



Supplement of

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

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S1 Beam size and intensity distribution

Beam sizes were measured using a CCD camera (Thorlabs DCC1545M-GL). The measured light intensity was calibrated using a power sensor (Thorlabs S121C). Images were analysed using ImageJ software (Fig. S1). The peak intensities of 1.9 W/mm2 and 2.1 W/mm2 have been obtained for the 532 and the 1064 nm channels, respectively.



Figure S1. Diameters and non-calibrated intensities for probe beam a), 532 nm pump beam b) and 1064 nm pump beam inside the measurement chamber as a function of distance from the axicon.

S2 Heating curves

Heating curves describe the average change of photodiode voltage during the modulation period (1/91 s for the 532 nm channel, 1/96 s for the 1064 nm channel). The curves were obtained by averaging the signal from several thousand intervals (Fig. S2). Because in the infrared channel the signal is lower, the noise is more pronounced (Fig. S2b). The pump laser being switched ON during the first half of the interval induces exponential increase of the signal voltage. During the OFF phase an exponential reduction is observed. The time constants for both channels are similar.



Figure S2. Average photodiode voltage during the heating and cooling parts of the modulation period for the 532 nm channel (a) and the 1064 nm channel (b) obtained for nigrosin particles. The durations of the modulation period are 11.1 ms and 10.4 ms for the corresponding channels. The curves are obtained by averaging the photodiode PD1 voltage over more than 10000 modulation periods.

S3 Interferometer noise analysis

Interferometer noise was investigated by performing fast Fourier transform analysis of the interferometer signal on photodiode PD1 (Fig. S3). Figure S4 shows signal, noise and noise/signal ratio for the selected modulation frequencies. In general, both signal and noise are larger at lower frequencies. There is also some increased noise at 60 and 240 Hz, the latter is most probably connected to the resonance of the beam splitter block. Measurement frequencies of 91 Hz and 96 Hz were selected for their best performance.



Figure S3. Fast Fourier transform of photodiode PD1 signal.



Figure S4. Lock-in signal and (noise/signal) ratio vs. modulation frequency for the 532 nm channel (a) and the 1064 nm channel (b). Noise was determined as the standard deviation of the signal.

S4 NO₂ absorption

The 532 nm channel is calibrated using a mixture of 1 μ mol mol⁻¹ NO₂ in synthetic air. To calculate the absorption coefficient we need to know the absorption cross-section σ of NO₂ at the laser wavelength. We measured the emission spectrum of our 532 nm laser (Fig. S5a) and multiplied it with the absorption cross-section spectra (Fig. S5b) measured by Vandaele et al (2002). We obtained the absorption cross-section of 1.47E-19 cm², which is close to 1.45*10⁻¹⁹ cm² obtained by Osthoff et al. (2006). Changes of the laser spectrum during warm-up (23° C–29.3° C) resulted in 0.5% change in the absorption cross-section.



Figure S5. Normalised spectrum of our 532 nm laser (a). High resolution absorption cross section of NO₂ (Vandaele et al., 2002) obtained from MPI-Mainz UV/VIS spectral atlas (Keller-Rudek et al., 2013).

The absorption coefficient of 1 μ mol mol⁻¹ NO₂ is then:

$$b_{abs} = \frac{N}{V}\sigma,\tag{S1}$$

where N/V is a number density of NO_2 molecules:

$$\frac{N}{V} = 1 \ ppm * \ \frac{N_{air}}{V} = 1 \ ppm * \ \frac{p_0 * N_a}{R * T_0}.$$
(S2)

For 1 μ mol mol⁻¹ NO₂ at 100 kPa and 25 °C we obtain the absorption cross section of 357.3 Mm⁻¹.

S5 Determination of the optical properties of nigrosin

S5.1 Measurements of the real part of the refractive index

Thin film samples of nigrosin were prepared by drying nigrosin solution N4 on microscopy slides following the procedure described in section 2.1. The sample with smooth surface was selected for measurement. The nigrosin film was thick enough that almost no light was transmitted, so that the reflection from the glass substrate did not influence the measured reflection.

Measurements were conducted by changing the angle of the sample between 45 and 65 degrees and determination of the maximum reflected beam power. The real part of refractive index was determined by fitting the Fresnel equation to the measured data.

Measurements of refractive index of fused silica glass (Suprasil, UQG Optics, UK) show good agreement with the specification (Fig. S6) with deviation of +/- 0.01. Measured refractive index was on average 0.03 lower compared to Bluvstein et al. (2017).



c)

Figure S6. Examples of Brewster angle measurements on Fused silica glass and nigrosin film (a,b). The data was fitted with the Fresnel equation. Real part of the refractive index for fused silica and nigrosin (c) compared with literature data from Bluvstein et al. (2017) and fused silica glass specification.

S5.2 Absorbance of aqueous nigrosin solution

A spectrometer measures absorbance A of the sample with 10 mm optical path *I*. The absorption coefficient of the solution is calculated as:

$$b_{abs,sol} = \frac{atn}{l},\tag{S4}$$

where the attenuation atn is:

$$atn = A * \ln(10). \tag{S5}$$

The bulk absorption of the nigrosin is then:

$$b_{abs,bulk} = \frac{b_{abs,sol} * \rho_{nigrosin}}{\frac{m_{nigrosin}}{V_{sol}}},$$
(S6)

where nigrosin density ($\rho_{nigrosin}$) of 1600 kg/m³ and nigrosin mass concentration in the solution ($m_{nigrosin}/V_{sol}$) of 0.132 kg/m³ is used. The imaginary part of the refractive index is then:

$$k = b_{abs,bulk} \frac{\lambda}{4\pi}.$$
 (S7)



Figure S7. Imaginary part of the refractive index of aqueous nigrosin solution determined by absorbance measurements.

S5.3 Absorbance measurement of solid nigrosin

Samples with different thicknesses (designated N2, N3, N4) in triplicate (designated a, b, c) were prepared (Fig. S8). During drying of the nigrosin solution a thick edge was formed with uniform sample in the middle (Fig. S9). The absorbance of each sample was measured 3 times with the measurement beam in the middle of the sample (Fig. S9.a).



Figure S8. Solid nigrosin film samples on microscopy slides.



Figure S9. Absorbance image of nigrosin sample n3b (a) with marked position (dashed yellow line) of the measurement beam during integrating sphere measurements. Figure (b) shows a plot profile for the red line on the image (a).

To calculate the imaginary part of the refractive index, the sample thickness was measured using atomic force microscopy. Sample thickness (Table S1) was determined by measuring the depth of the groove generated with a sharp plastic tip (Fig. S10). Because the sample was destroyed during the sample preparation, only samples N2b, N3b and N4b were analysed.



Figure S10. 3D image of the groove in the nigrosin sample measured by the atomic force microscope (a). Sample thickness is defined as a difference in plateau and depression height (b).

Table S1. Nigrosin sample thickness measu	ared by atomic force microscope.
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Sample	Sample thickness (nm)
N2b	4-5
N3b	65
N4b	850

The absorbance of solid nigrosin was measured in a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer. The sample was placed at the entrance to the integrating sphere with the nigrosin layer facing the measurement beam (Fig. S11). Part of the light was reflected out of the integrating sphere.



Figure S11. Integrating sphere measurement setup (a). Measured transmittance T for different nigrosin samples (b).

Absorbance measurements in the integrating sphere were validated with an absorptive neutral density filter (Thorlabs NE10B), which was measured both in the integrating sphere and with the collimated beam at 520 and 1064 nm (Fig. S12). There is a good agreement between the measurements.



Figure S12. Comparison between absorptive neutral density filter transmittance measured with integrating sphere and collimated beam at 520 and 1064 nm.

The absorbance is calculated most reliably for the N4 and N0 sample pair, but it needs to be corrected for the illumination lost due to the reflection on the surface of the nigrosin layer. Fresnel equations were used to model the reflection of a thin absorptive film at 532 and 1064 nm (Fig. S13a). These values are compared to the measured reflectance (Fig. S13b). Modeled reflectance is lower compared to measurements because it does not include reflection from the back of the glass substrate, which is most pronounced for samples N0 and N2 where the absorption of the returning beam is small. There seem to be some discrepancy between modelled and measured reflectance which can result in the uncertainty in refractive index of about 3%.



Figure S13. Modelled reflectance of a clean glass substrate (N0) and nigrosin films N2b, N3b and N4b (a). The reflection from the back of the glass substrate is not taken into account. Reflectance measured using collimated beams on the samples N0b, N2b, N3b and N4b (b).

Modelled first-surface reflectance was 4% for clean sample (N0) and 7% for N4b sample at both wavelengths. The following correction scheme is used:

$$A_c = A + \log\left(\frac{1 - R_{N4b}}{1 - R_{N0}}\right),\tag{S8}$$

the imaginary part of the refractive index was calculated similarly as for the aqueous solution. First the attenuation is calculated:

$$atn = A * \ln (10). \tag{S9}$$

The bulk absorption coefficient can then be calculated for the sample of the thickness d:

$$b_{abs,bulk} = \frac{atn}{d} \,. \tag{S10}$$

The imaginary part of the refractive index is then:

$$k = b_{abs,bulk} \frac{\lambda}{4\pi}.$$
 (S11)

The imaginary part of the refractive index was determined in the 400-1200 nm range with some missing data between 900-1000 nm (Fig. S14).





S5.4 Proposed values of nigrosin refractive index

Refractive index of nigrosin was determined by measurements of the Brewster angle and absorbance of nigrosin film (Table S2). The uncertainty for the real part is 0.02 and for imaginary part 3%.

Wavelength (nm)	Refractive index
450	1.58 + i0.167
532	1.62 + i0.223
633	1.75 + i0.231
808	1.78 + i0.119
1064	1.73 + i0.0419

S5.5 Mie calculation

Absorption coefficients for nigrosin are obtained using Mie calculation with the known refractive index and particle size distributions (Fig. S15). The procedure was conducted during the AeroTox and Ljubljana 2021 campaigns. Size distributions below 400 nm were used for the calculation since the errors in the larger particle data results in an increased error. The following absorption ratios have been obtained for different experiments:

a) AeroTox 2020_10_01: b_{1064}/b_{532} = 0.0785

- b) Ljubljana 2020_12_02: $b_{1064}/b_{532} = 0.0782$
- c) Ljubljana 2021_05_07: $b_{1064}/b_{532} = 0.0781$



Figure S15. Particle size distributions determined during the following experiments: AeroTox 2020_10_01 (a), Ljubljana 2020_12_02 (b) and Ljubljana 2021_05_07 (c)

S5.6 Sensitivity analysis of Mie calculation

Sensitivity analysis of absorption coefficient on variation of the refractive index was performed for aerosolized nigrosin sample N2. Real part of refractive index was varied in the range 1.5 - 1.9 and resulted in positive slope of the absorption coefficient at 450 nm and negative slope for 808 and 1064 nm (Fig. S16); for these two wavelengths the absolute change of 0.1 resulted on 3.5% to 5.5% change in absorption coefficient (Table S3). 10% change in the imaginary part of the refractive index resulted in 5.6% to 8.7% change in absorption coefficient. Measurement error of 0.03 for *n* and 3% for *k* results in absorption coefficient uncertainty of 1.5% each and the combined uncertainty of 2%.



Figure S16. Absorption coefficient calculated using Mie theory for different values of refractive index

Table S3. Relative change of the absorption coefficient for absolute change of 0.1 of the real part and 10% change of the imaginary poart of the refractive index.

Wavelength (nm)	$\Delta b_{abs}(n + 0.1)/b_{abs}$	$\Delta b_{abs}(k+10\%)/b_{abs}$
450	0.012	0.086
532	-0.0067	0.087
808	-0.035	0.056
1064	-0.055	0.070

S6 Scanning electron microscopy of filter samples

Various aerosols were sampled on a Nuclepore[®] membrane. Diesel exhaust particles consist of small agglomerates with 2-4 globules and sizes between 80 and 180 nm (Fig. S17). The agglomerates for the propane soot are much larger, 260-400 nm (Fig. S18). Nigrosin samples show spherical particles with size increasing with the concentration of the nigrosin solutions used in the nebulizer (Fig. 19, 20 and 21).



Figure S17. SEM image of particles from diesel exhaust



Figure S18. SEM image of propane soot particles



Figure S19. SEM image of N1 nigrosin particles



Figure S20. SEM image of N2 nigrosin particles



Figure S21. SEM image of N3 nigrosin particles

S7 The experiment setup



Figure S22. The experiment setup for Ljubljana ambient winter campaign 2020



Figure S23. The experiment setup for Ljubljana laboratory campaign 2020



Figure S24. The experiment setup for Ljubljana laboratory campaign 2021

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