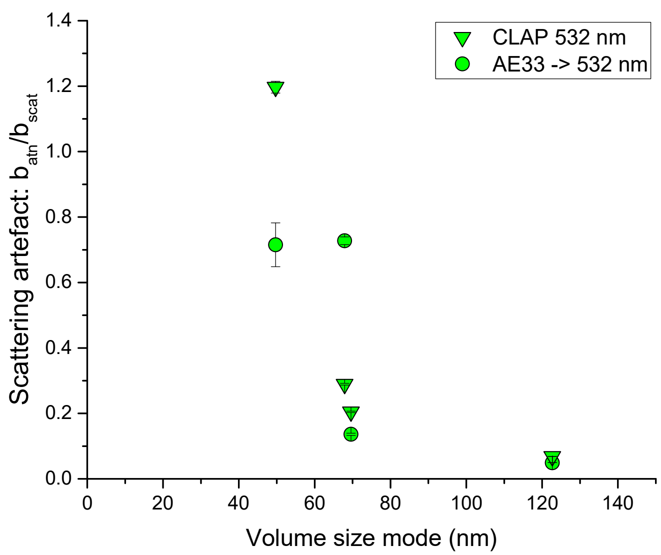
stanBC

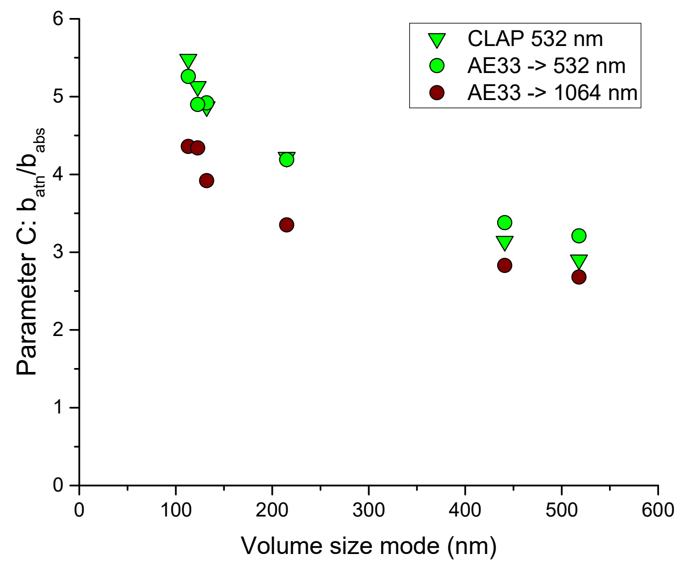
Absorption reference: Photothermal interferometry and extinction-minus-scattering
Transfer standard: photoacoustic spectrometer PAX
Characterized instruments: filter photometers



$$BC = \frac{b_{atn}}{C * MAC_{BC}}$$

b_{atn} – attenuation coefficient – influenced by scattering artefact
C – multiple scattering parameter – depend on particle size
MAC – mass absorption cross-section

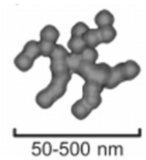


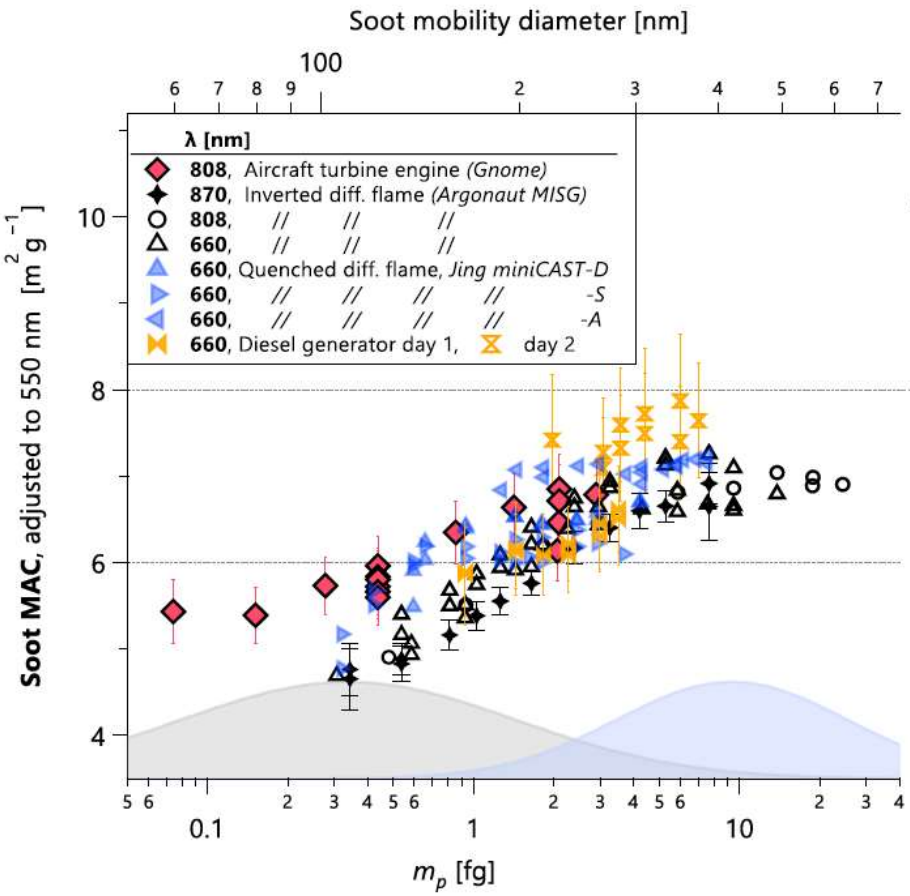


MAC variability

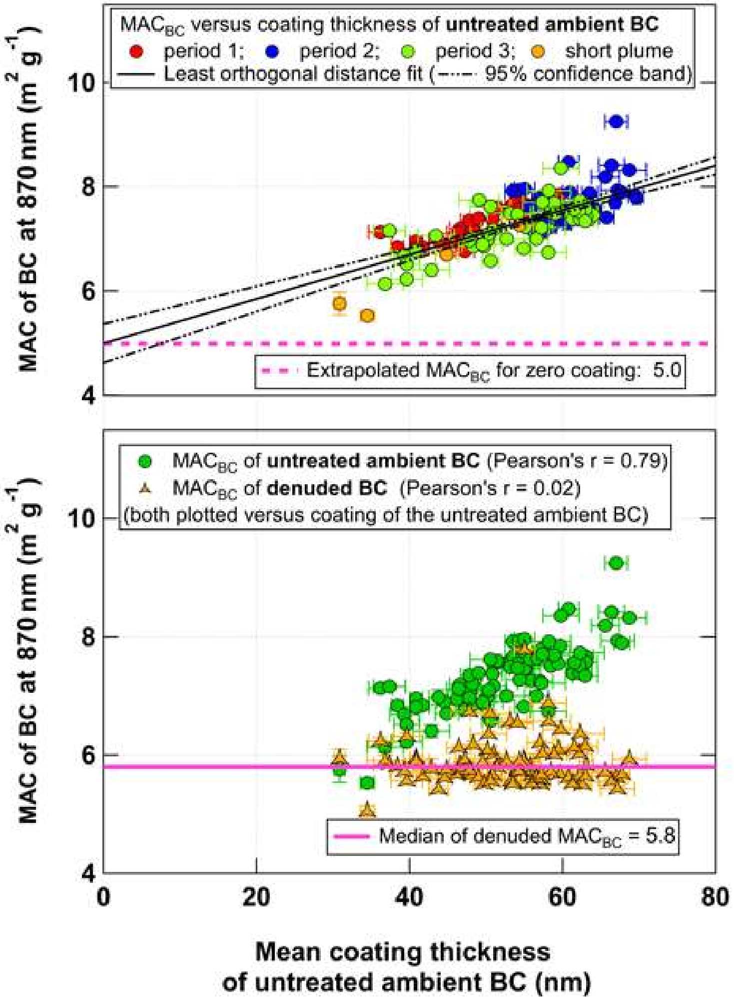
Yuan et al., 2021

- particle size
- structure
- coating



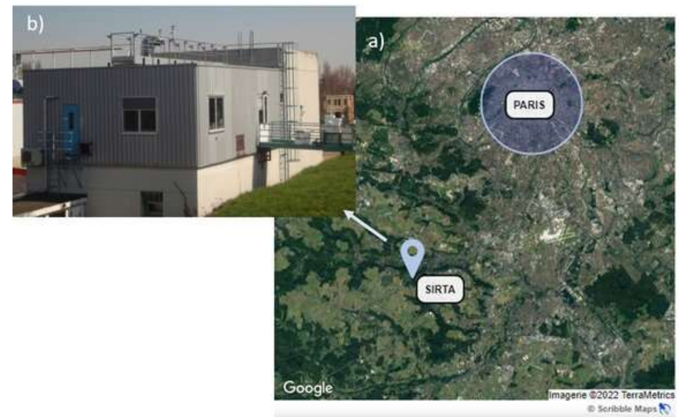


Corbin et al., 2022



Coating-dependent ambient black carbon mass absorption cross-section using direct aerosol absorption measurements with PTAAM-2λ and different mass metrics

EAC
2023
MALAGA
SPAIN
3-8 SEPTEMBER

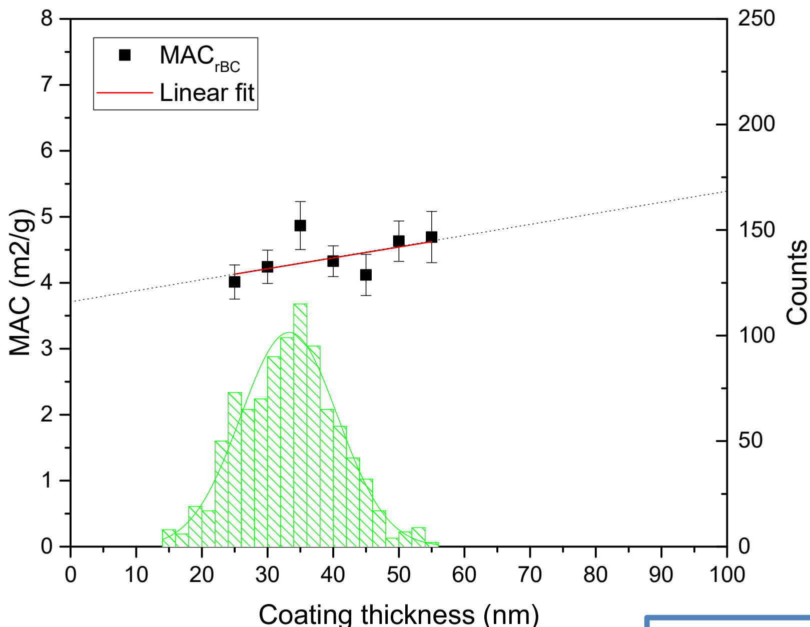


	Angstrom exp. PTAAM	EC (µg/m3)	EC/OC	SSA
Ljubljana	1.30	1.49	0.16	0.86
Deskle	1.31	1.05	0.19	
Sirta - March	1.21	0.646	0.17	0.91

Results – absorption enhancement E

	MAC_{EC}(1064 nm) (m2/g)	EC (µg/m3)	E
Ljubljana	6.06	1.49	2.1
Deskle	4.70	1.05	1.6
Sirta - March	3.17	0.646	1.1

Sirta – SP2 measurements



- Average coating thickness=33 nm
- E=1.1
- use MAC_{EC} to calculate E in Ljubljana and Deskle

- Highest absorption enhancement E in Ljubljana
- high E concurrent with high EC

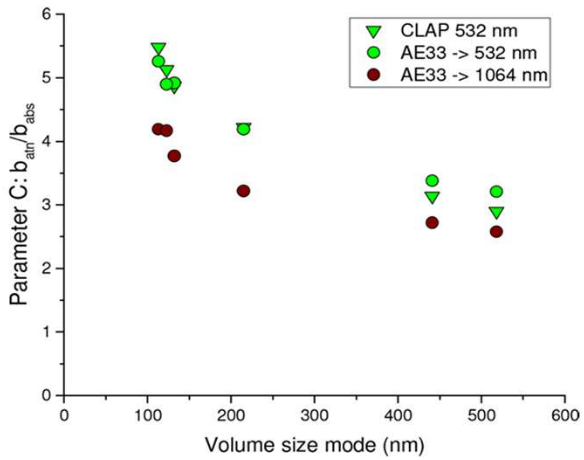
Results – BC/EC

$$BC = \frac{b_{atn}}{C * MAC_{BC}}$$

Filter photometers – AE33:
b_{atn}: attenuation coefficient
C: multiple scattering parameter: fixed value
MAC_{BC}: fixed value

Drinovec et al., 2022

	MAC_{EC} @1064 nm (m2/g)	C_{1064nm}	BC/EC
Ljubljana	6.06	3.25	2.16
Deskle	4.70	3.32	1.72
Sirta - March	3.17	4.33	1.49



- coated particles are bigger and have lower C value
- higher MAC due to coating coincides with lower C

-> resulting variation of BC/EC is lower than variation of MAC_{EC}

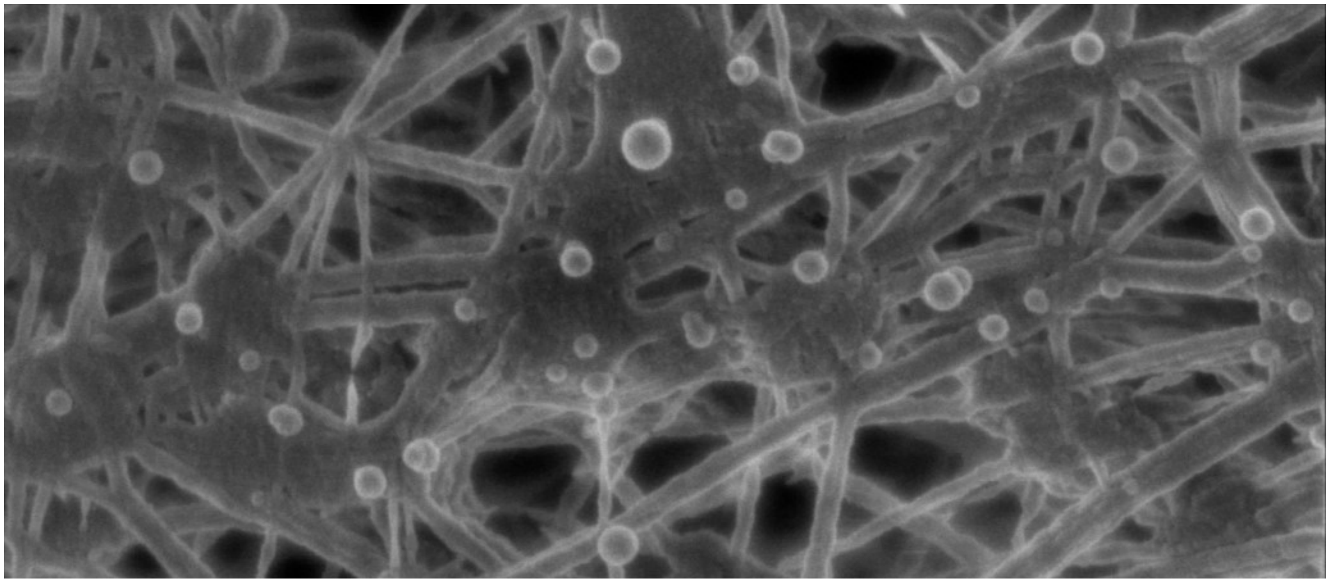
Conclusions

Filter photometer signal is sensitive to scattering and particles size

- high uncertainty for absorption measurement
- good for BC measurement – variation of MAC is counteracted by variation of C

Absorption coefficient should be measured using in-situ techniques

Acknowledgements



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