

Response to comments:

Photoacoustic and nephelometric spectroscopy of aerosol optical properties with a supercontinuum light source

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We would like to thank the reviewers for positive feedback and constructive criticisms.

Anonymous Reviewer 1

General comment

The application of a supercontinuum laser and photoacoustics for the measurement of light absorption by particles is to my knowledge presented here for the first time. The whole idea is excellent because at least in principle it makes it possible to measure the whole absorption spectrum in the true aerosol phase. And the instrument presented here also measures extinction and scattering so it essentially also has the means to have an independent absorption calibration. The principle of the method is clearly described but it is also shown that it still has fairly high noise levels in order to deploy it to background air measurements, leaving space for technical improvement. But all in all, I consider the paper definitely worth publishing after some fairly small revisions, suggested in the detailed comments below.

Authors Reply:

We appreciate the reviewer's support and positive comments. We also agree with the reviewer that at the present stage the instrument would not be sensitive enough for background measurements, as we discussed in the paper; however, it can still have value in laboratory studies, or sites with high pollution. The sensitivity of the current system is mostly limited by the low laser power within each wavelength band that could be mitigated by a multipass design or with enhanced supercontinuum laser power, as newer laser models already provide. An advantage of low laser power is that laser radiation effects on aerosol morphology or chemical and physical characteristics are probably negligible with respect to high laser power systems.

Detailed Comments

Reviewer comment 1: P6294L23: "Entrained mineral dust particles ..." Why do you have the word "entrained" there?

Authors Reply: The term "entrained" was removed.

Reviewer comment 2: P6295 L9 – 10 "... solar radiation depends upon particles characteristics like ..." remove "s"

Authors Reply: "particles" was replaced by "particle".

Reviewer comment 3: P6299 L 13 – 15 "The selection of different wavelength bands is achieved by using a series of singlebandpass filters (BrightLine filters by Semrock) mounted on a rotating filterwheel (Edmund Optics)". What is the rotating speed? In other words, at what frequency do you get data from any selected wavelength? Does the wheel stop for each wavelength filter for a selected time and then take the next wavelength or is it rotating continuously?

Authors Reply: Thanks for the question. The rotation of the filterwheel was controlled manually. This point is clarified in the manuscript at P6299 L 13 – 15.

While calibrating the instrument, measurements on each filter were done for about three-four minutes after which the wheel was rotated to select the next wavelength band.

A sentence clarifying this point is included in Section 4 of the revised manuscript.

During the experiments, the total time spent on a filter was approximately 3-4 minutes with one-minute sample measurement performed between two background measurements, of one minute each. Then the filterwheel was rotated to select the next wavelength.

This has already been mentioned in the manuscript in Section 5.

Reviewer comment 4: P6301 L14 – 16 “The background signal obtained for scattering and absorption were in the order of 10^3 and 10^2 Mm^{-1} , respectively.” Please give averages and standard deviations and the time that was used for collecting the respective data. That would make this info more quantitative and link it to detection limits.

Authors Reply: Good suggestion.

Background measurements were done at each filter before and after each sample measurement. Table 1 shows statistics (average, standard deviation and count) for the background signals for absorption and scattering as measured at each filter. All data used in the statistics, corresponded to a measurement time of about 2-3 seconds.

Table 1

Filter center wavelength [nm]	Absorption		Scattering		Number of measurements
	Average	St. Dev.	Average	St. Dev.	
417	39	12.4	2264	345	1106
475	6	8.0	2254	7.3	1061
542	35	4.4	2134	6.4	1035
607	80	3.0	1833	8.2	1068
675	65	3.2	1958	197	1101

A similar table with a short discussion was added to the revised version of the manuscript in section 2.

Reviewer comment 5: P6302 L13 “Because our instrument operated only at one wavelength-band at a time...” Now this comes back to my question for P6299: for how long does the instrument measure each wavelength and at what frequency?

Authors Reply: Answered in reply to comment#3.

Reviewer comment 6: P6302, L 16 ... Description of the iron lung. I understand that you present the details in the submitted manuscript but please give some more details also here: how big is the lung? How long does it take to fill it? What is the time resolution you achieve with it?

Authors Reply: The iron lung is a steel cylindrical drum having a diameter of 64 cm and height of 86 cm. It is lined with a conductive liner and has a capacity of 277 l. It takes 15-20 min to be fully filled with kerosene soot (diluted with air) with a flow rate of ~20 lpm. The sampling time was much longer (about 2 hours) as the flow used by the instruments added up to a total of about ~2 lpm.

Reviewer comment 7: P6302, instrument calibration. I understand you need high concentrations for the extinction calibration because of the short pathlength but why don't you calibrate scattering

with CO₂ like any nephelometer? That would be exact and there would not be the inevitable uncertainty that is always associated with aerosol production. And I would trust absorption calibration with NO₂ more than with soot, the absorption spectrum of NO₂ is well known. Still about the extinction measurement: if so high concentrations are needed for the calibration, what is the detection limit for extinction? In Table 2 you just present the detection limits for scattering and absorption – give also extinction.

Authors Reply: In table 2 below, we report calculated CO₂ (minus Air) scattering coefficients for the conditions of the experiments as performed in Reno, NV (at about 846 mb and ambient temperature). Depending on the wavelength, scattering from CO₂ is insufficient to give a signal significantly higher than the minimum detection limit of the instrument, and would therefore not provide a precise mean of calibrating the current instrument for all wavelengths. As we prefer to use the same calibration procedure for all wavelengths, we think that using the aerosol extinction measurement is a reasonable approach. In addition, the absorption calibration described in the paper critically depends on the scattering calibrated data. The fact that the photoacoustic signal as calibrated with aerosols compares well with the NO₂ absorption data, provides some additional evidence that the scattering calibration obtained with salt is also accurate. This calibration approach has been discussed carefully in (Abu-Rahmah, Arnott et al. 2006). Abu-Rahmah et al. also point out another advantage of this approach by writing: “The scattering coefficients of particle-free air and CO₂ are generally lower than the aerosol coefficients in an urban area of average pollution. Thus another calibration method extending the calibration range is desirable”. However, we also agree with the reviewer that future embodiments of our instrument -with possibly improved detection limits- should be at least compared against, if not calibrated with, CO₂.

Table 2: Calculated scattering coefficients of CO₂ minus Air:

Filter center wavelength [nm]	Scattering Coefficients [Mm ⁻¹]
417	43.93
475	27.24
542	16.38
607	10.76
675	7.08

We thank the reviewer for asking about the minimum detection limit for extinction. That data should have been added to the paper at its initial submission. In the following table 3 we report the extinction detection limit for 60s integration time, as it has been calculated using the Allan variance method used for scattering and absorption and discussed in the paper. These values have been added also to the table 2 in the revised manuscript.

Table 3: Minimum detection limit of extinction for 60s integration time:

Filter center wavelength [nm]	MDE[Mm ⁻¹]
417	1800
475	2300
542	1500
607	1400
675	750

Reviewer comment 8: P6307, sections 5.1 & 5.2. Why don't you also give results from modeling with a Mie code? You have nice and clear size distributions; they could easily be used for

calculating scattering and absorption and the associated SAE and AAE.

Authors Reply: The main focus of this paper was to present the design, development, calibration scheme, performance and limitations of the instrument. The comparison of the instrument with a commercial 3-wavelength photoacoustic (DMT Inc.), using two previously studied aerosol species (kerosene soot and salt) demonstrate the good agreement between the instruments, with an advantage for our instrument of being able to measure at two additional wavelengths. Since the aerosols sampled from the iron lung were irregularly shaped particles (soot and salt) and we do not know the details of their morphology it would be difficult to accurately simulate the expected scattering and absorption coefficients from the size distribution alone. Mie simulations, that assume spherical symmetry, would poorly reproduce the optical properties of soot and salt particles introducing substantial uncertainty in such comparison. However, we agree with the reviewer that using spherical aerosols of known size and index of refraction and comparing the results with those from Mie calculations would definitely be interesting and it should be included in future studies using for example nigrosin and latex spheres of selected size.

Reviewer comment 9: P6310 L23 – 24 ”... even in environemtns with ...”. Typing error.

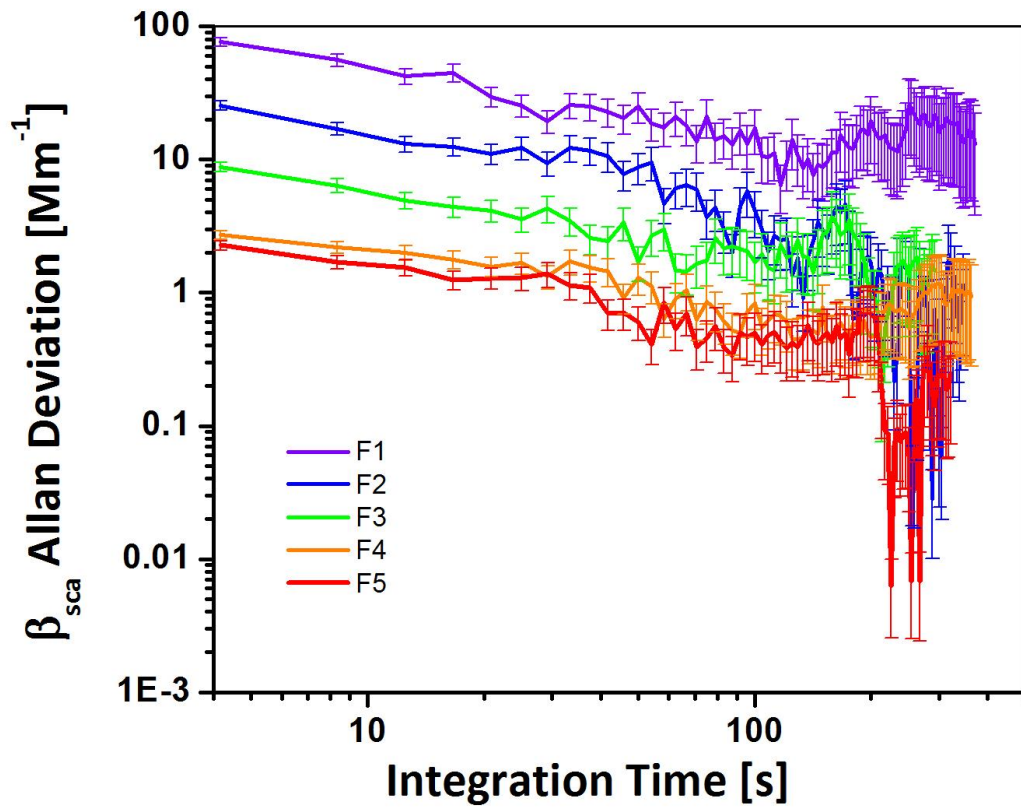
Authors Reply: Thanks for pointing this out, “environemtns” was replaced with “environments”.

Reviewer comment 10: Figure 8. Why do you have two y axes in both subplots? The ranges and units are the same both on the left and on the right. Confusing.

Authors Reply: One of the Y-axis in both plots represents the photoacoustic signal that is recorded from the response of the microphone, which corresponds to the absorption only when other relaxation processes are negligible (e.g. negligible photodissociation, or negligible fluorescence). When also scattering is negligible, this should correspond to the extinction, as is the case for NO₂ that is an absorbing gas at these wavelengths. Therefore, even though we are comparing similar quantities with same units and approximate same range, the quantities in place are inherently different: extinction, absorption, and photoacoustic signal. With the different coloring and axis we attempt to draw the reader attention to this distinction, which is particularly important when discussing the effect of photodissociation on the NO₂ photoacoustic signal at shorter wavelengths (the photoacoustic signal is lower than the absorption due to energy transfer in the photodissociation process). Only, when adjusted for photodissociation, the photoacoustic signal falls in close agreement with the measured extinction and expected absorption. We clarified this issue in the revised manuscript.

Reviewer comment 11: Figure 9. How come the Allan deviations have so clear minima at around 250 s and then again increase? Is this just due to some mathematical reasons or is this also true in measurement data? I find it hard to believe that by integrating over about 250 s your scattering noise would be about 0.01 Mm⁻¹ which is much better than that in the commercial nephelometers, specially dedicated for scattering.

Authors Reply: Allan deviation for white noise decreases proportionally to the square root of the integration time, which is shown as a grey line on the plots. When system drifts become significant, the Allan deviation starts increasing with integration time (Werle, Mücke et al. 1993). This is the reason why for some of the measurements we see a decrease in Allan deviation up to a certain integration time and an increase after that. However, the low value ($\approx 0.01 \text{ Mm}^{-1}$) at integration times around 250s is probably due to statistical fluctuations in the computed Allan deviations. In the figure below we added standard errors to the plots as calculated following the method described by Werle, Mücke et al. (1993). Evidently the errors increase at larger integration times. We did not include error bars on the plots in Figure 9 in the manuscript because that would clutter the graph making it difficult to read. It is evident that a detection limit of 0.01 Mm^{-1} at an integration time of 250s is unlikely.



References

- Abu-Rahmah, A., W. P. Arnott, et al. (2006). "Integrating nephelometer with a low truncation angle and an extended calibration scheme." *Measurement Science and Technology* **17**(7): 1723.
- Werle, P., R. Mücke, et al. (1993). "The limits of signal averaging in atmospheric trace-gas monitoring by tunable diode-laser absorption spectroscopy (TDLAS)." *Applied Physics B* **57**(2): 131-139.

Anonymous Reviewer 2

General Comment

The idea is very interesting, to avoid the use of filter for the measurement of the absorption in the aerosol phase. I also like the idea of measuring absorption and scattering in one single instrument which reduces the uncertainties (even if it is not suitable for remote sites).

The technical description is complete and well documented.

Authors Reply:

Thanks for the supporting comment.

Detailed comments

Reviewer comment 1: P6301: L15: The background signal seems high, what would be the LOD?

Authors Reply: The LOD for absorption and scattering (inclusive of the effect of background subtraction) at all five filters are mentioned in Table 2 in the manuscript. The background statistics is discussed earlier on in this document in response to the first reviewer.

Reviewer comment 2: L18: Why did you connect the temperature and RH sensors at the outlet (and not the inlet)?

Authors Reply: The RH sensor is sensitive to aerosol contaminations and therefore we installed the RH sensor after a filter at the outlet of the instrument.

Reviewer comment 3: P6302 L3 and P6305 L8: at which frequency do you change filter? Maybe you could mention here the duration (always 1 minute?)

Authors Reply: As discussed in response to the first reviewer, the rotation of the filterwheel was controlled manually. This point has been clarified in the manuscript at P6299 L 13 – 15. Measurements on each filter were done for about three to four minutes during the calibration process after which the wheel was rotated to select the next wavelength band. A sentence clarifying this point is included in Section 4 of the revised manuscript.

On the other hand, during the experiments, once a wavelength was selected, background measurements were done for approximately one minute, followed by one-minute sample measurements. Background measurements were repeated after the sample measurements to record the background drifts. Therefore, the total time spent on a filter was approximately 3-4 minutes after which the filterwheel was rotated to select the next wavelength.

This has already been mentioned in the manuscript in Section 5.

Reviewer comment 4: L16: what are the dimensions of the iron lung?

Authors Reply: The iron lung is a steel cylindrical drum having a diameter of 64 cm and height of 86 cm. It is lined with a conductive liner and has a capacity of 277 l.

Reviewer comment 5: P6303: L16: why did not you use the CO2 to calibrate the nephelometer part?

Authors Reply: We discussed this issue in detail in response to comment 7 of reviewer 1.

Reviewer comment 6: P6305 L12: What is “a value too low”?

Authors Reply: The sentence that the reviewer refers to, was replaced by:

“The aerosol was sampled at a rate of 2 lpm from the iron lung, which has a capacity 277 l so we expect the lung to be able to deliver aerosols for ~2 h 20 min. The total time taken by 6 runs in an experiment was approximately 2 h 6 min, therefore after 6 runs we started noticing a rapid drop in the aerosol concentrations by a third of the original value and we stopped measuring.”