

Response to RC2

Review of "Traceable calibration of in-situ aerosol absorption instruments with monodisperse nigrosin" by Drinovec et al. (egusphere-2026-1501)

General comments

This is a careful, well-organised and timely metrological study on a problem of real importance to the AMT readership. Traceable calibration of in-situ absorption instruments is a recognised bottleneck, and the systematic side-by-side evaluation of DMA, CPMA and tandem classification, together with an explicit uncertainty budget, is a valuable and practically useful contribution. The identification and quantification of the two competing biases (multiply-charged particles in the DMA, neutral particles in the CPMA) is a genuinely useful result, and the recommendation of the tandem configuration follows logically from it. The experimental work appears sound and the manuscript is clearly written. I recommend publication after the following points have been addressed. Several of them are substantive and, in my view, amount to a major revision, but all should be tractable with the data already in hand.

We would like to thank the Reviewer for the positive feedback and the insightful comments, which have helped us improve the quality of the manuscript. Please find below the answers to the questions raised.

1. The size dependence of the measured nigrosin density deserves a deeper analysis (Table 1, p. 6; Fig. 3B, p. 5; L188-191, p. 5).

This is, in my opinion, the most interesting and the least developed result of the paper. If D_p and D_m from Table 1 are recast as a difference rather than a ratio, one obtains $D_p - D_m = 3.8, 4.2, 4.3, 4.4$ and 3.8 nm for $m_p = 0.1, 0.3, 1, 3$ and 10 fg. In other words, the discrepancy is an essentially constant additive offset of ~ 4 nm in diameter over two decades in particle mass, and the apparent "size dependence of the density" is simply the geometrical consequence of that constant offset. This is a strong constraint on the physical explanation, and it is not consistent with the explanation currently offered in the text (fusion of incompletely dried particles, L188-191), which would produce a size-dependent void fraction rather than a constant diameter offset. A constant offset of this kind - equivalent to a shell about 2 nm thick - is much more suggestive of, e.g., residual water on these hygroscopic particles at the operating RH, a residual solute or surfactant layer, or a systematic offset between mobility and volume-equivalent diameter for this material. I would encourage the authors to present the data in this form and to discuss the candidate explanations explicitly - it would considerably strengthen the paper. Note also that the polystyrene bead validation (0.8 % in density, i.e. ~ 0.25 nm in diameter, Table S1) rules out a simple DMA sizing offset and therefore points to a material-specific effect. This matters beyond bookkeeping: if the particles carry a thin low-index shell, the homogeneous-sphere Mie model is not strictly appropriate, and the sign of the residual bias in Figs. 6B and 10B may be related.

The reviewer proposes an alternative model based on residual water or surfactant on the surface of the particles. It is not expected to have water on the surface of the particle because nigrosin is water soluble and is expected to dissolve in contact with water. The surfactant model seems to be counterindicated because the same behaviour of increasing effective density with diameter is observed for laboratory-grade ammonium sulphate.

Our model predicts the non-spherical shape of nigrosin particles. The discrepancy from the spherical shape is quite small: 4.3 nm for D_p of 110 nm for example. For irregular particles without internal voids, DeCarlo et al. (2002) reports that the electrical mobility diameter is overestimated, which results in a lower measured effective density (see below).

D



Irregular
(no voids)

$d_{me} = d_{ve}$
 $d_m > d_{ve}$

$\rho_p = \rho_m$

$\chi' = \chi > 1$

d_p	physical or geometric diameter
d_{ve}	volume equivalent diameter
d_e	envelope equivalent diameter (same as d_{ve})
d_{me}	mass equivalent diameter
d_m	electrical mobility diameter

DeCarlo, P. F., Slowik, J. G., Worsnop, D. R., Davidovits, P., and Jimenez, J. L.: Particle Morphology and Density Characterization by Combined Mobility and Aerodynamic Diameter Measurements. Part 1: Theory. *Aerosol Science and Technology*, 38(12), 1185–1205. <https://doi.org/10.1080/027868290903907>, 2004.

There are reports of nigrosin swelling under increased humidities:

- our results show 1% increase of D_p between 35% and 53% relative humidity.
- Flores et al. (2012) reported a 12% increase of D_p between 0% and 90% relative humidity
- The measured absorption coefficient of nigrosin is stable between 30% and 60% (Langridge et al., 2013). See below:

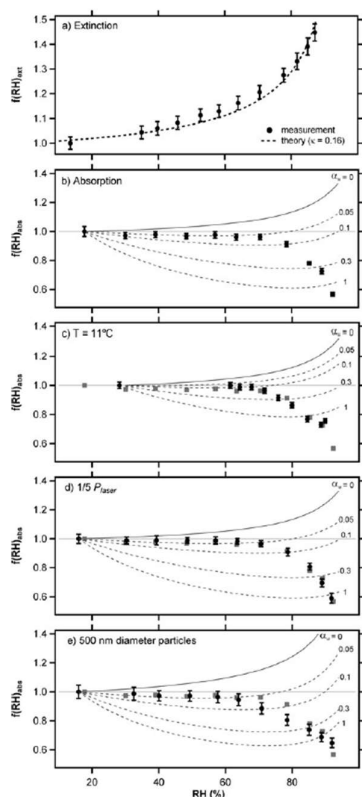


FIG. 4. Extinction (a) and absorption (b–e) measurements for size-selected nigrosin as a function of RH. Unless otherwise stated, experiments were performed using 200 nm dry diameter particles at a temperature of 25°C. Model predictions shown for each experiment $f(RH)_{\text{meas,dry}}$ (solid line) and $f(RH)_{\text{meas,air}}$ (dotted lines) are described fully in the main text. Measurements of $f(RH)_{\text{abs}}$ shown in (b) are repeated in (c–e) to facilitate comparison (gray squares).

These results indicate that nigrosin is quite insensitive to relative humidity at our experimental humidities around 30%.

Langridge, J. M., Richardson, M. S., Lack, D. A., Brock, C. A., and Murphy, D. M.: Limitations of the Photoacoustic Technique for Aerosol Absorption Measurement at High Relative Humidity. *Aerosol Science and Technology*, 47(11), 1163–1173. <https://doi.org/10.1080/02786826.2013.827324>, 2013.

Flores, M.J., Bar-Or, R. Z., Bluvshstein, N., Abo-Riziq, A., Kostinski, A., Borrmann, S., Koren, I., Koren, I., and Rudich, Y.: Absorbing aerosols at high relative humidity: linking hygroscopic growth to optical properties, *Atmos. Chem. Phys.*, 12, 5511–5521, <https://doi.org/10.5194/acp-12-5511-2012>, 2012.

In response to the comment, we updated the text in section 3.1: “The low experimental values in the effective particle density for nigrosin might be due to the non-spherical shape of the nigrosin particles as observed in some of the filter samples analyzed by SEM (Supplement – Fig. S5). Non-spherical particles could form inside the drier by fusion of semi-dry particles. This process might be enhanced by non-dried inlet air used in our nebulizer. Non-spherical particles have a larger electrical mobility diameter compared to the particle physical diameter (DeCarlo et al., 2012) which results in a lower effective density than the material density of 1.6 g cm^{-3} .”

2. The uncertainty budget omits the contribution of the assumed material density (Table 2, p. 10).

The manuscript states (L194-195, p. 5) that basing the Mie calculation on D_p rather than D_m changes the calculated absorption coefficient by 5-20 %, which shows that the result is strongly sensitive to the assumed particle density. Yet D_m is obtained from the CPMA-selected mass together with an assumed $\rho = 1.6 \text{ g cm}^{-3}$, and the paper itself demonstrates that the measured effective density deviates from this value by up to 20 %. Table 2 contains a 2 % component for CPMA mass and a 2 % component for the Mie calculation and refractive index, but no component for the density / mass-equivalent-diameter conversion. Please add this component explicitly, state the sensitivity coefficient ($d \ln \text{babs} / d \ln \rho$), and justify the value adopted. Depending on the answer to point 1, this could be one of the larger terms in the budget, and it would affect the ranking of the three configurations.

The Mie calculation is based on the physical particle diameter (same as the geometrical diameter, determined with microscopy). For non-spherical particles the mass-equivalent diameter is the same as the physical diameter but the electrical mobility diameter is overestimated (DeCarlo et al., 2004 – Table 1D). The overestimation of electrical mobility diameter is reflected in the effective particle density being lower than the material density. The uncertainty in the absorption coefficient based on the electrical mobility diameter was estimated as the difference between the absorption coefficients calculated using D_p and D_m : 13%, 8% and 5% for 1 fg, 3 fg and 10 fg particles correspondingly. This uncertainty has now been added to Table 2. Combined uncertainties for absorption coefficient based on D_p have been added to Table 2.

The following text has been added to section 3.6: “Mie calculation is based on the physical particle diameter. For non-spherical particles the electrical mobility diameter is larger than the physical particle diameter (DeCarlo et al., 2004). This results in an overestimated absorption coefficient when D_p is used for Mie calculation with the resulting uncertainty increasing with the decreasing particle mass from 5% at 10 fg to 13% at 1 fg.”

An uncertainty has been added to Table 2: “F: Mie calculation based on D_p 5% - 13%”.

The material density of 1.6 g cm^{-3} for nigrosin was reported by Moteki et al. (2010). The authors used a similar experimental setup for nigrosin density but did not report the uncertainty in the reported value. Our results show agreement of measured density with the material density of polystyrene beads within 0.8%. This is much lower than the combined uncertainty of CPMA and DMA of 9.2%. If the experimental system is calibrated with the same polystyrene beads, the actual method uncertainty is much lower. We have included the uncertainty of 2% for the material density of nigrosin in the calculation of combined uncertainty of absorption coefficient based on D_m . When calculating the absorption coefficient using D_m we get $dbabs/d\rho=1$. The uncertainty of calculated absorption coefficient due to the uncertainty of the material density is then 2%.

Text is added to section 3.6: “The material density of 1.6 g cm^{-3} for nigrosin as reported by Moteki et al. (2010) was selected with instruments similar to DMA and CPMA, which would result in an uncertainty of 9.2%. If both instruments are calibrated with the same polystyrene beads, the uncertainty in the measured density is much lower as validated by our measurements of polystyrene beads density (Supplement S2). The uncertainty of the absorption coefficient based on D_m is the same as the assumed uncertainty of the material density of 2%.”

The uncertainty of 2% is added to Table 2: “G: Mie calculation based on D_m 2%”.

3. The particle-based method is validated only at 450 nm, although its main motivation is the near-IR.

The Introduction motivates particle-based calibration by the fact that NO₂ absorption is too weak for sub-ppm calibration in the near-IR (L79-80, p. 2). The PTAAM P02 has an 808 nm channel, and the 808 nm calibration is stated to be transferred from 450 nm using the Mie-calculated $b_{abs}(808)/b_{abs}(450)$ ratio (L136-138, p. 4). However, all measured-versus-calculated comparisons presented (Figs. 4B, 6B, 8B, 10B) are at 450 nm. The central practical claim of the paper - that monodisperse nigrosin enables calibration where NO₂ cannot be used - is therefore not directly tested. If 808 nm data were recorded, please show the same comparison at 808 nm; if not, please state this limitation explicitly in the Discussion and Conclusions and temper the corresponding claims. The wavelength dependence of the multiple-charge and neutral-particle biases (both of which act through the size dependence of the mass absorption cross-section) would also be worth a sentence.

The aim was to develop a traceable calibration method for aerosol instruments in the visible to near infra-red range. As noted by the reviewer the method was compared to the reference method only at 450 nm. The only uncertainty component which could depend on the wavelength is the DMA uncertainty after charge correction.

The text in section 3.6 has been updated: “We have checked the influence of measurement wavelength for the uncertainty of component K). The correction for multiple charges at 808 nm is between 17% and 25%, in the same range as correction for 450 nm (13-27%).”

The uncertainty of the component C) is stated at 2% for both wavelengths. The sensitivity analysis showed (Drinovec et al., 2022b) that compared to 450 nm the calculated absorption coefficient at 808 nm is more sensitive to the error in the real part of the refractive index but less sensitive to the error in the imaginary part. See the citation below:

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

The text in section 3.6 has been updated for multiple charge correction of DMA selected particles: “When monodisperse nigrosin is size-selected with a DMA, the calculated absorption coefficient must take into account the multiply-charged particles which account for 13-27% of the absorption.”

The abstract and Conclusions already state that the comparison was performed only at 450 nm.

The text in the Introduction is updated: “Here we develop and evaluate a calibration method for aerosol absorption instruments based on monodisperse nigrosin particles. In this study, we experimentally tested size- and mass- selection techniques using a DMA, a centrifugal particle mass analyzer (CPMA) and a tandem configuration of both in series and compared the calculated absorption coefficient at 450 nm with the measured absorption by a NO₂-calibrated instrument. The DMA provides electrical mobility selection, whereas the CPMA enables mass selection; their tandem use constrains both size and mass simultaneously, improving control over particle properties used for calibration. We assess the performance of these approaches and discuss implications for reducing

calibration uncertainty and improving intercomparability across absorption measurement techniques.”

4. Please clarify the traceability claim and the logic of the comparison.

The title and abstract present the nigrosin method as a "traceable calibration". Strictly, the traceable chain demonstrated here runs NO₂ permeation standard -> CAPS -> PTAAM (450 nm); the nigrosin comparison then relies on Mie theory plus a literature refractive index, neither of which is traceable to SI in the metrological sense.

We have modified the title of the manuscript to properly reflect the way to achieve traceability. A new section after the discussion describes the traceability chain as achievable by a well-instrumented laboratory at a national metrology institute:

“5. Traceability to SI units

For the traceable calibration of an aerosol absorption monitor all quantities used in calculations need to be traceable to SI units. For calibration with NO₂ this amounts to determination of NO₂ amount fraction, cross-section of NO₂, emission spectrum of measurement light, pressure, relative humidity and temperature (Table 4).

Traceable calibration with monodisperse nigrosin is based on the determination of the nigrosin refractive index, material density, particle electrical mobility or particle mass for the determination of the particle diameter, particle number or charge, temperature, relative humidity and pressure. The refractive index of nigrosin can be determined in a traceable manner using ellipsometry. Nigrosin material density can be obtained from particle mass and electrical mobility diameter of spherical particles. All parameters and methods with references for the traceable calibration of the required parameters are listed in Table 5.

Table 4. Parameters and methods required for the traceable calibration of aerosol absorption monitors with NO₂

Parameter	Method	Reference
NO ₂ amount fraction	Permeation	Haerri et al., 2017
NO ₂ cross-section	High-resolution Fourier transform spectroscopy	Vandaele et al., 2002
Spectrum of measurement beam	VIS-NIR spectrometer calibrated against accurately known spectral lines	
Pressure		Perkin et al., 2008
Relative humidity		Lochlainn et al., 2024
Temperature		Sparasci et al., 2024

Table 5. Parameters and methods required for the traceable calibration of aerosol absorption monitors with monodisperse nigrosin

Parameter	Method	Reference
Nigrosin refractive index	Ellipsometry	ISO 23131:2021

Particle mass-to-charge ratio	CPMA traceably calibrated using mass-certified polystyrene spheres	Ehara et al, 2006 Takahata and Sakurai, 2026
Particle electrical mobility diameter	DMA traceably calibrated with size-certified polystyrene spheres	ISO 15900:2020 Vasilatou et al., 2025
Nigrosin material density	CPMA and DMA	see above
Number of particles	CPC traceably calibrated against a FCAE	ISO 27891:2015 Vasilatou et al., 2025
Particle charge	FCAE traceably calibrated against a primary standard for electric current	
Pressure		Perkin et al., 2008
Relative humidity		Lochlainn et al., 2024
Temperature		Sparasci et al., 2024

“

New references are included in the list:

Haerri, H.-P., Macé, T., Waldén, J., Pascale, C., Niederhauser, B., Wirtz, K., Stovcik, V., Sutour, C., Couette, J., and Waldén, T.: Dilution and permeation standards for the generation of NO, NO₂ and SO₂ calibration gas mixtures, Meas. Sci. Technol., 28, 035801, <https://doi.org/10.1088/1361-6501/aa543d>, 2017.

Vandaele, A. C., Hermans, C., Fally, S., Carleer, M., Colin, R., Merienne, M. F., Jenouvrier, A., and Coquart, B.: High-resolution Fourier transform measurement of the NO₂ visible and near infrared absorption cross sections: Temperature and pressure effects, J. Geophys. Res.-Atmos., 107, ACH 3-1–ACH 3-12, <https://doi.org/10.1029/2001jd000971>, 2002.

Vasilatou, K., Iida, K., Kazemimanesh, M., Olfert, J., Sakurai, H., Sipkens, T.A. and Smallwood, G.J.: Aerosol physical characterization: A review on the current state of aerosol documentary standards and calibration strategies, J. Aerosol Sci., 183, 106483- , <https://doi.org/10.1016/j.jaerosci.2024.106483>, 2025.

Perkin, M., Picard, A., Lecollinet, M., Fen, K., Sardi, M., Müller, A., Agarwal, A., Jescheck M. and Wüthrich C.: Final report on CCM key comparison CCM.P-K2: Pressure (10 kPa to 120 kPa) absolute mode. Metrologia, Volume 45(1A). 10.1088/0026-1394/45/1A/07002. 2008.

Lochlainn, D.M., Mitter, H., Aytekin, S.O., Panman, M., Senn, R., Šestan, D., Smorgon, D., Stevens, M. and Zvizdić, D.: Comparison in humidity (dew-point temperature high range) dew point temperature +30 °C to 95 °C. Metrologia, Volume 61(1A). 10.1088/0026-1394/61/1A/03008. 2024.

Sparasci, F., Risegari, L., Martin, C., Hermier, Y., Lopardo, G., Steur, P.P.M, Pearce, J., Bünger, L., Rudtsch, S., de Bruin-Barendregt, C., Panman, M., Peruzzi, A., Hofstätter-Mohler, C., Turzó-András, E., Nedialkov, S., Spasova, S., Petrusova, O., Martín Hernandez, M.J., del Campo Maldonado, D., García Izquierdo, C., Strnad, R., Simic, S., Stepanovic, V., Nielsen, J., Kokkini, E., Gaidamovičiūtė, L., Galkauskas, L., Mikalauskas, K., Kozicki, M., Zvizdić, D., Šestan, D., Mutapčić, N., Stratulat, C., Neagu, M., Eusébio, L., Olsen, Å.A.F., Bergerud, R.A., Opel, K., Kvernmo, G., Högström, R., Heinonen, M., Bojkovski, J., Žužek, V., MacLochlainn, D., Holmsten, M., Senn, R., Dobre, M., Pavlasek, P. and Kalemci, M.: EURAMET.T-K9 regional key comparison ITS-90 SPRT calibration from the Ar TP to the Zn FP. Metrologia, Volume 61(1A). 10.1088/0026-1394/61/1A/03005. 2024

Ehara, K., Takahata, K., & Koike, M.: Absolute Mass and Size Measurement of Monodisperse Particles Using a Modified Millikan's Method: Part I—Theoretical Framework of the Electro-Gravitational Aerosol Balance. *Aerosol Science and Technology*, 40(7), 514–520. <https://doi.org/10.1080/02786820600714379>, 2006.

Takahata, K. and Sakurai, H.: Development and certification of a 300 nm monodisperse spherical particle reference material with SI-traceable diameter and mass. *Advanced Powder Technology*, Volume 37(4). doi.org/10.1016/j.appt.2026.105211. 2026.

International standard organization: Ellipsometry — Principles, ISO 23131:2021, <https://www.iso.org/standard/74663.html> (Last access: 23 Sept 2026), 2021.

International standard organization: Determination of particle size distribution — Differential electrical mobility analysis for aerosol particles, ISO 15900:2020, <https://www.iso.org/standard/67600.html> (Last access: 23 Sept 2026), 2020.

International standard organization: Aerosol particle number concentration — Calibration of condensation particle counters, ISO 27891:2015, <https://www.iso.org/standard/44414.html> (Last access: 23 Sept 2026), 2015.

What the experiments demonstrate is a validation of the nigrosin-based method against an NO₂-traceable calibration, with the residual differences (+5 to +11 %, -2 to -3 %, +2 to +8 %) setting a floor on the achievable agreement. For a paper of this metrological character I think this distinction should be made explicitly, and the wording in the title, abstract and conclusions adjusted accordingly. Relatedly, please state whether the residual differences are statistically consistent with the combined uncertainty of the comparison (which must combine the calibration uncertainty and the Mie-calculation uncertainty), or whether an unexplained bias remains.

We have modified the title of the manuscript to properly reflect the way to traceability. We have modified the abstract to reflect this change in:

“We developed a traceable calibration method based on monodisperse nigrosin particles and showed how to make it traceable to primary units. “

Differences between measured and calculated absorption are not significantly different using $k=2$ uncertainties except for a single measurement marked by * on Fig 5b.

Text is added to the discussion: “The uncertainties for calculations based on D_p are larger and depend on the particle size. The measured and calculated absorption are not significantly different (using $k=2$ uncertainties) except for the one experiment (Figure 5b).”

5. Refractive index provenance and batch dependence.

The manuscript itself notes that nigrosin optical properties vary between batches (L93-94, p. 3, citing Foster et al., 2019), and then adopts refractive index values determined previously (L171-173, p. 5). Please state explicitly whether the nigrosin batch used here is the same physical batch as in Drinovec et al. (2022), and if not, how the transfer was justified. If nigrosin is to be recommended as a practical transfer standard, the procedure should specify whether the refractive index must be re-determined for each batch, and what that adds to the uncertainty. A short, explicit step-by-step recommended protocol (classification settings, R_m , solution concentration, required checks) would substantially increase the practical value of the paper for AMT readers.

The same nigrosin as in Drinovec et al. 2022 has been used here as noted in section 2.4. The text in section 2.1 has been updated to include the batch designation “Lot # SHBL0637”

Section 3.6 has been updated to mark the importance of using the batch specific refractive index: “Because of differences in the refractive index between different batches of nigrosin, each sample’s properties need to be determined. Here, we used the sample already characterized in a past study (Drinovec et al., 2022). The uncertainties in the real and imaginary part of the refractive index of this nigrosin batch are 2% and 3%, respectively. Using the sensitivity coefficients from Drinovec et al. (2022b) we get the uncertainties of the calculated absorption coefficient of 2.6% and 2.1% at 450 and 808 nm, respectively.

The following text has been added to the Discussion: “The proposed step-by-step protocols for calibration with monodisperse nigrosin are presented in Supplement S12.”

New section has been added to the Supplement: “

S12. Step by step protocols for calibration with monodisperse nigrosin

S12.1 Selection with DMA

- prepare 0.1 g l⁻¹ nigrosin solution
- check sample RH
- build the setup illustrated in Fig. 2a and measure density of particles with $D_p=150$ nm
- select $D_p=150$ nm, sheath flow=15 l min⁻¹
- build the setup as illustrated in Fig. 2c and measure multiply-charge particle fraction
- build the setup as illustrated in Fig. 2b and measure absorption and particle concentration for 15 minutes

S12.2 Selection with CPMA

- prepare 1 g l⁻¹ nigrosin solution
- check RH
- build the setup illustrated in Fig. 2d
- set $m_p=3$ fg, $R_m=10$, set to measured sample flow

- measure absorption and particle current for 15 minutes

S12.3 Selection with CPMA + DMA

- prepare 1 g l-1 nigrosin solution
- check RH
- build the setup illustrated in Fig. 2a
 - set CPMA: mp=3 fg, Rm=5, set to measured sample flow
 - set SMPS: sheath flow=10 l min⁻¹
 - measure Dp and identify distribution peak
- build the setup illustrated in Fig. 2f
- set DMA to peak Dp, sheet flow=10 l min-1
- measure absorption and particle number for 15 minutes

“

6. Generality beyond the PTAAM.

The title refers to "in-situ aerosol absorption instruments" in general, but only the PTAAM is tested, and the conflict of interest statement notes that three authors are employed by the manufacturer (which is properly declared and is not in itself a problem). To support the general claim it would be valuable to apply the method to at least one independent instrument, e.g. a photo-acoustic spectrometer. If that is not possible, please discuss explicitly what would change for PAS - for instance microphone/resonator response, sensitivity to gas-phase absorbers and to relative humidity - and consider narrowing the title.

The intention was to separate filter-based and in-situ instruments. The proposed calibration method is not useful for filter photometers as their response changes with the particle size and shape. The reported calibration method could be adapted for photo-acoustic instruments taking into account their sensitivities, especially the one to humidity.

To clarify the issue, we decided to change the title to “Development of a traceable calibration method for photothermal aerosol absorption monitor using monodisperse nigrosin”

The short discussion of applicability of the calibration method for the photoacoustic instruments has been added to section 4.:

“The calibration method using monodisperse nigrosin can be extended to other in-situ absorption methods like photo-acoustic spectroscopy, which has been demonstrated in several studies (Radney and Zangmeister, 2015; Lack et al., 2006; Bluvshstein et al., 2017; Cotterell et al., 2020; Kuula et al., 2025; Lawson et al., 2025). Care should be taken with the photo-acoustic method because its response has been shown to be highly sensitive to relative humidity (Langridge et al., 2013).”

A new reference has been added to the list:

Langridge, J. M., Richardson, M. S., Lack, D. A., Brock, C. A., and Murphy, D. M.: Limitations of the Photoacoustic Technique for Aerosol Absorption Measurement at High Relative Humidity. *Aerosol Science and Technology*, 47(11), 1163–1173. <https://doi.org/10.1080/02786826.2013.827324>, 2013.

7. Repeatability and the interpretation of the error bars.

Figures 4B, 6B, 8B and 10B carry error bars on both the measured and the calculated values, but the captions do not state what these represent - the standard deviation of the raw signal, the standard error, or the combined uncertainty of Table 2 - nor how many independent repetitions underlie each point. For a calibration method, repeatability is a key figure of merit. Please define the error bars in the captions, state the number of repetitions and the period over which they were acquired, and, if the bars represent within-run scatter only, add a statement of day-to-day reproducibility. The latter would be particularly convincing for a method intended as a transfer standard.

The results in Figures 4B, 6B, 8B and 10B show the mean value for one experiment. The error bars represent the parameter uncertainty (the figure captions were updated). The repeatability of instrumental response is already contained in the uncertainty component K: Stability of PTAAM response in Table 2. The uncertainty of 3% is stated. When we repeated the tests in our laboratory the repeatability was 0.3% during 5 consecutive days (see below). The 3% uncertainty in Table 2 includes the increased noise during laboratory experiments (see new Fig. 1b).

New measurement of the instrument response repeatability is added to the supplement:

“S10. Repeatability of the PTAAM-2λ (version P02) response

Repeatability of instrument response was tested by performing daily calibrations (Table S9). The calibration procedure:

A) Testing 450 nm channel response

- wavelength calibration of the spectrometer Thorlabs SC100/M using a calibration lamp Thorlabs SCL1
- measurement of the 450 nm channel laser diode (LD450) emission spectrum using the spectrometer Thorlabs SC100/M
- calculation of the absorption cross-section of NO₂ for the LD450 spectrum
- measurement of NO₂ concentration of the calibration sample using NO₂ CAPS
- measurement of the PTAAM response at 450 nm
- calculation of the 450 nm channel response

B) Testing the 808 nm channel response

- measurement of the nigrosin size distribution with the SMPS
- calculation of the absorption ratio using Mie theory: $\text{babs_Mie_808/babs_Mie_450}$
- measurement of absorption of polydisperse nigrosin with the PTAAM
- calculation of the absorption ratio $\text{babs_PTAAM_808/babs_PTAAM_450}$
- calculation the 808 nm channel response

Table S11. The results of PTAAM-2λ calibrations performed on consecutive days. Results are calculated relative to the first day.

Day	CS	Calculated	Measured	Channel 1	Mie calculated	Measured	Channel 2
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	(10 ⁻¹⁹ cm ²)	babs/no2 (Mm-1*ppb ⁻¹)	babs/NO2 (Mm-1*ppb ⁻¹)	relative response	babs808/babs450	babs808/babs450	relative response
1.	4.857	1.201	1.201	1.000	0.3239	0.3239	1.000
2.	4.858	1.200	1.120	0.933	0.3240	0.3259	0.939
3.	4.880	1.206	1.205	0.999	0.3240	0.3249	1.002
4.	4.848	1.198	1.198	1.000	0.3230	0.3247	1.005
5.	4.851	1.199	1.198	0.999	0.3236	0.3250	1.003
SD	0.3%	0.3%	0.3%	0.3%	0.2%	0.2%	0.3%

“

Specific comments

p. 1, L33-34 (Abstract): The phrase "Calculated versus measured absorption coefficients differed by ..." would be clearer if the sign convention were stated, i.e. that positive values mean the Mie calculation exceeds the measurement. Please also state that all these values refer to 450 nm.

The text was updated: “The difference between Mie calculated and measured absorption coefficient at 450 nm for different monodisperse selection techniques was between +5% to +11% for the DMA, -2% to -3% for the CPMA and +2% to +8% for tandem of the CPMA and the DMA.”

p. 2, L43-58 (List of Abbreviations): SMPS is used in Sect. 3.1 (L180, p. 5) and rho / Rm are used throughout but none appears in the list. Please add SMPS, Rm and the density symbols. Also, Dp is defined as "electrical mobility diameter" here but referred to as "mobility diameter" and "particle diameter" elsewhere; please use one term consistently.

List of abbreviations has been updated to include all used parameters: “

mp Particle mass
Dg Physical or geometric diameter
ρ0 Material density of nigrosin
peff Effective particle density calculated with Dp and mp
Rm Resolution parameter Rm=mp/FWHM”

The text has also been updated with respect to electrical mobility diameter.

p. 3, L124-127 (PTAAM version): P02 uses laser diodes at 450 and 808 nm, whereas P01 used DPSS lasers at 532 and 1064 nm. Laser diodes have a considerably broader and more temperature-sensitive emission spectrum. Given that the NO₂ absorption cross-section is strongly structured near 450 nm, the effective wavelength, the spectral width (FWHM) and its stability are critical for the calibration. The text mentions that the pump spectrum was measured with a CCS100/M spectrometer (L133-135), which is good practice, but please report the measured centre wavelength and FWHM, describe how the convolution with the NO₂ cross-section was performed, and include the resulting uncertainty contribution in Table 2.

The calculation of the NO₂ cross-section is the same as described in Drinovec et al. (2022). For clarity a new section was added to the Supplement:

“S9. Calculation of absorption cross-section of NO₂ for 450 nm laser diode

The absorption cross-section of NO₂ is wavelength dependent. The exact absorption cross-section needs to be calculated using a high-resolution absorption cross-section of NO₂ (Vandaele et al., 2002)

and the measured spectrum of the 450 nm laser diode (Fig. S9). The effective cross-section CS was calculated as follows:

$$CS = \frac{\sum CS_i \cdot I}{\sum I} ,$$

where CS_i is the wavelength-dependent cross-section and I is the emission spectrum of laser diode. The emission spectrum of the laser diode depends on temperature and electric current, which have to be kept stable.

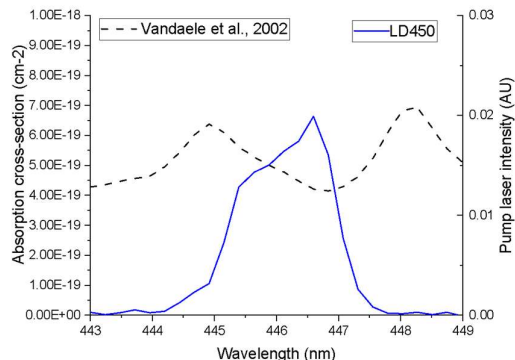


Figure S9. Spectra of the absorption cross-section and 450 nm laser diode.

The laser diode spectrum was measured using a Thorlabs CCS100/M spectrometer, which was wavelength-calibrated using a neon spectral lamp (Thorlabs CSL1) just before the measurement. The uncertainty comes from the limited spectral resolution of the spectrometer: 0.5 nm. The decrease in spectral resolution of the Vandaele et al. (2002) cross-section measurement from 0.25 nm to 0.5 nm results in an uncertainty of 0.7%. The difference between the cross-section measured by the Thorlabs CCS100/M spectrometer compared to a high-resolution spectrometer (Edinburg Photonics FLS920) with a 0.07 nm resolution (Fig. S10) was 0.6% which falls within the estimated uncertainty.

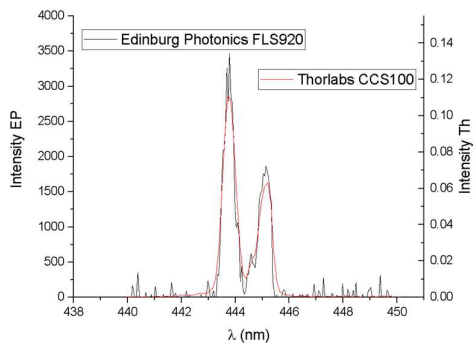


Figure S10. Measured emission spectra of 450 nm laser diode using spectrometers Edinburg Photonics FLS920 and Thorlabs CCS100/M.”

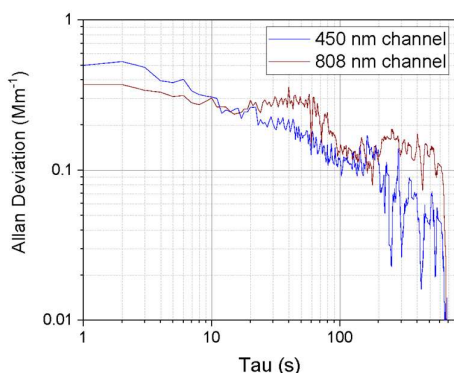
The uncertainty in the NO₂ cross-section due to errors in measurement of the laser diode emission spectrum has been added to Table 2.

p. 4, L136-138: Since the refractive index values are quoted "at 450 nm and 808 nm" from a study performed at 532 and 1064 nm, please state whether these were measured directly at 450/808 nm or interpolated from a measured spectrum, and give the associated uncertainty.

The refractive index values measured at 450 and 808 nm are listed in Drinovec et al. (2022). The values were directly copied to section 2.4 of this article: "The refractive index of the Nigrosin batch used in this study had been determined previously over a large interval of wavelengths including 450 nm and 808 nm, and was taken as $1.58 + i0.167$ at 450 nm and $1.78 + i0.119$ at 808 nm (Drinovec et al., 2022b) for the calculation of absorption coefficients."

p. 4, L140-146 and Fig. 1: The 15 min Allan deviation is 0.03 Mm^{-1} , but the "actual measurement uncertainty for 15 min experiments" is stated as 0.3 Mm^{-1} , a factor of ten larger. Please explain the origin of this factor more quantitatively. At the signal levels used for the monodisperse comparisons (babs = $14.5\text{--}38 \text{ Mm}^{-1}$, Table 3) this corresponds to 0.8-2 %, which is not negligible relative to the 5.2-6.9 % combined uncertainty; please state whether it is already covered by component K.

An additional Allan plot describing an example of instrument stability during laboratory experiments has been added to Fig 1.



The actual stability of the instrument tested for 5 days was 0.3%. The uncertainty of 3% in the stability of the PTAAM response in Table 2 covers any additional uncertainty related to the increased noise.

p. 4, L152-154: "at sample flow of 3 L min^{-1} sample flow" - the phrase "sample flow" is duplicated. Please also state the RH after the diffusion drier more precisely than "below 30 %", since residual water is directly relevant to the density discussion (General comment 1).

Text is updated to: "The nebulizer was connected to a diffusion drier to reduce the relative humidity to $33 \pm 3\%$."

p. 5, L183-185 and Fig. 3: The sentence "Effective particle density and particle volume were calculated based on the selected particle mass (Fig. 3A) and the mobility diameter, respectively" is hard to follow on first reading. The reference to Fig. 3A is presumably to the selected masses shown in the legend, whereas the resulting densities are plotted in Fig. 3B, which is where a reader would expect the callout to point. Please rephrase so that it is clear which quantity is taken from which panel.

How the density was calculated is already explained in the same paragraph. The text has been updated as follows: "Particle density was measured for monodisperse particles whose mass m_p was selected by the CPMA and electrical mobility diameter D_p measured by the SMPS as shown in Fig. 2a. The CPMA was run at $R_m=10$ which resulted in a distribution width of 10% of their selected mass. The number size distributions (Fig. 3a) show two peaks corresponding to the electrical mobility diameter of the doubly- and singly-charged particles. The distributions were fitted with two Gauss functions to obtain the peak electrical mobility diameter. For nigrosin, the effective density increases with particle mass (Fig. 3b) toward the nominal value of 1.6 g cm^{-3} (Moteki et al., 2010)."

p. 5, Fig. 3 caption, L204: "coverage factor_k= 1" - formatting error; should read "coverage factor k = 1".

The text has been corrected.

p. 5, L188-191: "The low experimental values in the particle density for nigrosin might be due to fusion of particles before being completely dry." Please see General comment 1. In addition, if fused (doublet or higher) particles are present in significant numbers, this also undermines the homogeneous-sphere assumption in the Mie calculation. Please quantify the fraction of fused particles seen in the SEM images (Fig. S5) and bound the resulting error, e.g. by comparing with a dynamic shape factor estimate.

The type of substrate (fibrous structure) and analysis (SEM instead of TEM) make the particle shape analysis uncertain. The difference between D_p and D_m (4.3 nm for D_p of 110 nm, for example) indicates a small deviation from spherical shape.

The text has been updated as follows: "The low experimental values in the effective particle density for nigrosin might be due to the non-spherical shape of the nigrosin particles as observed in some of the filter samples analyzed by SEM (Supplement – Fig. S5). Non-spherical particles could form inside the drier by fusion of semi-dry particles. This process might be enhanced by the use of non-dried inlet air used in our nebulizer. Non-spherical particles have a larger electrical-mobility diameter compared to the particle physical diameter (DeCarlo et al., 2012) which results in a lower effective density than the material density of 1.6 g cm^{-3} ."

p. 6, Table 1 caption: "mobility dimeter" -> "mobility diameter". Please also add a column for $D_p - D_m$ (see General comment 1), and state the measured effective density uncertainty (9.2 %) alongside the tabulated values rather than only in the caption.

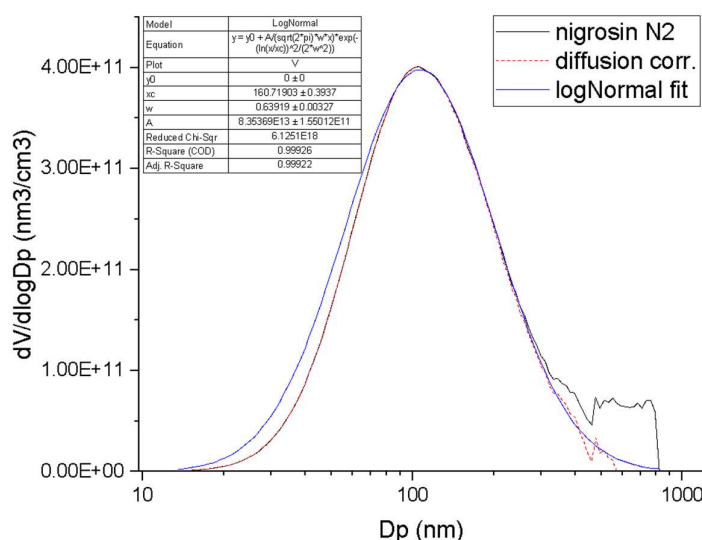
The table has been updated:

Table 1. Measured electrical mobility diameter D_p , effective density and mass-equivalent diameter D_m for nigrosin particles selected according to particle mass (m_p). Errors represent $k=1$ uncertainties.

m_p (fg)	D_p (nm)	Effective density (g cm^{-3})	D_m (nm)	$D_p - D_m$ (nm)
0.1 ± 0.002	53.0 ± 1.6	1.28 ± 0.03	49.2 ± 0.5	3.8 ± 2.1
0.3 ± 0.006	75.2 ± 2.3	1.35 ± 0.03	71.0 ± 0.7	4.2 ± 3.0
1 ± 0.02	110.4 ± 3.3	1.42 ± 0.03	106.1 ± 1.1	4.3 ± 4.4
3 ± 0.06	157.4 ± 4.7	1.47 ± 0.03	153.0 ± 1.5	4.4 ± 6.2
10 ± 0.2	232.3 ± 7.0	1.52 ± 0.03	228.5 ± 2.3	3.8 ± 9.3

p. 6, L215-218: The volume size distribution shows a non-negligible contribution above 350 nm that is attributed to an artefact of the inversion algorithm, and particles above 400 nm are simply excluded from the Mie calculation. This is a fairly consequential ad hoc choice. Please quantify how much the calculated polydisperse absorption changes if the cut-off is moved to, say, 300 or 500 nm, so that the reader can judge the sensitivity of the +10 % polydisperse result to this choice.

Particles above 400 nm represent 5% of the total absorption coefficient. This is about the same value we get if we subtract 700 particles from the distribution, which then follows the log-normal distribution (see figure below). The artefact is due to the short scan time of 1 minute during which some residual particles remained in the SMPS. When extending the scan time to 5 minutes the artefact was gone.



The text is updated: "The volume size distribution shows the presence of particles above 350 nm, which represent a non-negligible fraction of total volume. Experiments with an impactor (not shown) failed to reduce the number of these particles. We later found out that the artefact was present only when a short SMPS scan duration of 1 minute was used. This indicates that some residual particles were influencing the measurement. For the Mie calculation of the sample absorption, only particles smaller than 400 nm were used which resulted in 5% lower absorption coefficient."

p. 6, Fig. 4 caption, L226: "nigrosine" -> "nigrosin" (used elsewhere throughout).

The text is corrected.

p. 7, L253-256: "the absorption was then calculated as the sum of the absorption of singly-charged particles with mass m_0 , doubly-charged particles with mass $3.5 \cdot m_0$ and triply-charged particles with mass $6.6 \cdot m_0$ ". Please state how the factors 3.5 and 6.6 were obtained (presumably from the measured mass-mobility relation) and give their uncertainty, since these directly determine the 15-25 % correction. Also, "multiply-charged particles accounted for 15 % and 25 % of the total light absorption" gives two numbers, whereas three particle masses (0.7, 2.4 and 5.7 fg) are compared in Fig. 6B; please give the value for each of the three settings.

A table with the corrected absorptions when taking into account the multiply-charged particles is added to the Supplement:

“Table S2. Fitted peak positions, particle masses (m1, m2, m3) and number of particles (n1, n2, n3) for singly, doubly and triply-charged particles. E450 and E808 show the increase of calculated absorption when taking into account the higher mass of multiply-charged particles compared to assigning all particles the mass m1.

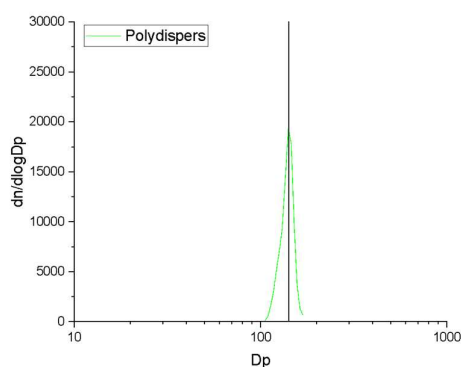
Dp (nm)	Peak1 (fg)	Peak2 (fg)	Peak3 (fg)	m1 (fg)	m2 (fg)	m3 (fg)	n1	n2	n3	E450	E808
100	0.707+/-0.002	1.23+/-0.05	1.6+/-0.3	0.708	2.44	4.68	4877	213	39	1.18	1.17
150	2.39+/-0.01	4.2+/-1.2	5.2+/-4.1	2.39	8.4	15.6	1442	22	27	1.27	1.20
200	5.71+/-0.03	9.8+/-2.7	12.8+/-4.2	5.71	19.6	38.4	418	3.4	8.9	1.13	1.25

”

Article text is updated: “The numbers of singly-, doubly- and triply-charged particles were calculated by fitting Gauss functions to the measured distribution and integrating each peak to obtain the number of these particles (Supplement – Fig. S4). Mass of the singly-charged particles (m_0) corresponds to the peak position of the left-most peak. Because CPMA selects particles by their mass-to-charge ratio, the actual mass of the doubly-charged particles is a double of the second peak position and triple for the third peak (Table S2). The absorption was then calculated as the sum of the absorption of singly-charged particles with mass m_0 , doubly-charged particles with mass $3.5*m_0$ and triply-charged particles with mass $6.6*m_0$. In our experiment, multiply-charged particles accounted for between 13% and 27% of the total light absorption (Table S2).”

p. 7, L257-259: A resolution of $R_m = 1.5$ is very broad. Please state the resulting width of the selected mass distribution and quantify the error introduced by treating such a broad distribution with a single mass-equivalent diameter in the Mie calculation (the mass absorption cross-section varies with size, cf. Fig. S3).

The equation for calculating the distribution width is stated in L258 :“ $R_m = m_p / \text{FWHM} = 1.5$ ”. For example, the full width at half maximum for particles with $m_p = 2.4$ fg is 1.6 fg. See the figure below:



The bias when using monodisperse distribution depends on the skewness of the distribution. Here, the absorption coefficient based on the monodisperse distribution was higher than the polydisperse between 3% and 7%. The text is updated: “Because of the distribution width there is a positive bias when calculating the absorption coefficient using the monodisperse aerosol approach: 5%, 3% and 7% for 0.7, 2.4, and 5.7 fg, respectively.”

p. 8, L296-301 and Fig. 8A: The neutral-particle contribution is quantified as 2.6 % of total absorption at $R_m = 3$ and then described as "negligible" at higher R_m . Fig. 8A shows data at $R_m = 3$, 7 and 15, so please give the measured numerical values for $R_m = 7$ and 15 rather than the qualitative statement, and state the detection limit of the electrostatic precipitator method.

The text is updated: "The absorption coefficients of -0.2 Mm^{-1} and 0.0 Mm^{-1} for neutral particles were measured at $R_m=7$ and $R_m=15$, respectively."

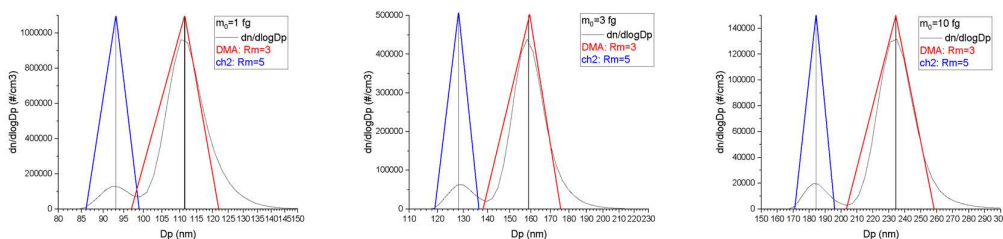
The measurement uncertainty of 0.3 Mm^{-1} has already been stated in section 2.2.

p. 8, L276-277: "Because the fraction of the multiply charged particles is several times smaller compared to the singly charged particles the error is smaller than 1 % and the correction was not applied." Please give the measured fraction and show the arithmetic leading to $<1\%$

The text has been updated "In the mass range of the selected particles, the MAC of nigrosin slowly increases with particle mass (Supplement Fig. S3). For example, the MAC of a 2 fg particle is 2% higher compared to that of a 1 fg particle. Because singly-charged particles represent about 90% of the selected particles, the assumption of constant MAC results in a 0.4% underestimation of the calculated absorption coefficient. For the sake of simplicity, the correction for mass-dependent MAC was not applied."

p. 9, L321-325: In the tandem configuration the CPMA is run at $R_m = 5$ and the DMA at $R_m = 3$. Please state explicitly the resulting mass and mobility transmission windows, and confirm quantitatively that doubly-charged particles ($D_p = 93 \text{ nm}$ for $m_0 = 1 \text{ fg}$, as stated at L312-313) are indeed outside the DMA transfer function at $R_m = 3$, since 93 nm and 110.4 nm differ by only about 16 %.

The transmission windows were approximated with triangular profiles for $R_m=5$ and $R_m=3$ around the measured peak positions. There is a small overlap for the experiment with $m_p=1 \text{ fg}$ particles which accounts for less than 0.2% of the doubly-charged particles.



The text has been updated: "We checked that the transmission window of the DMA did not overlap with the electrical mobilities of multiply-charged particles transmitted by the CPMA."

p. 10, L336-338: "The combined uncertainty is calculated as the square-root of the linear sum of squared standard uncertainty components" - the wording is confusing. Please rephrase as "the root sum of squares of the standard uncertainty components", and state explicitly the assumption that the components are uncorrelated (which is stated in the Table 2 caption but should also appear in the text).

The text is updated: "The combined uncertainty for uncorrelated components is calculated as the root sum of squares of the standard uncertainty components:

$$\sigma = \sqrt{\sum \sigma_i^2} \quad "$$

p. 10, Table 2: (i) Please add the density / mass-equivalent-diameter component (General comment 2) and the particle-loss-correction component (comment on L138-139). (ii) Component C, "Mie calculation & nigrosin refractive index", is given as 2 % from 2 % and 3 % uncertainties in the real and imaginary refractive index; please show the sensitivity coefficients, since these are size- and wavelength-dependent.

The sensitivity parameters for variation of the absorption coefficient for changes of the refractive index are provided in Drinovec et al. (2022b).

The text is updated to show the uncertainties for both wavelengths: "Because of the difference in the refractive index between different batches of nigrosin, each sample property needs to be determined. Here, we used the sample already characterized in a past study (Drinovec et al., 2022). The reported uncertainties in the real and imaginary part of the refractive index of this nigrosin are 2% and 3%, respectively. Using the sensitivity coefficients from Drinovec et al. (2022b), we obtain uncertainties of the calculated absorption coefficient of 2.6% and 2.1% at 450 and 808 nm, respectively."

The uncertainty of Mie calculation & nigrosin refractive index is increased to 3% to include not the average of both wavelengths but the worst-case scenario (450 nm).

(iii) Please indicate for each component whether it is Type A or Type B, as is conventional in a metrological uncertainty budget.

Type B uncertainties are used in Table 2. The Table caption is updated: "Sources of uncertainty (type B) and combined standard uncertainties"

p. 10, L349-350: "We accessed 5 % additional uncertainty" -> "We assessed". Please also state how the 5 % was arrived at.

The text is updated: "When monodisperse nigrosin is produced with DMA, the calculated absorption coefficient must take into account the multiply charged particles which account for 13-27% of absorption. This correction is uncertain because of the deviation between measured and fitted distribution shapes, too high number of triply-charged particles compared to the Boltzmann charge distribution and the fact that multiple charges were not measured at the same time as the absorption coefficient. We assessed 5% additional uncertainty in the calculated absorption coefficient caused by errors in multiple-charge correction."

p. 10, L357-358: The CPC uncertainty is taken as 3 % from the literature. Since both a CPC and an FCAE were available in this study, a direct CPC-versus-FCAE intercomparison would substantiate this value at essentially no extra experimental cost, and would strengthen the traceability argument for the DMA and tandem configurations. Was such a comparison performed?

The instrument intercomparison is added to the supplement:

“S11. Intercomparison of particle concentration measured with CPC and FCAE

Monodisperse singly-charged nigrosin particles were selected with a tandem of CPMA ($m_p=1$ fg, $R_m=5$) and DMA (Sheet flow = 10 l min^{-1} , $D_p=110.4$ nm). Particle concentration was measured using CPC with 0.984 l min^{-1} and FCAE with 0.526 l min^{-1} sample flows as reported at 25°C and 100 kPa . Fig. S11 shows a slope of 0.997 ± 0.006 between particle concentrations measured with FCAE and CPC.

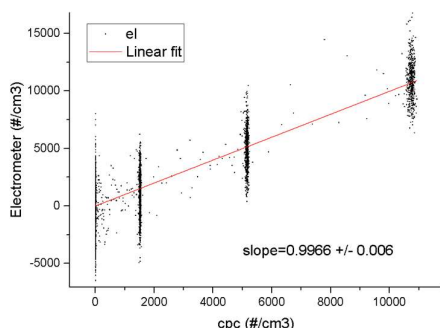


Figure S11. Correlation between measured particle concentrations at 1 s time resolution using FCAE and CPC.”

p. 11, L395-397: The AAC comparison is a useful addition. Since the AAC selects by aerodynamic diameter, converting to mass again requires a density assumption; given the present results this caveat is worth one sentence.

The text is added: “The calculation of physical particle diameter (needed for the calculation of the absorption coefficient) from the aerodynamic diameter requires the knowledge of particle density.”

p. 12, Table 3: The entry “Resolution parameter $R_m = 0.1$ ” for the polydisperse case is not meaningful, as a polydisperse distribution has no resolution parameter. Please replace it with “n/a” or with the geometric standard deviation of the distribution.

Corrected.

p. 12, L424-426 (Conclusions): The tandem configuration is declared “optimal” on the basis of a combined uncertainty of 5.2 % versus 5.8 % for the CPMA alone. Given the size of the individual budget components, this difference is not significant. I would suggest presenting the two as essentially equivalent in uncertainty and distinguishing them on the practical grounds the authors already give (signal level versus experimental simplicity), which is the more defensible and more useful message.

We agree. The text is updated: “Configuration with a CPMA and a FCAE is the simplest calibration method because it requires only a CPMA and a FCAE without the need for post processing. A tandem of the CPMA and the DMA in series avoids the biases caused by neutral and multiply-charged particles and provides high absorption signal. CPMA and tandem selection methods have essentially equivalent uncertainties and are both proposed for calibration of absorption instruments with monodisperse nigrosin”

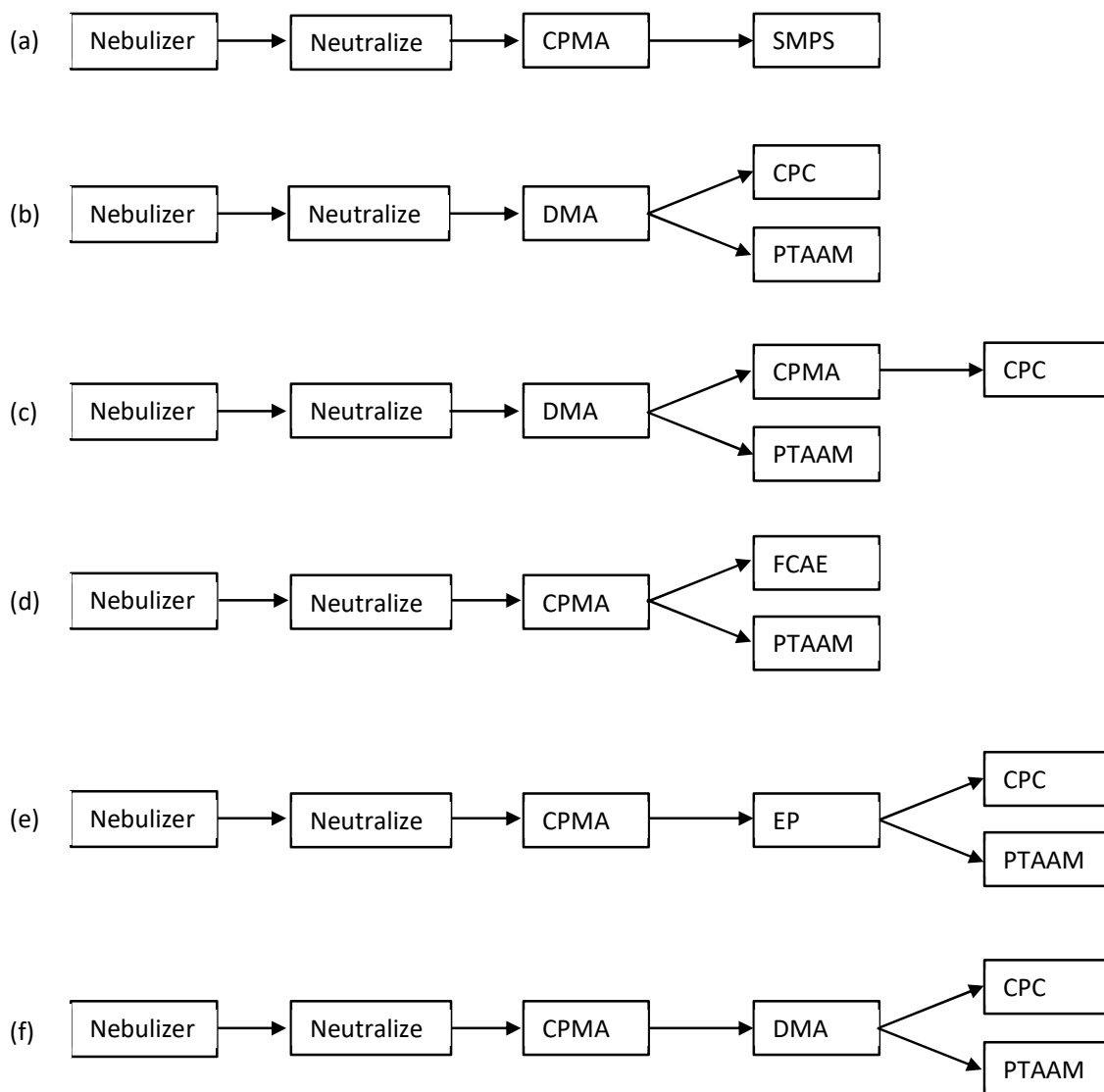
p. 12, L410-412 (Conclusions) and Abstract: "preferable" -> "preferable" (occurs in both the Abstract, L32, and the Conclusions, L411).

Corrected.

Figures 2, 5, 7 and 9: These four schematic diagrams each occupy a separate figure but consist of only four to six boxes. Combining them into a single four-panel figure would save considerable space and, more importantly, would let the reader compare the four configurations at a glance, which is the central comparison of the paper.

A new figure is introduced:

Figure 2. Schematic diagrams of the experimental setup for particle density measurement (a), selection of particles with DMA (b), analysis of multiply-charged particles (c), selection of particles with CPMA (d), analysis of neutral particles transmitted by CPMA (e), selection of particles with a tandem of CPMA and DMA (f).



Figures 3, 4, 6, 8 and 10: The plots are presented in a spreadsheet-style default format. Axis label and tick font sizes are small and inconsistent between panels, and the panel identifiers (A)/(B) sit below the panels rather than within them. Please redraw to a consistent style and at publication resolution, following the AMT figure guidelines. In the bar charts (Figs. 4B, 6B, 8B and 10B) a difference plot (calculated minus measured, in %) as a second panel would convey the key result far more directly than the side-by-side bars.

A difference plot would not show the signal intensity. Signal intensity is important because it limits the resolution used in particle selection.

The images will be prepared for publication following the AMT figure guidelines.

References: The reference list contains an entry "Drinovec, L., Jagodic, U., Pirker, L., et al.: A dual-wavelength photothermal aerosol absorption monitor ..., 2022" and a second entry "Supplement of: A dual-wavelength photothermal aerosol absorption monitor ..., 2022b", but there is no entry labelled "2022a". The in-text citations therefore mix "Drinovec et al. (2022)" and "Drinovec et al. (2022b)", leaving the "b" suffix orphaned. Please relabel the two entries as 2022a and 2022b consistently, or cite the supplement as part of the main reference. Please also check "Romshoo et al, 2022" (L71, p. 2), which is missing a period after "al", and the inconsistent rendering of "Yus-Diez et al., 2021" versus "Yus- Diez et al., 2025" (also L71, p. 2), the latter carrying a stray space.

The errors have been corrected.

Previews of the updated manuscript and supplement are shown below.

Development of a traceable calibration method for photothermal aerosol absorption monitor using monodisperse nigrosin

Luka Drinovec^{1,2}, Jesus Yus-Díez^{1,2}, Tobias Bühlmann³, Maitane Iturrate-Garcia³, Tobias Hammer⁴, Konstantina Vasilatou⁴, Arun Babu Suja⁵, Thomas Müller⁵, Krzysztof Ciupek⁶, Alejandro Keller⁷, Ernest Weingartner⁷, Jorge Saturno⁸, Maria I. Gini⁹, Kostas Eleftheriadis⁹, John Backman¹⁰, Eija Asmi¹⁰, Griša Močnik^{1,2,11}

¹Center for Atmospheric Research, University of Nova Gorica, Nova Gorica, 5270, Slovenia

²Haze Instruments d.o.o., Ljubljana, 1000, Slovenia

³Laboratory Gas Analysis, METAS, Federal Institute of Metrology METAS, Bern, 3003, Switzerland

⁴Particles and Aerosols Laboratory, Federal Institute of Metrology METAS, Bern, 3003, Switzerland

⁵Atmospheric Microphysics Department, Leibniz Institute for Tropospheric Research, 04318 Leipzig, Germany

⁶Air Quality and Aerosol Metrology Group, National Physical Laboratory, Teddington, TW11 0LW, UK

⁷University of Applied Sciences and Arts Northwestern Switzerland, CH-5210 Windisch, Switzerland

⁸Physikalisch-Technische Bundesanstalt, 38116 Braunschweig, Germany

⁹Institute of Nuclear Technology and Radiation, NCSR Demokritos, Paraskevi, Attiki, 15310, Greece

¹⁰Finnish Meteorological Institute, 00560 Helsinki, Finland

¹¹Department of Environmental Sciences, Jozef Stefan Institute, Ljubljana, 1000, Slovenia

Correspondence to: Luka Drinovec (luka.drinovec@ung.si)

Abstract. The absorption coefficient of light absorbing aerosols is difficult to measure with low uncertainty and improvements of measurement procedures based on traceable calibration are needed. Reducing measurement artefacts can be achieved by using in-situ direct measurement methods such as photo-acoustic spectroscopy and photo-thermal interferometry. We developed a calibration method based on monodisperse nigrosin particles and showed how to make it traceable to primary units. Nebulized nigrosin forms nearly spherical particles for which it is possible to calculate the absorption coefficient in the UV-NIR range using Mie theory. In the presented study, we have experimentally tested size- and mass-selection techniques using a differential mobility analyzer (DMA), a centrifugal particle mass analyzer (CPMA) and a tandem of both in series to compare Mie-calculated absorption coefficient with the measured one using the photo-thermal aerosol absorption monitor PTAAM, traceably calibrated with NO₂. We observed that the nigrosin particle density changes with particle size, which is due to the irregular shape of the particles produced by our nebulizer. For the irregular particles the electrical mobility diameter is larger than the particle physical diameter, which results in an overestimated Mie calculated absorption coefficient. Mass-equivalent diameter based on the material density of 1.6 g cm⁻³ was used instead. The difference between Mie calculated and measured absorption coefficient at 450 nm for different monodisperse selection techniques was between +5% to +11% for the DMA, -2% to -3% for the CPMA and +2% to +8% for tandem of the CPMA and the DMA. Combined standard uncertainties (coverage factor $k=1$) for PTAAM calibrated with monodisperse nigrosin particles selected by the DMA, the CPMA, and the CPMA and the DMA tandem are 7.5%, 6.6% and 6.0%, respectively. The optimal classification setup is a tandem of the CPMA and the DMA which avoids the systematic bias of both neutral (in the CPMA) and multiply-charged (in the DMA) particles and provides a high enough absorption signal. Experimentally the simplest selection method is based on the CPMA.

List of Abbreviations

PTAAM	Photo-thermal aerosol absorption monitor
PTI	Photo-thermal interferometry
PAS	Photo-acoustic spectroscopy
TMPG	Traceable mobile permeation generator
IR	Infrared
UV	Ultraviolet
DMA	Differential mobility analyzer
D_p	Electrical mobility diameter
CPMA	Centrifugal particle mass analyzer
D_m	Mass-equivalent diameter
EMS	Extinction minus scattering
CAPS	Cavity attenuated phase shift
FCAE	Faraday cup aerosol electrometer
CPC	Condensation particle counter
EP	Electrostatic precipitator
b_{abs}	Aerosol absorption coefficient
m_p	Particle mass
D_g	Physical or geometric diameter
ρ_0	Material density of nigrosin
ρ_{eff}	Effective particle density calculated with D_p and m_p
R_m	Resolution parameter $R_m = m_p / FWHM$

1. Introduction

Absorption and scattering of sunlight by ambient aerosol influence the Earth radiation budget and accurate and precise measurements are required to validate climate models (Bond et al., 2013; Zanatta et al., 2016; Saleh et al., 2018; Samset et al., 2018; Szopa et al., 2021). The aerosol absorption coefficient remains challenging to measure with low uncertainty and improvements in the measurement procedures based on a traceable calibration are needed (Vasilatou et al., 2025). The most common absorption instruments are filter photometers which measure attenuation of light transported through the filter on which particles are continuously collected. These methods suffer from various artefacts caused by the interaction of the particles with the filter matrix, such as cross-sensitivity to scattering (Collaud Coen et al., 2010), filter loading effect (Virkkula et al., 2007; Drinovec et al., 2015), multiple scattering within the filter (Weingartner et al., 2003), and size dependent response (Moteki et al., 2010; Yus-Díez et al., 2021; Romshoo et al., 2022; Drinovec et al., 2022a; Yus-Díez et al., 2025). Such artefacts can bias derived intensive properties (eg., single scattering albedo) and aerosol absorption optical depth, propagating into uncertainties in aerosol direct radiative forcing.

Reducing measurement artefacts is possible by using methods which are in-situ and direct, such as photo-acoustic spectroscopy (PAS; Arnott et al., 1999) and photo-thermal interferometry (PTI; Sedlacek, 2006; Drinovec et al., 2022a). Measurement methods require calibration, which is usually performed with absorbing gases. The most common absorbing gas used for calibration of PAS is NO_2 , which absorbs strongly in the lower half of the visible wavelength range (Arnott et al., 2000; Schnaiter et al. 2023). However, NO_2 absorption in the near-IR region is too low to allow calibration with sub-ppm concentrations. The main drawback with NO_2 for calibration is reaction with the surface material, which reduces sample concentration in tubes and containers (Flores et al., 2021) and complicates the realization of stable, traceable reference concentrations.

Ozone has also been used for calibration of photo-acoustic instruments; however, problems with photo-dissociation and interaction with N_2 have been reported (Bluvshstein et al., 2017; Davies et al., 2018; Fischer and Smith, 2018). Recently, Corbin et al. (2025) proposed a calibration with O_2 at 760 nm, enabling calibration with ambient air. The method is limited to a single wavelength.

An alternative calibration procedure is based on absorbing particles. For spherical particles with known size distribution and refractive index it is possible to calculate the absorption coefficient using Mie theory (Mie, 1908). A popular calibration material is a water-soluble version of nigrosin which can be nebulized to generate polydisperse spherical particles that absorb over a wide spectral range from the UV to the near-IR. The refractive index of the nigrosin sample must be predetermined, for example by using spectroscopy on thin films (Bluvshstein et al., 2017; Drinovec et al., 2022b). Care should be taken due to differences in optical properties between batches of nigrosin (Foster et al., 2019). Foster et al. (2019) observed a good agreement between calculated and measured absorption of polydisperse nigrosin. Drinovec et al. (2022a) used polydisperse nigrosin to transfer the calibration from the "green" (532 nm) to the IR channel (1064 nm).

Calibration uncertainty can be further reduced by using monodisperse nigrosin particles (Radney and Zangmeister, 2015). To this end, the particle size has been selected using either an aerodynamic aerosol classifier (AAC) (Lawson et al., 2025) or a differential mobility analyzer (DMA) (Lack et al., 2006; Bluvshstein et al., 2017; Cotterell et al., 2020; Kuula et al., 2025).

Here we develop and evaluate a calibration method for aerosol absorption instruments based on monodisperse nigrosin particles. In this study, we experimentally tested size- and mass- selection techniques using a DMA, a centrifugal particle mass analyzer (CPMA) and a tandem configuration of both in series and compared the calculated absorption coefficient at 450 nm with the measured absorption by a NO₂-calibrated instrument. The DMA provides electrical mobility selection, whereas the CPMA enables mass selection; their tandem use constrains both size and mass simultaneously, improving control over particle properties used for calibration. We assess the performance of these approaches and discuss implications for reducing calibration uncertainty and improving intercomparability across absorption measurement techniques.

2. Materials and methods

2.1 Chemicals

Nigrosin (Acid black 2, Nigrosin water soluble, CAS 8005-03-6, Lot # SHBL0637) and ammonium sulfate (Mascagnite, ReagentPlus®, CAS 7783-20-2) were obtained from Sigma-Aldrich. Aqueous solutions of nigrosin and ammonium sulfate were prepared by dissolving chemicals in ultra-pure water (Milli-Q). Nigrosin solutions labeled Nig2 (0.1 g L⁻¹) and Nig3 (1 g L⁻¹) have been used for nebulization.

Polystyrene beads (Sigma-Aldrich 433025ML-F) with a particle diameter of 95 nm ± 4% and a density of 1.05 g cm⁻³ were used to validate particle size and mass measurements.

A bottle with a nominal amount fraction of 1 μmol mol⁻¹ NO₂ in synthetic air (Traceline, Messer Schweiz AG) was acquired for the PTAAM calibration. For calibration a Tedlar® SCV gas sampling bag (Sigma-Aldrich) was filled with 10 L of sample from the bottle.

2.2 Aerosol absorption measurements

The absorption coefficient was measured using the version P02 of the PTAAM. The PTAAM P02 is based on version P01 described in Drinovec et al. (2022a). Instruments differ in the pump lasers used for thermal excitation, with laser diodes (450 nm and 808 nm) being used in P02 instead of diode-pumped solid-state lasers (532 nm and 1064 nm).

The instrument was calibrated following the procedure described by Drinovec et al. (2022a). In short, the 450 nm channel was calibrated using a premixed sample of about 1 μmol mol⁻¹ NO₂ in synthetic air from the Tedlar bag filled with a bottle sample. The exact amount fraction of the premixed sample was measured using a NO₂ cavity attenuated phase shift analyzer (CAPS, Aerodyne Research Inc., USA), which was calibrated using the so-called traceable mobile permeation generator (TMPG, Haerri et al., 2017). NO₂ absorption was calculated based on the spectrum at 450 nm (pump beam) measured with

a CCS100/M spectrometer (Thorlabs, USA) and the NO₂ absorption spectrum from Vandaele et al. (2002).

The 808 nm channel was calibrated using polydisperse nigrosin particles transferring the calibration from the blue channel (450 nm) using the Mie calculated $b_{\text{abs}_808 \text{ nm}}/b_{\text{abs}_450 \text{ nm}}$ ratio. Absorption measurements with the PTAAM were corrected for losses, 2% for NO₂ and 5% for particles (Supplement S7).

The PTAAM was running with 2-minute intervals containing 45 s of background absorption measurement, which was then subtracted from the measured total absorption. Typical instrument noise under controlled laboratory conditions (using filtered room air) is shown in Fig. 1 with 15 min average noise of 0.03 Mm⁻¹. During actual experiments there are influences caused by e.g. pressure oscillations due to several instruments connected to the sample line, or by a possibility of larger variation in room temperature. Actual measurement uncertainty for 15 min experiments of 0.3 Mm⁻¹ was determined by the variation of the absorption coefficient for the filtered sample.

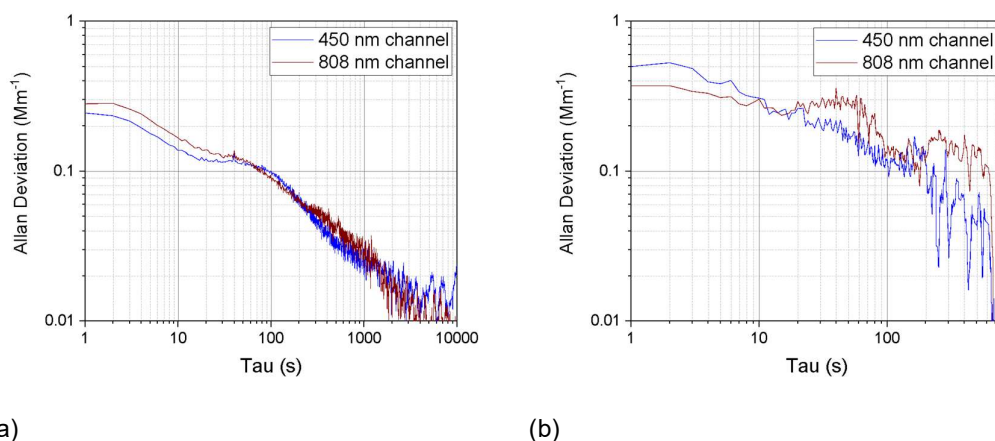


Figure 1. Allan deviation plot for absorption coefficient measured with PTAAM version P02 using filtered room air under stable laboratory conditions (a) and during actual experiments (b). Tau denotes the observation time.

2.3 Aerosol generation and classification

Nigrosin and ammonium sulfate aerosols were generated using the ATM 226 nebulizer (Topas GmbH, Germany) at sample flow of 3 L min⁻¹. The nebulizer was connected to a diffusion drier to reduce relative humidity to $33 \pm 3\%$

Particle mass was measured/selected using a centrifugal particle mass analyzer (CPMA, model Mk II, Cambustion Ltd.), as described by Olfert and Collings (2005). CPMA classifies particles by mass-to-charge ratio using opposing centrifugal and electric forces. For a given rotational speed and applied voltage only particles with selected mass-to-charge ratio are transmitted. The distribution width is defined by a resolution parameter $R_m = m_p/\text{FWHM}$, where m_p is the selected particle mass and FWHM is full width at half maximum of the distribution. The CPMA was operated with positive polarity.

Particle electrical mobility diameter was measured/selected using a Vienna-type differential mobility analyzer (DMA, model 2083; TSI Inc., USA). The DMA was operated with negative polarity.

A neutralizer with a Kr-85 source (model 3077A, TSI Inc., USA) was installed upstream of the CPMA and DMA to obtain the Boltzmann charge distribution in the aerosol sample. Particle charge was measured with Faraday-cup aerosol electrometer (FCAE, model 3068B from TSI Inc, USA). Particle number was measured with a condensation particle counter (CPC, model 3750; TSI Inc., USA).

Conductive tubes with internal diameter of 6.35 mm were used. The length of the tubes after the size selection were between 1 and 2 meters. Sample flows of the instruments were 1 l min⁻¹ for CPC, and 0.5 l min⁻¹ for FCAE and PTAAM.

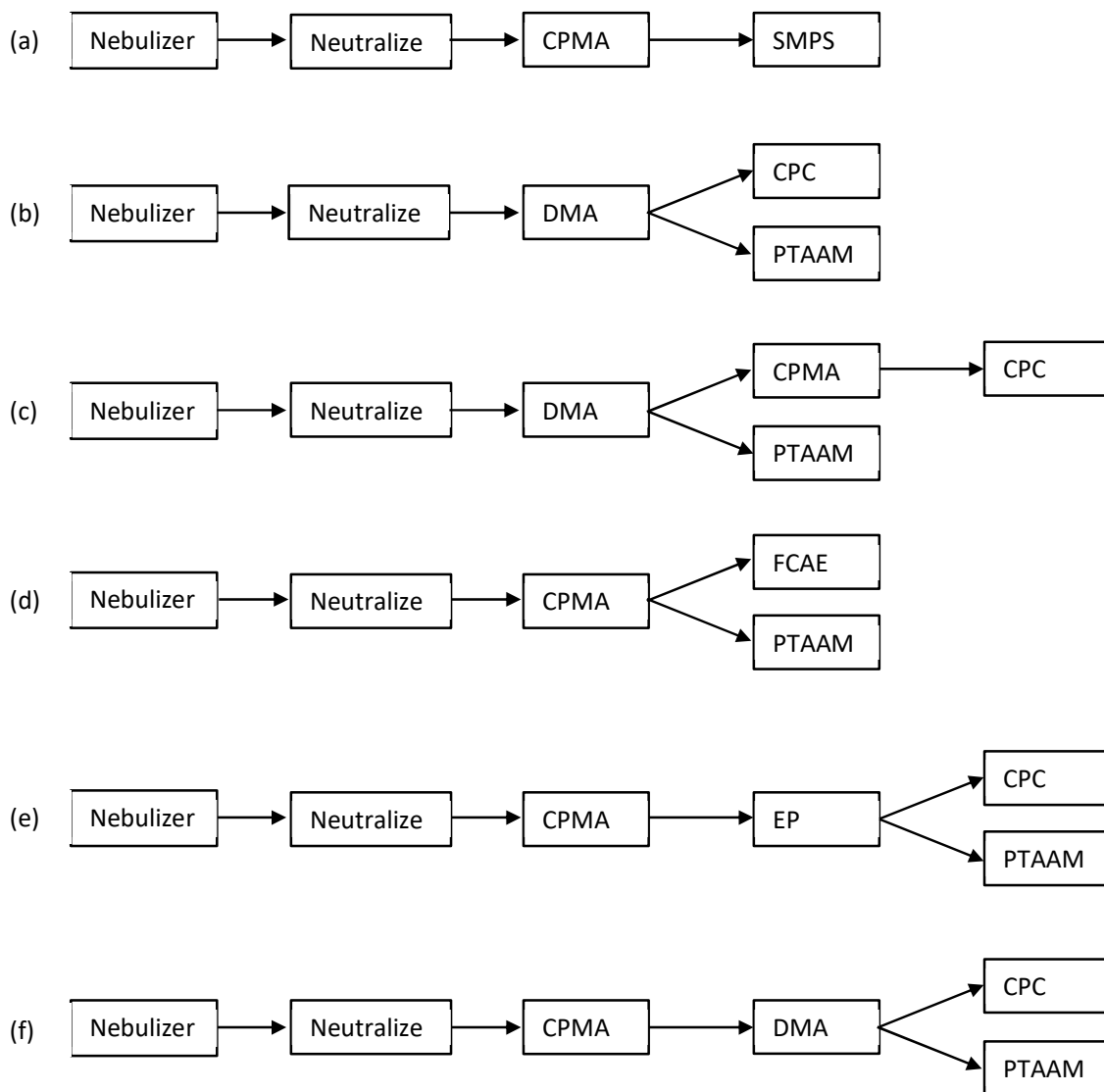


Figure 2. Schematic diagrams of the experimental setup for particle density measurement (a), selection of particles with DMA (b), analysis of multiply-charged particles (c), selection of particles with CPMA (d), analysis of neutral particles transmitted by CPMA (e), selection of particles with a tandem of CPMA and DMA (f).

2.4 Data evaluation

All aerosol concentrations were recalculated and reported at conditions of temperature and pressure of 25 °C and 100 kPa.

Mie calculations were performed using MATLAB routines for homogeneous spheres (Mätzler, 2002). The refractive index of the Nigrosin batch used in this study had been determined previously over a large interval of wavelengths including 450 nm and 808 nm, and was taken as $1.58 + i0.167$ at 450 nm and $1.78 + i0.119$ at 808 nm (Drinovec et al., 2022b) for the calculation of absorption coefficients.

Measurement noise (standard error) was 0.1-0.2% for the CPC, 0.5-1.5% for the FCAE and 0.3-0.5% for the PTAAM. A typical experiment time series is shown in Supplement (Fig. S1).

3. Results

3.1 Density of nigrosin particles

Particle density was measured for monodisperse particles whose mass m_p was selected by the CPMA and electrical mobility diameter D_p measured by the SMPS as shown in Fig. 2a. The CPMA was run at $R_m=10$ which resulted in a distribution width of 10% of their selected mass. The number size distributions (Fig. 3a) show two peaks corresponding to the electrical mobility diameter of the doubly- and singly-charged particles. The distributions were fitted with two Gauss functions to obtain the peak electrical mobility diameter. For nigrosin, the effective density increases with particle mass (Fig. 3b) toward the nominal value of 1.6 g cm^{-3} (Moteki et al., 2010). Similar behavior was observed for the nebulized ammonium sulfate (Supplement - Fig. S2) but not for the 95 nm polystyrene beads, where the measured density agreed with the nominal value within 0.8% (Supplement – Table S1). The low experimental values in the effective particle density for nigrosin might be due to the non-spherical shape of the nigrosin particles as observed in some of the filter samples analyzed by SEM (Supplement – Fig. S5). Non-spherical particles could form inside the drier by fusion of semi-dried particles. This process might be enhanced by the non-dried inlet air used in our nebulizer. Non-spherical particles have a larger electrical mobility diameter compared to the particle physical diameter (DeCarlo et al., 2012) which results in a lower effective density than the material density of 1.6 g cm^{-3} .

For particles which are not completely spherical it is better to use the mass-equivalent particle diameter D_m rather than D_p for Mie calculations. D_m is calculated as

$$D_m = \left(\left(\frac{6}{\pi} \right) \left(\frac{m_p}{\rho_0} \right) \right)^{1/3}, \quad (1)$$

where m_p is the particle mass and ρ_0 the material density of nigrosin. D_m is smaller than D_p for all the measured sizes by about 4 nm (Table 1). The absorption coefficients calculated based on the measured electrical mobility diameter results in 5-20% higher values compared to calculations based on D_m .

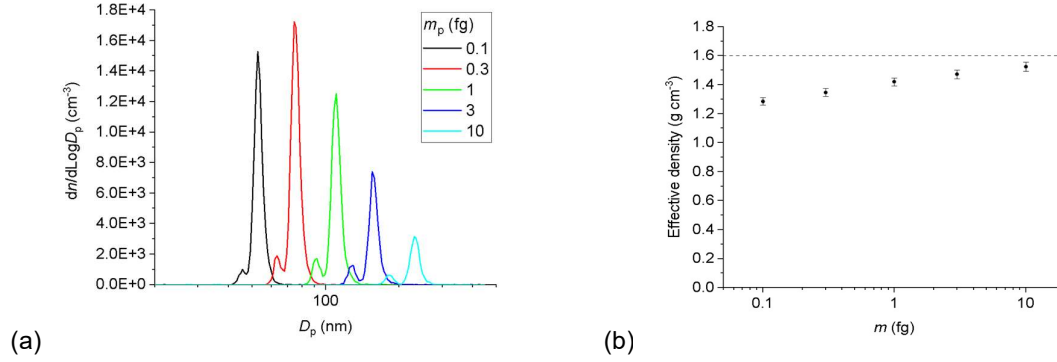


Figure 3. Electrical mobility number size distributions for nigrosin particles at different target masses (a), shown without correction for multiple charge. Effective nigrosin particle density (b) as a function of particle mass. Error bars represent measurement uncertainty of 9% (coverage factor $k=1$; 68% confidence interval). The dashed line represents a density of 1.6 g cm^{-3} , as reported by Moteki et al. (2010).

Table 1. Measured electrical mobility diameter D_p , effective density and mass equivalent diameter D_m for nigrosin particles selected according to particle mass (m_p). Errors represent $k=1$ uncertainties.

m_p (fg)	D_p (nm)	Effective density (g cm^{-3})	D_m (nm)	$D_p - D_m$ (nm)
0.1 ± 0.002	53.0 ± 1.6	1.28 ± 0.03	49.2 ± 0.5	3.8 ± 2.1
0.3 ± 0.006	75.2 ± 2.3	1.35 ± 0.03	71.0 ± 0.7	4.2 ± 3.0
1 ± 0.02	110.4 ± 3.3	1.42 ± 0.03	106.1 ± 1.1	4.3 ± 4.4
3 ± 0.06	157.4 ± 4.7	1.47 ± 0.03	153.0 ± 1.5	4.4 ± 6.2
10 ± 0.2	232.3 ± 7.0	1.52 ± 0.03	228.5 ± 2.3	3.8 ± 9.3

3.2 Absorption of polydisperse nigrosin particles

For a polydisperse distributions measured by SMPS, the absorption coefficients calculated for each size bin were summed. These depend on the correct charge inversion algorithm which predicts the total particle number concentration from that obtained for singly-charged particles corrected for multiply-charged particles and diffusion losses using the instrument's internal algorithm. The calculated number and volume size distribution are shown in Fig 4a.

The volume size distribution shows the presence of particles above 350 nm, which represent a non-negligible fraction of total volume. Experiments with an impactor (not shown) failed to reduce the number of these particles. We later found out that the artefact was present only when a short SMPS scan duration of 1 minute was used. This indicates that some residual particles were influencing the measurement. For the Mie calculation of the sample absorption, only particles smaller than 400 nm were used which resulted in 5% lower absorption coefficient.

Because of the nigrosin density size dependence (Fig. 3b), a size distribution based on the mass-equivalent diameter D_m was used for the Mie calculation. The calculated absorption coefficient was 10% larger than the measured one at 450 nm (Fig. 4b). Because of the charge inversion, the uncertainty of particle number concentration for the polydisperse size distribution is 10% (Wiedensohler et al., 2018) which strongly influences the combined uncertainty for the calibration with polydisperse nigrosin (Table 2).

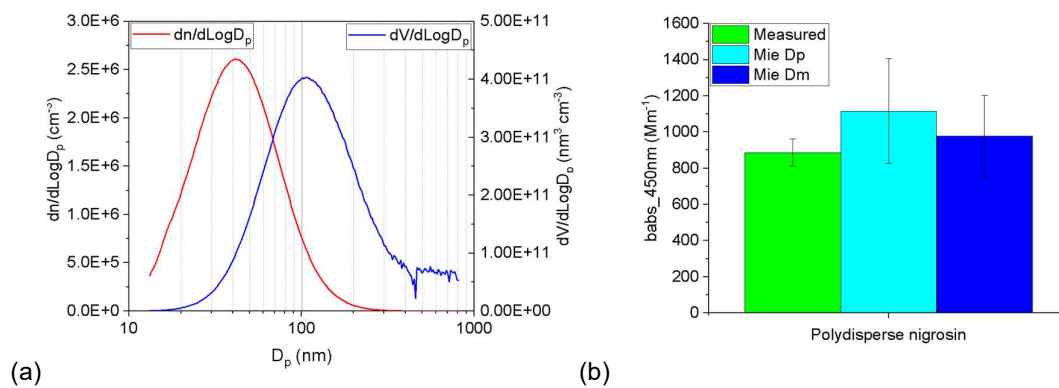


Figure 4. Measured particle size distributions of nigrosin aerosols (solution Nig2) shown as number-based and volume-based distributions as a function of electrical mobility diameter (a). Comparison between measured absorption coefficient and the absorption coefficient calculated using Mie theory based on the particle electrical mobility diameter D_p and mass equivalent diameter D_m (b). Error bars represent $k=2$ uncertainty. Calculated absorption coefficients are not significantly different from the measurement.

3.3 Monodisperse nigrosin particles selected with a differential mobility analyzer (DMA)

The first particle selection approach investigated in this study is based on size selection, performed using electrical mobility classification with a DMA. For each selected electrical mobility diameter, the particle number concentration and absorption coefficient were measured using a CPC and a PTAAM, respectively (Fig. 2b). DMA-based size selection is likely to remain the most common. However, electrical mobility selection intrinsically includes both singly charged particles at the target electrical mobility diameter and larger multiply charged particles with the same mobility, which must be considered when interpreting size-resolved number, mass, and absorption measurements. To reduce the fraction of multiply-charged particles (and the corresponding error), we shifted the selection to the descending side of the volume size distribution. This was achieved by nebulizing a more diluted nigrosin solution (Fig. 5a).

We quantified the bias due to the multiply-charged particles, transmitted by the DMA, on the measured absorption coefficient. The number of multiply-charged particles was determined by measuring the particle mass distribution using a CPMA followed by a CPC downstream of the DMA, essentially inserting the CPMA between the DMA and CPC in Fig. 2b. The numbers of singly-, doubly- and triply-charged particles were calculated by fitting Gauss functions to the measured distribution and integrating each peak to obtain the number of these particles (Supplement – Fig. S4). Mass of the singly-charged particles (m_0) corresponds to the peak position of the left-most peak. Because CPMA selects particles by their mass-to-charge ratio, the actual mass of the doubly-charged particles is a double of the second peak position and triple for the third peak (Table S2). The absorption was then calculated as the sum of the absorption of singly-charged particles with mass m_0 , doubly-charged particles with mass $3.5*m_0$ and triply-charged particles with mass $6.6*m_0$. In our experiment, multiply-charged particles accounted for between 13% and 27% of the total light absorption (Table S2).

To obtain sufficient signal when using a more diluted nigrosin solution for nebulization a relatively broad size distribution was produced by using a low sample-to-sheet flow ratio of $1.5 \text{ L min}^{-1}/5 \text{ L min}^{-1}$. Because of the distribution width there is a positive bias when calculating the absorption coefficient using the monodisperse aerosol approach: 5%, 3% and 7% for 0.7, 2.4, and 5.7 fg, respectively. For the selected particle distributions, we measured an absorption coefficient of approx. 20 Mm^{-1} (Fig. 5b). Calculated absorption coefficients based on D_p are higher than measurement by 26%, 34% and 30% for particles mass of 0.7, 2.4, and 5.7 fg, respectively. Calculations based on D_m are higher than measurement by 5%, 11% and 7%. Due to particle deviation from the spherical shape D_p is overestimated (DeCarlo et al, 2004) and produces higher absorption compared to calculation based on D_m . The calculated values were compared to measured values using $k=2$ uncertainties (Table 2). Only babs for 5.7 fg particles calculated using D_p was significantly different from the measured one.

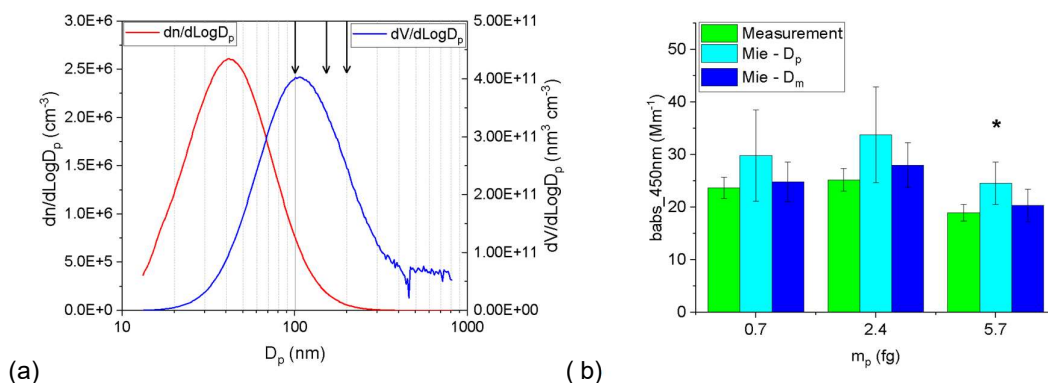


Figure 5. Measured particle size distributions of nigrosin aerosols, generated by nebulizing nigrosin solution Nig2 (0.1 g L^{-1}), shown as number based and volume-based distributions as a function of electrical mobility diameter. Arrows show the selected electrical mobility diameters (a). Comparison between measured absorption coefficient and the absorption coefficient calculated using Mie theory based on the particle electrical mobility diameter D_p and mass-equivalent diameter D_m (b). Error bars represent $k=2$ uncertainty. * denotes statistically significant difference from the measurement.

3.4 Monodisperse nigrosin particles selected with a centrifugal particle mass analyzer (CPMA)

The particles were selected with a CPMA and their charge is measured with a FCAE, as shown in Fig. 2d. CPMA select particles by their mass-to-charge ratio. For CPMA selected particles the mass of the charged particles is directly proportional to their charge, so that the measured current closely corresponds to the particle mass concentration. In the mass range of the selected particles, the MAC of nigrosin slowly increases with particle mass (Supplement Fig. S3). For example, the MAC of a 2 fg particle is 2% higher compared to that of a 1 fg particle. Because singly-charged particles represent about 90% of the selected particles the assumption of constant MAC results in a 0.4% underestimation of the calculated absorption coefficient. For the sake of simplicity, the correction for mass-dependent MAC was not applied.

The width of the mass distribution of the CPMA-selected particles depends on the resolution parameter R_m . At low R_m , we obtain higher particle number and absorption, together with neutral particles that leak through the classifier. These neutral particles are expected to have low mass, but their exact number and corresponding absorption is difficult to predict (Johnson et al., 2013). The relative number of neutral particles can be reduced by selecting the particles on the ascending part of the particle volume distribution. This was achieved by nebulizing a more concentrated nigrosin solution (Fig. 7a).

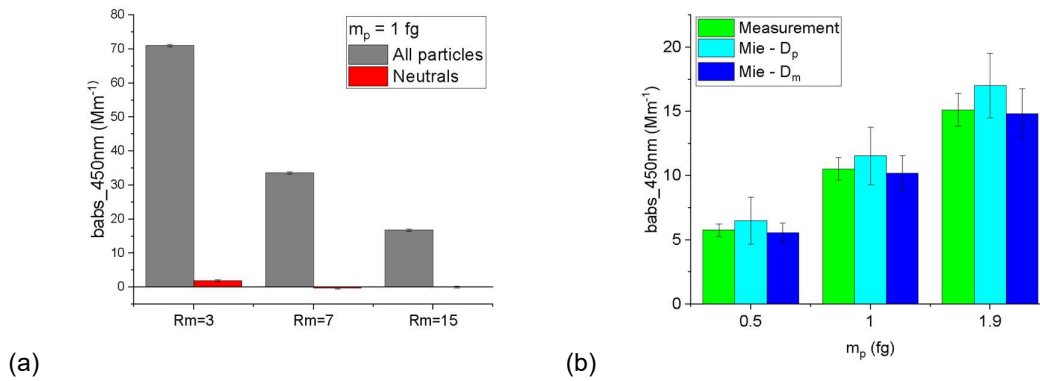


Figure 6 . The absorption coefficient of total and neutral-only particles transmitted through the CPMA for different values of the resolution parameter R_m (a). Comparison between measured absorption coefficient and the absorption coefficient calculated using Mie theory based on the particle electrical mobility diameter D_p and mass-equivalent diameter D_m by means of a CPMA with $R_m=15$ (b). Error bars represent $k=2$ uncertainty. Calculated absorption coefficients are not significantly different from the measurement. Calculated absorption coefficients are not significantly different from the measurement.

Neutral particles were analyzed by running the sample through an electrostatic precipitator (EL) as shown in Fig. 2e. DMA set to a voltage of -10000 V with the sheath flow off was used as a high efficiency electrostatic precipitator. When running the CPMA at $R_m=3$, neutral particles represent 2.6% of the total absorption (Fig. 6a). The absorption coefficients of -0.2 Mm⁻¹ and 0.0 Mm⁻¹ for neutral particles were measured at $R_m=7$ and $R_m=15$, respectively. At higher R_m values, the absorption due to neutral particles is negligible. A final comparison between measured and calculated absorption was performed for $R_m=15$ (Fig. 6b). There is a good agreement between the measured and calculated absorption based on D_m which is lower by 2-3%. Absorption coefficients based on D_m are higher compared to measurements by 13%, 10% and 13% for the particle mass of 0.5, 1 and 1.9, respectively. None of the calculated values differed significantly from the measurements. As discussed above, the $R_m=7$ setting would be sufficient to eliminate neutral particles and would double the absorption signal.

3.5 Monodisperse nigrosin particles selected with the tandem CPMA and DMA setup

In the tandem setup, particles are first selected by mass using the CPMA and then filtered by setting the DMA to the peak electrical mobility diameter for the selected mass point (Fig. 2f). The peak electrical mobility diameters were measured with SMPS for each selected mass point before the tandem experiment. For example, the CPMA set to $m_p=1$ fg was paired with DMA set to D_p of 110.4 nm. The main advantage of this setup is the elimination of neutral and multiply-charged particles. Neutral particles are filtered out by the DMA. Multiply-charged particles are likewise not transmitted because the CPMA and DMA behave differently: in the CPMA multiply-charged particles have multiple masses ($2*m_0$, $3*m_0$, ...). Doubly charged particles with $m_p=2$ fg have electrical mobility diameter of 139.1 nm. Because of the double charge these particles have the same electrical mobility as singly-charged particles with $D_p=92.7$ nm and are filtered out by the DMA set to 110.4 nm. Calculation of electrical mobility of multiply-charged particles is showed in the Supplement S8.

Because the neutral particles are removed, it is possible to set CPMA to lower resolution R_m and to obtain higher absorption signal. We run the classifiers CPMA with $R_m=5$ and DMA with $R_m=3$. We checked that the transmission window of the DMA did not overlap with the electrical mobilities of multiply-charged particles transmitted by the CPMA. Without neutral and multiply charged particles it was possible to measure the particle concentration using CPC instead of FCAE with the advantage of lower measurement noise. The results show that the calculated absorption based on D_m is higher than the measured one by 8%, 5% and 2% for 1 fg, 3 fg and 10 fg particles, respectively (Fig. 7b). Calculated absorption coefficient based on D_p is higher than measured by 24%, 17% and 11% for the selected particle masses. None of the calculated values differed significantly from the measurements.

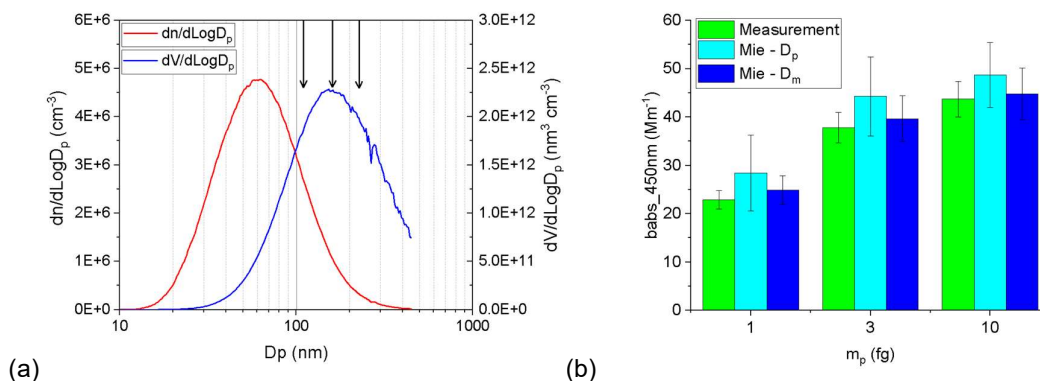


Figure 7. Measured particle size distributions of nigrosin aerosols, generated by nebulizing nigrosin solution Nig3 (1 g L⁻¹), shown as number based and volume-based distributions as a function of electrical mobility diameter. Arrows show the selected electrical mobility diameters (a). Comparison between measured absorption coefficient and the absorption coefficient calculated using Mie theory based on the particle electrical mobility diameter D_p and mass-equivalent diameter D_m (b). Error bars represent $k=2$ uncertainty. Calculated absorption coefficients are not significantly different from the measurement.

3.6 Uncertainty analysis of the PTAAM (version P02) for different calibration schemes

The uncertainty in the absorption coefficient measured with the PTAAM results from calibration method and instrumental uncertainties (Table 2). The combined uncertainty for uncorrelated components is calculated as the root sum of squares of the standard uncertainty components:

$$\sigma = \sqrt{\sum \sigma_i^2} \quad (2)$$

The coverage factor k determines the confidence in the data points within a certain standard deviation value. For normal distribution $k=1$ means there is a confidence that 68% of data points lie within one standard deviation, while $k=2$ means a confidence that 95% of the data points would lie within two standard deviations. The calibration of the 450 nm channel depends strongly on the uncertainty in the NO₂ amount fraction in the calibrating gas mixture. It was measured with NO₂ CAPS calibrated using NO₂ mixtures produced by the TMPG. For TMPG the standard uncertainty of the NO₂ amount fraction is below 2% (Haerri et al., 2017). Absorption cross-section of NO₂ is calculated using the reference absorption spectrum from (Vandaele et al., 2002; Orphal and Chance, 2003) and the emission spectrum of 450 nm laser diode (see Supplement S9). The uncertainties for these components are 2% and 1% respectively.

Because of differences in the refractive index between different batches of nigrosin, each sample properties need to be determined. Here, we used the sample already characterized in the past study (Drinovec et al., 2022b). The reported uncertainties in the real and imaginary part of the refractive index of this nigrosin batch are 2% and 3%, respectively. Using the sensitivity coefficients from Drinovec et al. (2022b) we obtain the uncertainties of the calculated absorption coefficient of 2.6% and 2.1% at 450 and 808 nm, respectively.

Mie calculation is based on the physical particle diameter. For non-spherical particles the electrical mobility diameter is larger than the physical particle diameter (DeCarlo et al., 2004). This results in an overestimated absorption coefficient when D_p is used for Mie calculation with the resulting uncertainty increasing with the decreasing particle mass from 5% at 10 fg to 13% at 1 fg.

The material density of 1.6 g cm⁻³ for nigrosin as reported by Moteki et al. (2010) was selected with instruments similar to DMA and CPMA, which would result in an uncertainty of 9.2%. If both instruments are calibrated with the same polystyrene beads, the uncertainty in the measured density is much lower as validated by our measurements of polystyrene beads density (Supplement S2). The uncertainty of the absorption coefficient based on D_m is the same as the assumed uncertainty of the material density of 2%.

The uncertainty in the measured number size distribution by the SMPS, which affects the calculation of polydisperse nigrosin absorption, is 10% (Wiedensohler et al., 2018). The influence of the size distribution on the absorption ratio $b_{\text{abs}}(808 \text{ nm})/b_{\text{abs}}(450 \text{ nm})$ is lower, having 4% uncertainty.

When monodisperse nigrosin is size-selected with a DMA, the calculated absorption coefficient must take into account the multiply charged particles which account for 13-27% of the absorption. This correction is uncertain because of the deviation between measured and fitted distribution shapes, too high number of triply-charged particles compared to the Boltzmann charge distribution and the fact that multiple charges were not measured at the same time as the absorption coefficient. We assessed 5% additional uncertainty in the calculated absorption coefficient caused by errors in multiple-charge correction.

Table 2. Sources of uncertainty and combined standard uncertainties (for 68% and 95% confidence intervals CI) of the absorption coefficient of PTAAM, which was traceably calibrated with gas and particles. Combined uncertainties were calculated using independent uncertainty components. The range of uncertainties results from the uncertainty differing with particle size.

Source of uncertainty	Type	Uncertainty <i>k</i> =1 (68% CI)	Uncertainty <i>k</i> =2 (95% CI)
A: NO ₂ amount fraction	B	2%	
B: Absorption cross-section of NO ₂	B	2%	
C: Emission spectrum of laser diode	B	1%	
D: Mie calculation & nigrosin refractive index	B	3 %	
E: Influence of particle size distribution error on absorption ratio babs(808 nm)/babs(450 nm)	B	4%	
F: Mie calculation based on D_p	B	5%-13%	
G: Mie calculation based on D_m	B	2%	
H: Particle number size distribution measured by SMPS	B	10%	
I: CPC measurement uncertainty	B	3%	
J: FCAE measurement uncertainty	B	4%	
K: DMA selection – remaining uncertainty after charge correction	B	5%	
L: CPMA mass uncertainty	B	2%	
M: Scattering and absorbing gases	B	1%	
N: Stability of PTAAM response	A	3%	
Combined uncertainties	Contributions		
PTAAM 450 nm: calibration with NO ₂	A, B, C, M, N	4.4%	8.8%
PTAAM 808 nm: NO ₂ + polydisperse nigrosin	A, B, C, D, E, M, N	6.6%	13.3%
Polydisperse nigrosin - D_m	D, G, M, N	10.9%	21.8%
Polydisperse nigrosin – D_p	F, G, M, N	13.3%	26.7%
Monodisperse nigrosin - D_m – DMA	D, G, H, J, M, N	7.5%	15.1%
Monodisperse nigrosin – D_m - CPMA	D, G, I, K, M, N	6.6%	13.1%
Monodisperse nigrosin – D_m - CPMA + DMA	D, G, H, K, M, N	6.0%	12.0%
Monodisperse nigrosin - D_p – DMA	D, F, H, J, M, N	8.8%-14.9%	17.7%-29.8%
Monodisperse nigrosin – D_p - CPMA	D, F, I, K, M, N	8.0%-14.4%	16.0%-28.8%
Monodisperse nigrosin – D_p - CPMA + DMA	D, F, H, K, M, N	7.5%-14.2%	15.1%-28.4%

We have checked the influence of measurement wavelength for the uncertainty of component K). The correction for multiple charges at 808 nm is between 17% and 25%, in the same range as correction for 450 nm (13-27%).

The uncertainty in the particle number concentration measured by the CPC depends on the calibration and flow measurement, resulting in 3% uncertainty (Wiedensohler et al., 2018). Due to high noise at low sample flow, a 4% uncertainty was used for the FCAE. The uncertainty in mass selection by the CPMA is 2% (Titosky et al., 2019).

Instrument operation can be influenced by the scattering artefact (0.1% as reported by Drinovec et al., (2022a)) and the presence of absorbing gases; absorption of gas fraction is measured on filtered sample and subtracted from the total absorption, however interactions from the adsorbed gas are also possible. The uncertainty contribution from the stability of the instrument response (3%) was determined by Kalbermatter et al. (2022). In stable environment the calibration repeatability is 0.3% (Supplement S9). The 3% value for the Stability of PTAAM response covers the increased noise (Fig. 1B) during complex experiments.

4. Discussion

A combination of DMA and CPMA has been extensively used in the past to measure the effective/material density of aerosols such as soot and organics. For nigrosin, we found that the effective particle density differed from the 1.6 g cm^{-3} value reported by Moteki et al. (2010), with the difference being higher for smaller particles. We have interpreted this result due to irregular shape of the particles produced by our nebuliser. Formation of irregular nigrosin particles in nebulizer has not been reported before. The main difference was the use of non-dried inlet air in our nebulizer compared to compressed air being used elsewhere (Radney and Zangmeister, 2015; Lawson et al., 2025; Lack et al., 2006; Cotterell et al., 2020;). For the irregularly shaped particles the electrical mobility diameter is larger than mass-equivalent diameter (DeCarlo et al., 2004) which generates a positive bias if the electrical mobility diameter is used for Mie calculation. Because D_m better describes the physical particle diameter of irregular particles a mass classifier (CPMA) is preferred over a size classifier (DMA). Mie-calculated absorption of polydisperse nigrosin based on D_m agrees within 10% with absorption measurements obtained with the PTAAM at 450 nm. The main source of uncertainty in the modeled absorption coefficient of polydisperse nigrosin is the charge correction in the SMPS. The calculated $k=2$ uncertainties for calibration with monodisperse nigrosin using a DMA, a CPMA or a tandem of the CPMA and the DMA in series based on D_m are much lower (15.1%, 13.1% and 12.0%, respectively) compared to the calibration with polydisperse nigrosin (21.8%). The uncertainties for calculations based on D_p are larger and depend on the particle size. The measured and calculated absorption are not significantly different (using $k=2$ uncertainties) except for the one experiment (Figure 5b).

When using a DMA for size selection, we have to correct for multiply-charged particles. To reduce the number of multiply-charged particles, it helps to select particles on the right side of the volume size distribution. This requires nebulizing a more diluted nigrosin solution. To obtain a high enough particle number concentrations, the resolution of the DMA must be decreased, which can reduce the accuracy of the monodisperse aerosol approach. The influence of multiple-charge with a DMA selection can be reduced by the impactor which removes bigger particles (Bluvshstein et al., 2017; Kuula et al., 2025).

When using a CPMA, we have to account for the contribution of neutral particles. Their contribution can be reduced by increasing the concentration of the nebulized nigrosin solution and using a sufficiently high R_m value ($R_m > 7$). Experimentally, calibration using a CPMA and FCAE is the simplest and requires no additional instrumentation. The highest absorption signal can be obtained using a tandem of the CPMA and the DMA for which there is no contribution from neutral and multiply-charged particles, and a medium R_m value can be used for both classifiers. A comparison between different methods is summarized in Table 3. The proposed step-by-step protocols for calibration with monodisperse nigrosin are presented in Supplement S12.

Particle size selection can also be performed using the AAC, resulting in a much higher absorption signal compared to the CPMA and the DMA, because for the AAC the particles are not filtered by

charge (Lawson et al. 2025). The calculation of physical particle diameter (needed for the calculation of the absorption coefficient) from the aerodynamic diameter requires the knowledge of particle density. A monodisperse particle size distribution can also be produced using a combination of unipolar charger and CPMA (Titosky et al., 2019). Unipolar charger produces a narrow distribution of highly charged particles resulting in a particle mass several times bigger than the CPMA setpoint, with the mass depending on the particle size and morphology (Hassim et al., 2025). For both selection methods an additional classifier is needed to determine the resulting particle mass.

The calibration method using monodisperse nigrosin can be extended to other in-situ absorption methods like photo-acoustic spectroscopy, which has been demonstrated in several studies (Radney and Zangmeister, 2015; Lack et al., 2006; Bluvshstein et al., 2017; Cotterell et al., 2020; Kuula et al., 2025; Lawson et al., 2025). Care should be taken with the photo-acoustic method because its response has been shown to be highly sensitive to relative humidity (Langridge et al., 2013).

Table 3. A comparison between the absorption calibration methods used in this study, based on polydisperse nigrosin particles and monodisperse nigrosin particles selected using a DMA, a CPMA or a tandem configuration of CPMA and DMA.

	Polydisperse	Monodisperse		
	/	DMA	CPMA	CPMA+DMA
Resolution parameter R_m	n/a	1.5	15	CPMA:5, DMA:3
$b_{abs_450\text{ nm}}$ (Mm-1)	887	25.2 ($m_p=2.4\text{ fg}$)	14.5 ($m_p=1.9\text{ fg}$)	38 ($m_p=3\text{ fg}$)
b_{abs} calculated vs. measured	+10%	+5 to +11%	-2% to -3%	+2% to +8%
Postprocessing	Density correction	Multiple charge correction	/	/
Needed instrumentation	DMA, CPMA, CPC	DMA, CPMA, CPC	CPMA, FCAE	DMA, CPMA, CPC
Uncertainty ($k=1$)	10.7%	6.9%	5.8%	5.2%

5. Traceability to SI units

For the traceable calibration of an aerosol absorption monitor all quantities used in calculations need to be traceable to SI units. For calibration with NO₂ this amounts to determination of NO₂ amount fraction, cross-section of NO₂, emission spectrum of measurement light, pressure, relative humidity and temperature (Table 4).

Traceable calibration with monodisperse nigrosin is based on the determination of the nigrosin refractive index, material density, particle electrical mobility or particle mass for the determination of the particle diameter, particle number or charge, temperature, relative humidity and pressure. The refractive index of nigrosin can be determined in a traceable manner using ellipsometry. Nigrosin material density can be obtained from particle mass and electrical mobility diameter of spherical particles. All parameters and methods with references for the traceable calibration of the required parameters are listed in Table 5.

Table 4. Parameters and methods required for the traceable calibration of aerosol absorption monitors with NO₂

Parameter	Method	Reference
NO ₂ amount fraction	Permeation	Haerri et al., 2017
NO ₂ cross-section	High-resolution Fourier transform spectroscopy	Vandaele et al., 2002
Spectrum of measurement beam	VIS-NIR spectrometer calibrated against accurately known spectral lines	
Pressure		Perkin et al., 2008
Relative humidity		Lochlainn et al., 2024
Temperature		Sparasci et al., 2024

Table 5. Parameters and methods required for the traceable calibration of aerosol absorption monitors with monodisperse nigrosin

Parameter	Method	Reference
Nigrosin refractive index	Ellipsometry	ISO 23131:2021
Particle mass-to-charge ratio	CPMA traceably calibrated using mass-certified polystyrene spheres	Ehara et al, 2006 Takahata and Sakurai, 2026
Particle electrical mobility diameter	DMA traceably calibrated with size-certified polystyrene spheres	ISO 15900:2020 Vasilatou et al., 2025
Nigrosin material density	CPMA and DMA	see above
Number of particles	CPC traceably calibrated against a FCAE	ISO 27891:2015 Vasilatou et al., 2025
Particle charge	FCAE traceably calibrated against a primary standard for electric current	
Pressure		Perkin et al., 2008
Relative humidity		Lochlainn et al., 2024
Temperature		Sparasci et al., 2024

6. Conclusions

Measured nigrosin particle density differed by up to 20% from the reference value of 1.6 g cm^{-3} , which is due to irregular shape of the particles produced by our nebulizer. For the irregular particles the electrical mobility diameter is larger than the particle physical diameter, which results in an overestimated Mie calculated absorption coefficient. Mass-equivalent diameter was used instead. Mie calculated absorption coefficient for polydisperse and monodisperse nigrosin particles was compared with measurements using the PTAAM at 450 nm, which was previously calibrated with NO_2 . Calibration of the absorption instruments with monodisperse nigrosin (selected with the CPMA or a tandem of the CPMA and the DMA) yields lower measurement uncertainty and better experimental agreement with measurements, compared to a polydisperse or a DMA selected sample.

The DMA selection method suffers from uncertainties due to multiply-charged particles, resulting in higher uncertainty compared to other methods. The CPMA selection requires a high enough resolution parameter R_m value to avoid the influence of neutral particles. Application of high R_m results in a lower particle number (and corresponding absorption coefficient) available for the calibration. Configuration with a CPMA and a FCAE is the simplest calibration method because it requires only a CPMA and a FCAE without the need for post processing. A tandem of the CPMA and the DMA in series avoids the biases caused by neutral and multiply-charged particles and provides a high absorption signal. CPMA and tandem selection methods have essentially equivalent uncertainties and are both proposed for calibration of absorption instruments with monodisperse nigrosin.

Calculated absorption coefficient of monodisperse nigrosin based on mass-equivalent diameter was not statistically different (using $k=2$ uncertainties) from measured absorption coefficient at 450 nm for any of the particle selection techniques.

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Conflict of interest statement

LD, GM and JYD are employed by Haze Instruments d.o.o., the PTAAM manufacturer. GM is an editor for AMT.

Data repository

Data is available at <https://repozitorij.ung.si/lzpisGradiva.php?id=11081>.

Author contributions

LD performed the experiments, evaluated the data and prepared the manuscript. EA provided and calibrated the FCAE. TB and MIG performed calibration of PTAAM and NO_2 CAPS with TMPG. All coauthors helped with manuscript preparation.

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Supplement of

Development of a traceable calibration method for photothermal aerosol absorption monitor using monodisperse nigrosin

Drinovec et al.

Correspondence to: Luka Drinovec (luka.drinovec@ung.si)

S1. Measurement time series

During experiment “2024_03_05 Monodisperse cpma” nigrosin particles were selected using a CPMA. Measurements of aerosol absorption, number of particles and current were measured using a PTAAM, a CPC and a FCAE correspondingly (Fig. S1).

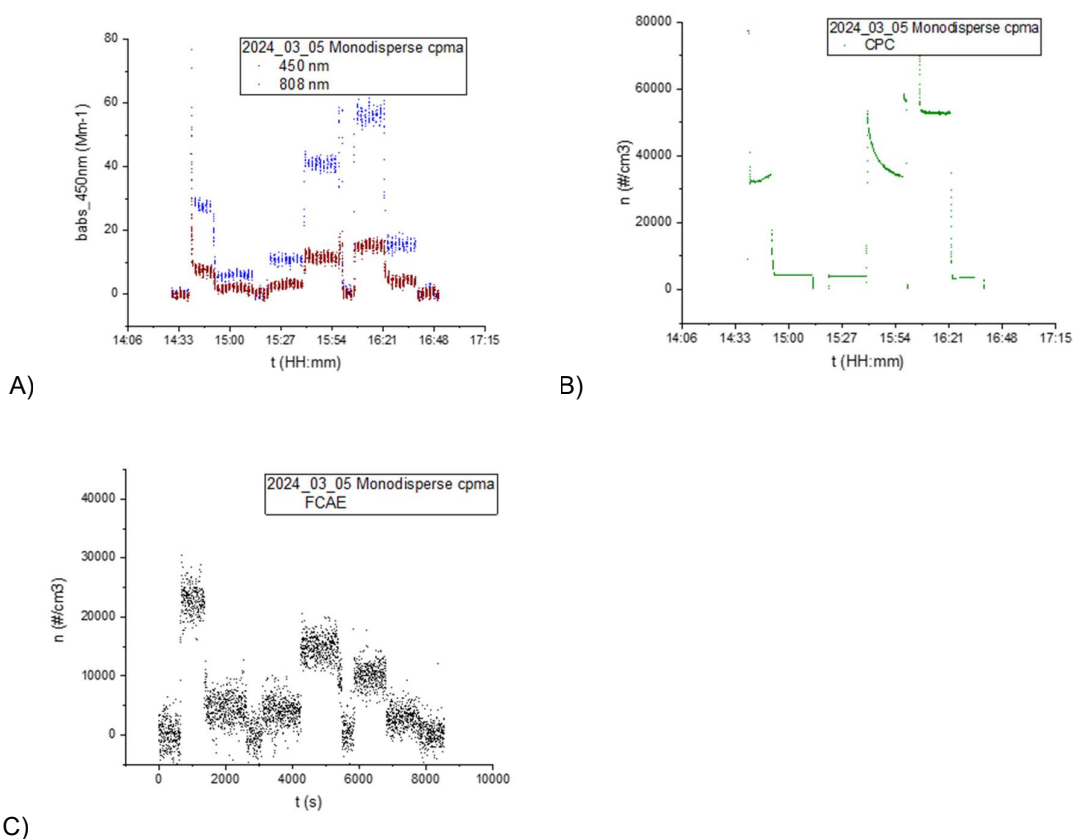


Figure S1. Time series of PTAAM (A), CPC (B) and FCAE (C) measurements for experiment “2024_03_05 Monodisperse cpma” with native 1 s time resolution.

S2. Effective density of polystyrene beads

Polystyrene beads were nebulized and sequentially analyzed with an SMPS and CPMA-CPC. Particle size/mass was determined by fitting a log-normal curve. The measured density differs from the nominal value by 0.8% (Table S1). Effective density of ammonium sulfate increases with particle mass towards the reference value of 1.77 g cm^{-3} (Haynes et al., 2017) (Fig S2).

Table S1. Reported and measured density of polystyrene beads. For measured data the fitting error is presented.

	Diameter (nm)	Mass (fg)	Density (g/cm ³)
Reported	95 +/- 4		1.05
Measured	94.988 +/- 0.05	0.5676 +/- 0.0005	1.042 +/- 0.002

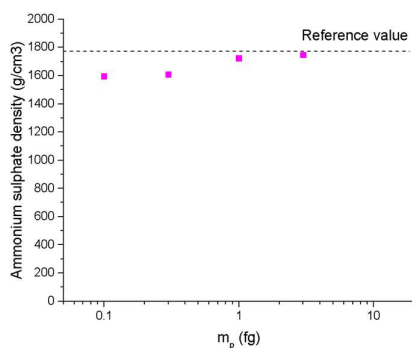


Figure S2. Effective density of nebulized ammonium sulfate particles.

S3. Mass absorption cross-section of nigrosin at 450 and 808 nm

The theoretical mass absorption cross-section of nigrosin was calculated using Mie theory based on a particle density of 1.6 g/cm^3 for refractive index values of $1.58 + i0.167$ at 450 nm and $1.78 + i0.119$ at 808 nm.

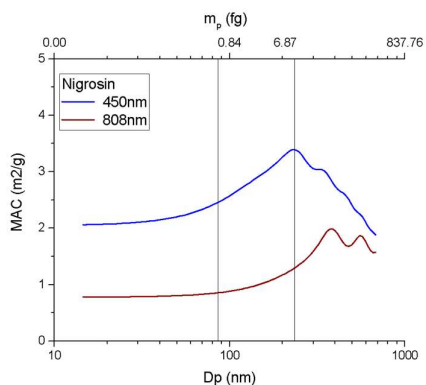


Figure S3. Mie calculated mass absorption cross-section for nigrosin particles of different sizes assuming a density of 1.6 g cm^{-3} . The vertical lines show the size range of particles used for the calibration.

S4. Measurement of multiply-charged particles in DMA-selected nigrosin

CPMA-CPC were installed after a DMA to measure number vs. mass particle distribution. Data were fitted with multiple Gauss peak functions, which described best the shape of the distribution. The first peak from the left side corresponds to singly-charged particles with the mass m_0 . The second peak corresponds to doubly-charged particles. Because CPMA selects particle by their mass-to-charge ratio the actual particle mass is the double of the observed peak position. For the triple-charged particles the actual particle mass is a triple of the observed peak position.

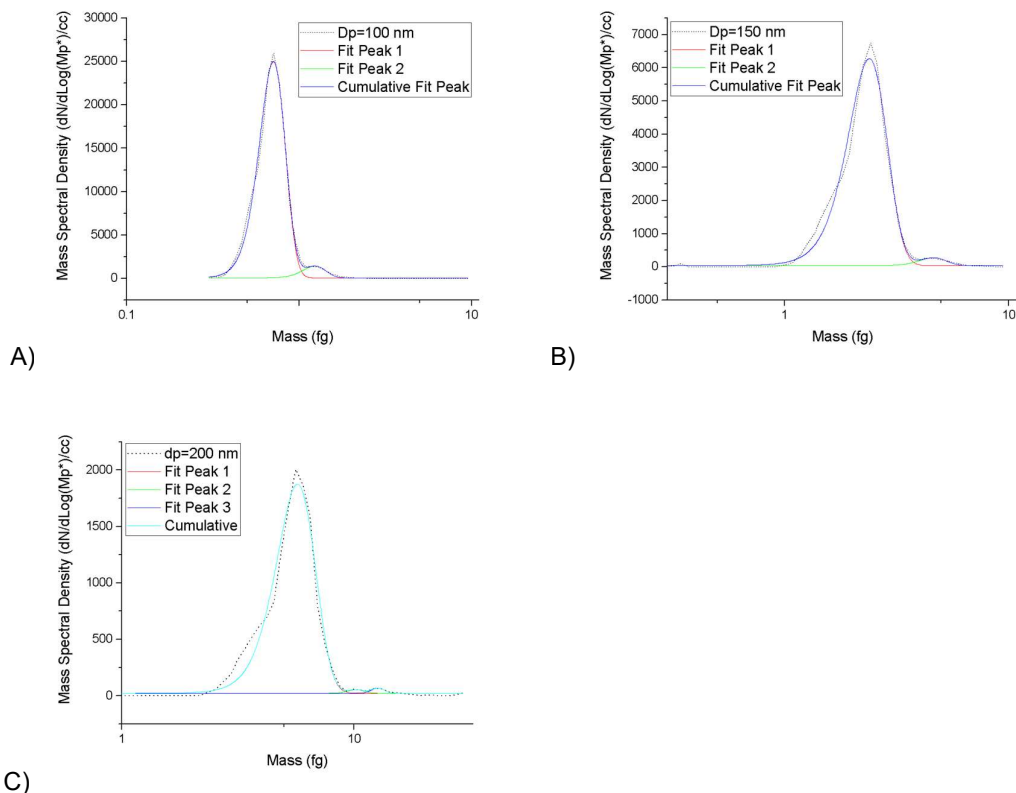


Figure S4. Number mass distribution of monodisperse nigrosin with mobility diameters of 100 nm (A), 150 nm (B) and 200 nm (C).

Table S2. Fitted peak positions, particle masses (m_1 , m_2 , m_3) and number of particles (n_1 , n_2 , n_3) for singly, doubly and triply-charged particles. E450 and E808 show the increase of calculated absorption at 450 nm and 808 nm when taking into account the higher mass of multiply-charged particles compared to assigning all particles the mass m_1 .

Dp (nm)	Peak1 (fg)	Peak2 (fg)	Peak3 (fg)	m_1 (fg)	m_2 (fg)	m_3 (fg)	n_1	n_2	n_3	E450	E808
100	0.707+/-0.002	1.23+/-0.05	1.6+/-0.3	0.708	2.44	4.68	4877	213	39	1.18	1.17
150	2.39+/-0.01	4.2+/-1.2	5.2+/-4.1	2.39	8.4	15.6	1442	22	27	1.27	1.20
200	5.71+/-0.03	9.8+/-2.7	12.8+/-4.2	5.71	19.6	38.4	418	3.4	8.9	1.13	1.25

S5. SEM image of fused nigrosin particles

Nigrosin particles were collected on Nucleopore filters and analyzed using a scanning electron microscope FEI HeliosNanolab 650 (Thermo Fisher Scientific, USA) operated at 1 kV accelerating voltage. The samples were mounted on SEM holders with a carbon tape and coated with a few nanometers of carbon to prevent charging effects.

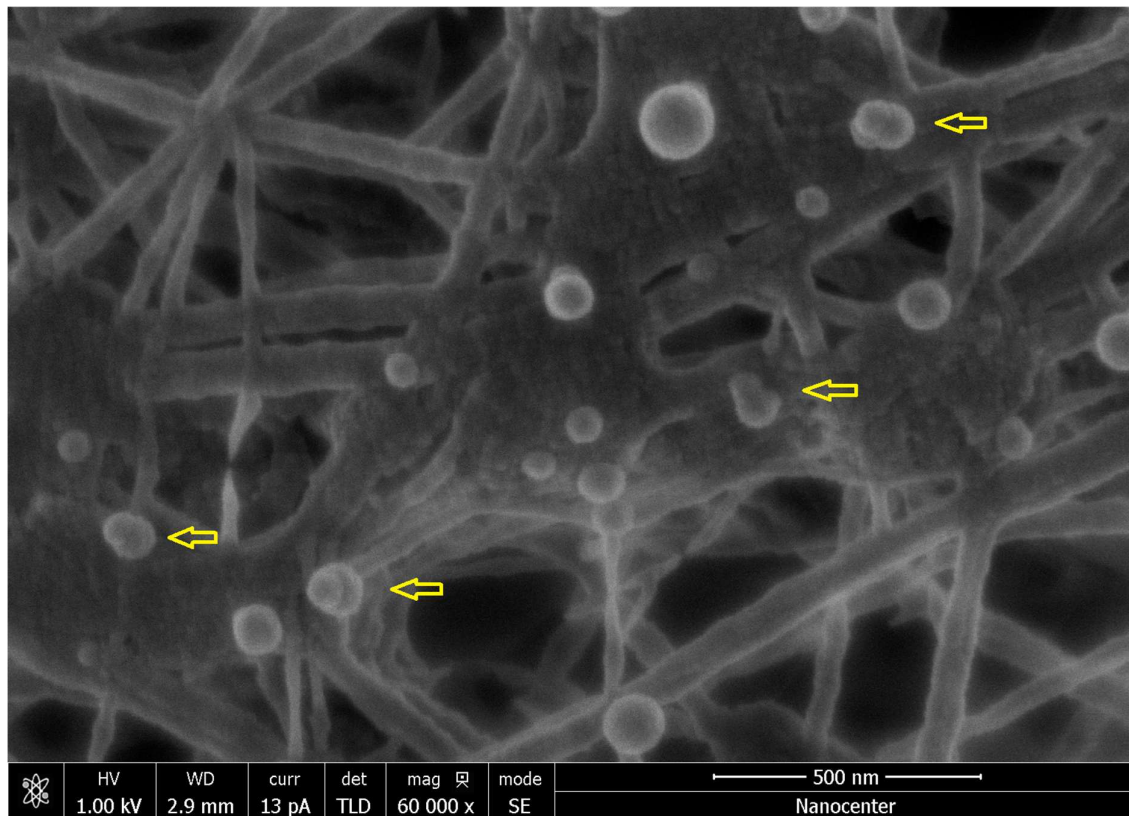


Figure S5. Scanning electron micrograph of nigrosin particles. Arrows designate fused, non-completely-spherical particles.

S6. Measured and calculated absorption of monodisperse nigrosin at 450 and 808 nm

The 450 nm channel of PTAAM was calibrated using NO₂, while the 808 nm channel was calibrated by transferring calibration from the 450 nm channel using the Mie-calculated absorption ratio $b_{\text{abs}_808\text{nm}}/b_{\text{abs}_450\text{nm}}$ for polydisperse nigrosin as described in Drinovec et al., 2022. PTAAM measurements are compared with Mie calculated absorption coefficient based on mobility diameter and mass equivalent diameter (Fig. S6 & Table S3).

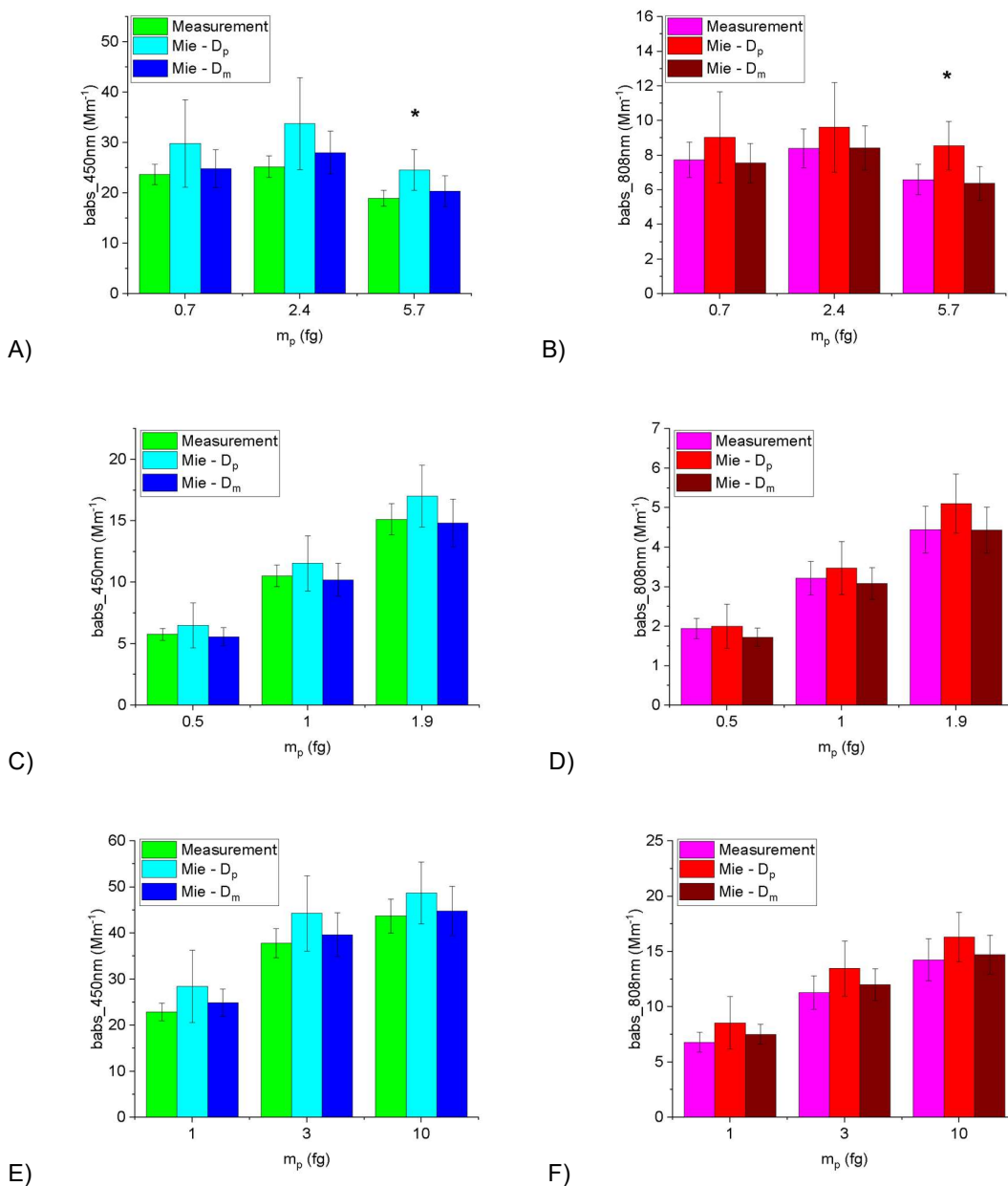


Figure S6. Measured and calculated absorption coefficient of monodisperse nigrosin at 450 nm (left: A, C, E) and 808 nm (right: B, D, F). Nigrosin was size-selected using a DMA (A & B), a CPMA (C & D) and a tandem of CPMA and DMA (E & F). Error bars represent $k=2$ uncertainty. * denotes statistically significant difference from the measurement.

Table S3. Measured and calculated absorption coefficient of monodisperse nigrosin at 450 nm and 808 nm. Nigrosin was size-selected using a DMA, a CPMA and a tandem of CPMA and DMA. Errors represent $k=2$ uncertainties.

Selection method	mp (fg)	Dp (nm)	babs_450nm (Mm-1)			babs_808nm (Mm-1)		
			PTAAM	Mie_Dp	Mie_Dm	PTAAM	Mie_Dp	Mie_Dm
DMA	0.7	100	23.7 ± 2.0	29.8 ± 8.7	24.8 ± 3.7	7.74 ± 1.0	9.0 ± 2.6	7.6 ± 1.1
DMA	2.4	150	25.2 ± 2.1	33.8 ± 9.1	28.0 ± 4.2	8.4 ± 1.1	9.6 ± 2.6	8.4 ± 1.3
DMA	5.7	200	19.0 ± 1.6	24.6 ± 4.1	20.3 ± 3.1	6.6 ± 0.9	8.6 ± 1.4	6.4 ± 1.0
CPMA	0.5	88.2	5.8 ± 0.5	6.5 ± 1.8	5.6 ± 0.7	1.95 ± 0.3	2.0 ± 0.6	1.73 ± 0.7
CPMA	1.0	110.1	10.5 ± 0.9	11.5 ± 2.2	10.2 ± 1.3	3.2 ± 0.4	3.5 ± 0.7	3.1 ± 1.3
CPMA	1.9	137.0	15.1 ± 1.3	17.0 ± 2.5	14.8 ± 1.9	4.4 ± 0.6	5.1 ± 0.8	4.4 ± 1.9
Tandem	1.0	110.4	22.8 ± 1.9	28.4 ± 7.8	24.9 ± 3.0	6.8 ± 0.9	8.6 ± 2.4	7.5 ± 0.9
Tandem	3.0	158.2	37.9 ± 3.2	44.3 ± 8.2	39.7 ± 4.8	11.3 ± 1.5	13.5 ± 2.5	12.0 ± 1.4
Tandem	10.0	235.0	43.7 ± 3.7	48.7 ± 6.7	44.8 ± 5.4	14.3 ± 1.9	16.3 ± 2.2	14.7 ± 1.8

S7. Measurement of NO₂ and particle losses in PTAAM

NO₂ losses between the instrument inlet and the measurement chamber were measured by running a known concentration of NO₂ sample through the instrument and being measured with CAPS NO₂ monitor. Sample flow through the PTAAM was kept at 0.45 L min⁻¹ by adding a fixed amount of NO₂ free air before entering the CAPS. NO₂ loss for sub 1 µmol mol⁻¹ sample was calculated by comparing the measured NO₂ concentration running through the PTAAM with the bypass configuration.

Particle losses were determined for monodisperse and polydisperse nigrosin particle distributions. Nigrosin particles were generated using the solution with 0.1 g L⁻¹ nigrosin. For monodisperse measurements the aerosol was routed through the neutralizer and the CPMA to the PTAAM. Sample was directed out of the sample cell and fixed amount of particle free sample was added before the CPC, keeping the sample flow through the instrument stable at 0.45 L min⁻¹. Measured number concentration was compared to the setup without the PTAAM. For polydisperse experiment the neutralized nigrosin particles passed the PTAAM before adding particle free air and being measured using the SMPS. The size dependent particle losses are shown in Table S4. Particle losses for single charged 100 nm particles are approx. 5%. Particle losses for mineral dust particles (Table S5) were measured in a similar manner using optical particle sizer Grimm 11-D (Durag Group, Germany).

Table S4. Measured nigrosin particle losses using monodisperse particles selected using CPMA or polydisperse particles analysed using SMPS after passing the inlet part of the PTAAM.

D _p (nm)	Loss_monodisperse	Loss_polydisperse	m _p (fg)
200	2.1%	2.9%	6.69
100	4.3%	5.6%	0.83
50	10.6%	12.5%	0.105
25	24.4%	26%	0.013
12.9	47.0%	47%	0.0018

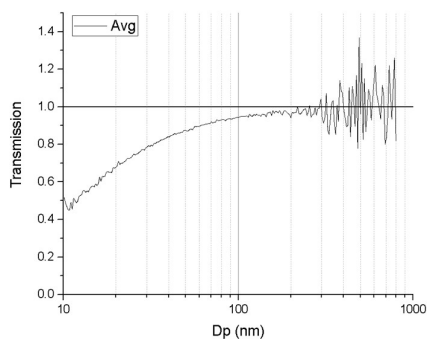


Figure S7. Penetration efficiency in PTAAM for single-charged nigrosin particles.

Table S5. Particle loss in PTAAM for different fractions of mineral dust particles

Particle size fraction	Particle loss
PM10 [ug/m3]	10.0%
PM4 [ug/m3]	9.4%
PM2.5 [ug/m3]	8.1%
PM1 [ug/m3]	3.8%

S8. Calculation of electrical mobility

Electrical mobility Z_p is calculated as:

$$Z_p = \frac{neC}{3\pi D_p} ,$$

where n is number of elementary charges on the particle, e is elementary charge (1.6022×10^{-19} As) and C is Cunningham slip correction defined as:

$$C = 1 + K_n \left[\alpha + \beta \cdot \exp\left(-\frac{\gamma}{K_n}\right) \right] ,$$

where $\alpha=1.165$, $\beta=0.483$ and $\gamma=0.997$. K_n is Knudsen number defined as:

$$K_n = \frac{2\lambda}{D_p} ,$$

where λ is gas mean free path (approximately 7×10^{-8} m).

It is difficult to calculate the inverse function $D_p(Z_p)$. To calculate D_p from Z_p we prepared the table with D_p and corresponding Z_p values. Then we use interpolation to calculate D_p corresponding to our Z_p .

S8.1 Example for particles selected by CPMA with mass-to-charge ratio of 1 fg

Singly-charged, single-mass particles: $m_p=1$ fg, $D_p=110.4$ nm.

Doubly-charged, double-mass particles: $m_p=2$ fg, $D_p=139.1$ nm

- calculate electrical mobility: $Z_p(n=2, D_p=139.1 \text{ nm}) = 3.27653 \times 10^{-8} \text{ m}^2 \text{s}^{-1} \text{V}^{-1}$
- calculate D_p of singly-charged particle with the same mobility:
 - $Z_p(n=1, D_p=?)=Z_p(n=2, D_p=139.1 \text{ nm})$
 - $D_p=92.4$ nm

Triply-charged triple-mass particles: $m_p=3$ fg, $D_p=159.2$ nm

- calculate electrical mobility: $Z_p(n=2, D_p=139.1 \text{ nm}) = 3.27653 \times 10^{-8} \text{ m}^2 \text{s}^{-1} \text{V}^{-1}$
- calculate D_p of singly-charged particle with the same mobility:
 - $Z_p(n=1, D_p=?)=Z_p(n=2, D_p=139.1 \text{ nm})$
 - $D_p=92.4$ nm

S8.2 Measurement of CPMA selected particles with SMPS

An example of SMPS measurement of particles selected by CPMA set to $m_p=1$ fg is shown in the Fig. S8. It is possible to observe the peak of singly-charged particles with $m_p=1$ fg appearing at 110.4 nm and the peak of doubly-charged particles with $m_p=2$ fg appearing at 92.5 nm. Triply-charged particles are not observed.

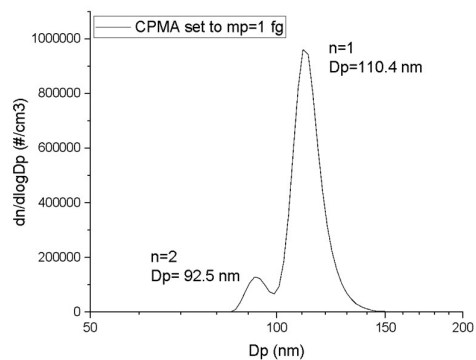


Figure S8. SMPS measurement of particle size distribution of nigrosin particles selected by CPMA set to $m_p=1$ fg.

S9. Calculation of absorption cross-section of NO₂ for 450 nm laser diode

The absorption cross-section of NO₂ is wavelength dependent. The exact absorption cross-section needs to be calculated using a high-resolution absorption cross-section of NO₂ (Vandaele et al., 2002) and the measured spectrum of the 450 nm laser diode (Fig. S9). The effective cross-section CS was calculated as follows:

$$CS = \frac{\sum CS_i \cdot I}{\sum I} ,$$

where CS_i is the wavelength-dependent cross-section and *I* is the emission spectrum of laser diode. The emission spectrum of the laser diode depends on temperature and electric current, which have to be kept stable.

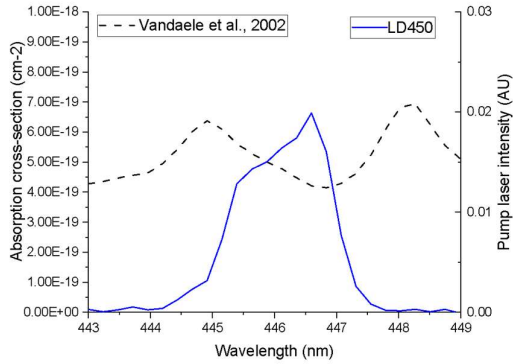


Figure S9. Spectra of the absorption cross-section and 450 nm laser diode.

The laser diode spectrum was measured using a Thorlabs CCS100/M spectrometer, which was wavelength-calibrated using a neon spectral lamp (Thorlabs CSL1) just before the measurement. The uncertainty comes from the limited spectral resolution of the spectrometer: 0.5 nm. The decrease in spectral resolution of the Vandaele et al. (2002) cross-section measurement from 0.25 nm to 0.5 nm results in an uncertainty of 0.7%. The difference between the cross-section measured by the Thorlabs CCS100/M spectrometer compared to a high-resolution spectrometer (Edinburg Photonics FLS920) with 0.07 nm resolution (Fig. S10) was 0.6% which falls within the estimated uncertainty.

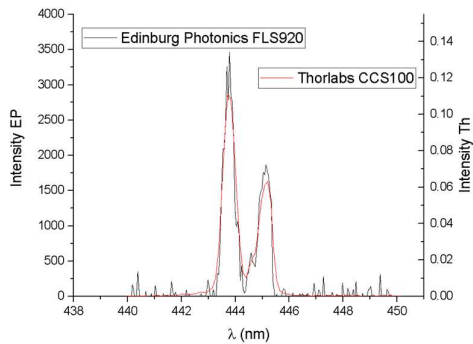


Figure S10. Measured emission spectra of 450 nm laser diode using spectrometers Edinburg Photonics FLS920 and Thorlabs CCS100/M.

S10. Repeatability of the PTAAM-2 λ (version P02) response

Repeatability of instrument response was tested by performing daily calibrations (Table S11). The calibration procedure:

A) Testing 450 nm channel response

- wavelength calibration of the spectrometer Thorlabs CCS100/M using a calibration lamp Thorlabs SCL1
- measurement of the 450 nm channel laser diode (LD450) emission spectrum using the spectrometer Thorlabs SC100/M
- calculation of the absorption cross-section of NO₂ for the LD450 spectrum
- measurement of NO₂ concentration of the calibration sample using NO₂ CAPS
- measurement of the PTAAM response at 450 nm
- calculation of the 450 nm channel response

B) Testing the 808 nm channel response

- measurement of the nigrosin size distribution with the SMPS
- calculation of the absorption ratio using Mie theory: $\text{babs_Mie_808/babs_Mie_450}$
- measurement of absorption of polydisperse nigrosin with the PTAAM
- calculation of the absorption ratio $\text{babs_PTAAM_808/babs_PTAAM_450}$
- calculation the 808 nm channel response

Table S11. The results of PTAAM-2 λ calibrations performed on consecutive days. Results are calculated relative to the first day.

Day	CS (10 ⁻¹⁹ cm ²)	Calculated babs/no2 (Mm ⁻¹ *ppb ⁻¹)	Measured babs/NO2 (Mm ⁻¹ *ppb ⁻¹)	Channel 1 relative response	Mie calculated babs808/babs450	Measured babs808/babs450	Channel 2 relative response
1.	4.857	1.201	1.201	1.000	0.3239	0.3239	1.000
2.	4.858	1.200	1.120	0.933	0.3240	0.3259	0.939
3.	4.880	1.206	1.205	0.999	0.3240	0.3249	1.002
4.	4.848	1.198	1.198	1.000	0.3230	0.3247	1.005
5.	4.851	1.199	1.198	0.999	0.3236	0.3250	1.003
SD	0.3%	0.3%	0.3%	0.3%	0.2%	0.2%	0.3%

S11. Intercomparison of particle concentration measured with CPC and FCAE

Monodisperse singly-charged nigrosin particles were selected with a tandem of CPMA ($m_p=1$ fg, $R_m=5$) and DMA (Sheet flow = 10 l min^{-1} , $D_p=110.4 \text{ nm}$). Particle concentration was measured using CPC with 0.984 l min^{-1} and FCAE with 0.526 l min^{-1} sample flows as reported at 25°C and 100 kPa . Fig. S11 shows a slope of 0.997 ± 0.006 between particle concentrations measured with FCAE and CPC.

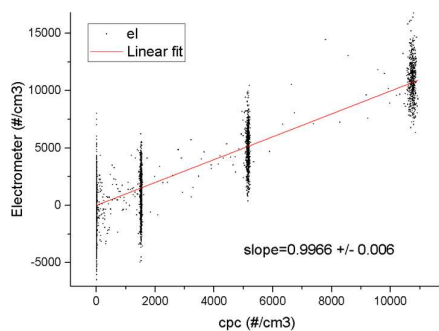


Figure S11. Correlation between measured particle concentrations at 1 a time resolution using FCAE and CPC.

S12. Step by step protocols for calibration with monodisperse nigrosin

S12.1 Selection with DMA

- prepare 0.1 g l⁻¹ nigrosin solution
- check sample RH
- build the setup illustrated in Fig. 2a and measure density of particles with $D_p=150$ nm
- select $D_p=150$ nm, sheath flow=15 l min⁻¹
- build the setup illustrated in Fig. 2c and measure multiply-charge particle fraction
- build the setup illustrated in Fig. 2b and measure absorption and particle concentration for 15 minutes

S12.2 Selection with CPMA

- prepare 1 g l⁻¹ nigrosin solution
- check RH
- build the setup illustrated in Fig. 2d
- set $m_p=3$ fg, $R_m=10$, set to measured sample flow
- measure absorption and particle current for 15 minutes

S12.3 Selection with CPMA + DMA

- prepare 1 g l⁻¹ nigrosin solution
- check RH
- build the setup illustrated in Fig. 2a
 - set CPMA: $m_p=3$ fg, $R_m=5$, set to measured sample flow
 - set SMPS: sheath flow=10 l min⁻¹
 - measure D_p and identify distribution peak
- build the setup illustrated in Fig. 2f
- set DMA to peak D_p , sheath flow=10 l min⁻¹
- measure absorption and particle number for 15 minutes

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