Response to Reviewers Manuscript Number: AMT-2015-100

Manuscript Title:

Spectral Aerosol Extinction (SpEx): A new instrument for in situ ambient aerosol extinction measurements across the UV/visible wavelength range

The comments from the referee are italicized, with our responses in plain text. All of the line numbers refer to the original manuscript.

Anonymous Referee #2

Received and published: 17 July 2015

Summary of the Work

This paper describes an instrument to measure aerosol extinction from 300 – 700 nm. It uses a Xenon arc lamp, White cell with 40 m path length, and a grating spectrometer with CCD. The authors measure spectra of NO2, polystyrene latex spheres, and a variety of aerosol types. They find agreement of their measurements with literature NO2 cross sections and calculated extinction for PSL. The authors determine the detection limit using an Allan deviation plot.

This work builds on a previous results by Chartier and Greenslade (2012).

This paper is well-written and well-organized. It represents the next step toward deploying the wavelength-resolved White cell as a field instrument.

We thank Referee #2 for their compliment.

Comments

- Determining weak wavelength-dependent absorption from extinction spectra is very difficult, and the paper seems to over-promise this potential in a few places:

We agree with this concern and have modified our language accordingly.

Pg 6471 lines 12-14: "SpEx can more accurately distinguish the presence of brown carbon from other absorbing aerosol due to its 300 nm lower wavelength limit compared to measurements limited to visible wavelengths."

This sentence has been revised to:

"SpEx measurements are expected to help identify the presence of ambient brown carbon due to its 300 nm lower wavelength limit compared to measurements limited to longer UV and visible wavelengths."

Pg 6475 lines 5-7: "However, in the UV, particularly at wavelengths as short as 300 nm, the absorption term may be expected to influence the shape of the extinction spectrum such that differences among these groups may be determined."

This sentence has been modified to:

"However, in the UV, particularly at wavelengths as short as 300 nm, the absorption term may influence the shape of the extinction spectrum revealing differences among these groups."

I would recommend softening these statements a bit. As an example, for an ambient extinction of 100 Mm-1 at 300 nm and a single-scattering albedo of 0.95, the absorption is 5 Mm-1. In the ambient atmosphere, 70% or more of that absorption may be due to black carbon. The actual brown carbon absorption signal that you are looking for would be 1.5 Mm-1. This is beyond the current detection limit of the instrument.

Your point is very well taken and we have tried to tone down our language. Your example makes an excellent point. However, if there are BrC sources that are independent of BC (e.g., colored dissolved organic matter (CDOM) and humic like substances (HULIS) in surface waters have absorption spectra akin to BrC), then one might find non-combustion related BrC aerosols with a distinctive extinction spectrum (in addition to a unique absorption spectrum). One of the reasons we are interested in making this measurement in ambient atmospheres is to learn whether BrC only arises from combustion or whether there are other sources that give rise to BrC aerosols (either primary or secondary).

- Is the Xenon lamp temperature-controlled? What is the part number for the Xenon lamp?

We did not control the temperature of the lamp (please see our response to Referee #1 for more details). We have made a note of this in the text (page 6480, lines 12-14) as follows:

"This may arise from thermal variability of the lamp (which was not temperature-controlled for these tests), temperature variations of the gas cell inducing minor fluctuations of the optics, or variability in the power source for the lamp."

The part number for the xenon lamp has been added to the text (page 6478 lines 13-15):

"SpEx (Fig. 1) was custom designed based on the UV 5000 gas analyzer system (Cerex Monitoring Solutions, LLC, Atlanta, GA) with a 150 W xenon lamp source (Cerex P/N CRX-X150W), integrated with an Ocean Optics, Inc. (Dunedin, FL) QE65Pro 16-bit spectrometer."

- What is the wavelength resolution of the grating spectrometer, determined using a narrow reference line source (such as a Hg or Ne penray lamp)? There is a mention of an offset in the wavelength calibration on pg. 6484, but no description of calibrating the wavelength using a standard.

See the following comment for updated text on the wavelength resolution of the spectrometer. Note, we did not calibrate the spectrometer. The Ocean Optics QE65 Pro was incorporated into the UV5000 system by Cerex Monitoring Solutions. The offset we discuss is strictly in relation to the NO_2 and monodisperse PSL tests conducted as a test of the instrument performance. The 1 nm shift we observed is unlikely to matter for ambient aerosol measurements where the particles will not be monodisperse.

- What is the wavelength resolution in terms of nm/pixel on the CCD?- Pg 6479 lines 17-19: How was the optimum path length determined? It is unclear in the text.

The text (page 6478 lines 19-20) has been updated to include the resolution:

"The QE65Pro includes their standard 1024 pixel detector and a composite grating providing 1.36 pixels per nm over a range of 750 nm starting at 200 nm resulting in a spectral resolution of approximately 0.7 nm."

To clarify the optimum path length the text has been modified (starting at line 13, page 6479):

"The White-type cell (Fig. 1) is designed to allow for a range of optical path lengths. As is evident from Eqn. 4, for any given difference between I and I_0, a longer path length (L) offers greater sensitivity in extinction, while for any given path length maximizing I_0 improves sensitivity of σ_{ext} to I. With a 48-inch (1.23 m) basepath between mirrors, an alignment with 6 spots across the top of the primary mirror (28 passes total) provides an optical path length of 34.4 m, while the maximum of 8 spots (36 passes total) extends the path to 44.3 m. Since a little light is lost at each reflection of the light beam, intensity decreases as the path length (i.e., the number of spots) increases. Hence, determining the optimum path length requires a balance in maximizing the intensity versus maximizing the number of spots. In tests at Cerex Monitoring Solutions, 7 spots (32 passes total) were found to offer the optimum path length of 39.4 m, given the light source and the efficiency of the mirror coatings over the UV/Vis range."

- Pg. 6479 lines 24-25: "Since the spot is larger than the fiber diameter (600 um). . ." Are the authors using a lens to collect and focus the light into the optical fiber? That would improve the light collection.

Text has been added at the end of line 21 page 6479 to note:

"Collimating lenses focus the light as it enters and exits the cell."

- How were the 100 ppb NO2 concentrations generated? One can use either a cylinder of NO2 in N2 or generate NO2 continuously by adding excess NO to a measured concentration of O3. It isn't clear what was done in this case, or why the flow was not continuous during the NO2 measurements.

We have amended the text in Section 3.1.1 (page 6483, starting at line 17) to clarify this:

"100 ppb NO_2 (diluted from a calibrated cylinder of 5 ppm NO_2) was measured (using a Los Gatos Research instrument model 907) across the sample-line filter showing negligible difference in mixing ratio between downstream and upstream locations, suggesting the filter is not modifying the NO_2 concentration between the filtered and unfiltered sampling lines. Additional tests using both O_3 (Thermo Environmental Instruments model 49C ozone analyzer) and NO_2 showed that O_3 is not being produced (conversely NO_2 is not lost) in the optical cell by the light sources with 70-80 lpm flow."

And in the following paragraph (page 6484 line 5):

"For NO_2, a series of four tests were done starting with an undiluted 5 ppm test from the calibrated cylinder, followed by a series of three dilutions (1 ppm, 250 ppb, and 100 ppb). NO_2 tests were performed by slowly filling the cell, capping it, then collecting spectra, in order minimize the volume of calibration gas that would have been consumed with the 17 l volume and typical 80 lpm flow rate. Stopping the flow led to increased surface losses. Correcting the SpEx absorption spectra for these losses, it is clear that SpEx obtained a curve that captured the expected features calculated from GOME/SCIAMACHY NO_2 cross-section data binned to 1 nm resolution (Fig. 3). Similar results were obtained in all four tests, only the 5 ppm results are shown here."

- Pg. 6484 line 21 – It would be better to consistently refer to the PSL diameters as 600 and 903 nm, instead of 600 and 900 nm, since those are the mean diameters given by the manufacturer.

The text and figure labels have been updated throughout the manuscript. Note, the 900 nm monodisperse curve shown in Fig. 4 remains unchanged to preserve clarity in contrast to the 904 nm curve.

- Pg. 6484 line 22 – Quantify "excellent agreement" in the text. - Pg. 6486 line 4 – Quantify "low noise" in the text.

In view of the suggestion regarding the use of "coarse" and "fine" in the comment below, we have removed the sentence on page 6486 (lines 3-6) for clarity and revised the text (page 6484 line 22) for "excellent agreement" as follows:

"The measured extinction spectra for 600 nm and 903 nm PSLs capture the structure of spectra (Fig. 4) calculated from the extinction cross-sections (C_{ext}, m^2/particle)."

- Figure 3 states that the GOME-SCIAMACHY NO2 spectrum was averaged to 1 nm resolution. The more correct approach is to convolve the reference spectrum with the instrument lineshape of the spectrometer. The lineshape is determined using a narrow reference line source.

It is not clear to us how a calibration with a narrow line source can be appropriately applied over the full wavelength range of the instrument. This was why we did the NO_2 and PSL tests, in order to compare the instrument performance to well-established theoretical calculations that applied over a broad spectral range. We have not done any tests with narrow line sources, so we are unable to follow this particular recommendation.

- Figure 4 - This data is very nice.

Thank you.

- "Coarse" and "fine" are unclear. Change to "low resolution" and "high resolution" throughout. It would also be useful to give an example of the wavelength range you mean when you first mention each, since ideas of "high resolution" vary.

This is a good point. At the first occurrence of coarse and fine (page 6484 starting at line 12) we have revised the language as follows:

"The comparison in Fig. 3 shows the ability of SpEx to capture the broad absorption peak centered around 400 nm over the 300-500 nm range, along with high spectral-resolution features down to a few nm width. In laboratory studies similar high-resolution features in spectra of monodisperse aerosols have been used to retrieve refractive indices (e.g, Chartier and Greenslade, 2012)."

There were no other uses of "coarse". There were only 4 remaining uses of "fine", two were simply changed to "high spectral-resolution". The final two uses were in the 2nd paragraph of Section 3.2 (page 6487 starting at line 9) revised as follows:

"This variability in shape arises from differences in the refractive indices of these materials, along with some variability that may be due to minor differences in the size distributions (e.g., the high spectral-resolution structure in the PSL spectrum arises from a nearly monodisperse size distribution whereas the DMA size selected AS and citric acid particles were more broadly dispersed). Spectral comparisons of particles with a constant size illustrate the utility of SpEx to measure spectral differences that arise from variability in chemical composition."