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 #3

Received and published: 27 July 2015

The manuscript "Spectral Aerosol Extinction (SpEx): a new instrument for in situ ambient aerosol extinction measurements across the UV/visible wavelength range" by Jordan et al., describes an instrument to measure the extinction coefficient of aerosols between 300 – 700nm. The authors measure NO2 and different aerosol types (purely scattering, brown carbon and black carbon proxies) to demonstrate its functionality and give its limitations. The manuscript is well written and clear; however, I think it needs several changes before it is publishable in AMT.

The title should be modified. It is not clear why the instrument is new. The authors are not presenting a new technique and the differences between the instrument presented here and the one by Chartier and Greendslade 2012 don't seem substantial to label the SpEx as a new instrument. The SpEx presents improvements in some aspects to the AE-DOAS; e.g., it has lower detection limits, but it's on the expense of size (the SpEx is double in length). On the other hand, the wavelength range is narrower: 300-700nm instead of 225-700nm. Also the authors do not present ambient measurements; all of the aerosol measurements presented are from laboratory measurements of aerosol proxies.

We respectfully disagree with the referee on this point. We used the language "a new instrument" purposefully. It is in fact a new individual instrument with unique capabilities compared to other existing instruments designed to make similar measurements (whether in laboratories or in the field). It is not a new technique nor methodology, which we make clear in the text. It does offer a new capability for field measurements that we are really excited about. The fact that we do not include field measurements in this manuscript, is because we felt that it was important to devote the first manuscript to laboratory tests that prove the instrument works properly. However, it was not designed to be a bench top instrument. It was designed for studies of the ambient atmosphere. So, the title is intended to state up front the intended purpose of this instrument. Therefore, we have not changed the title.

As an aside about the name, on more than one occasion, both Drs. Greenslade and Jordan have encountered colleagues who found the name AE-DOAS confusing, since the difference method used here is not the same as the traditional DOAS approach for gas measurements. At their urging, we adopted a new name for SpEx.

The statement that SpEx can distinguish BrC from other aerosols is not well supported. The SpEx is measuring total extinction not absorption.

We agree with all three referees on this point and have modified our language throughout the text as noted in our responses to each of the referees.

In page 6489 lines 5 and 6, the authors state "Clearly, cinnamaldehyde exhibits behaviour typical of BrC, while 2-CB does not." It is incorrect; the cinnamaldehyde extinction curve can very well be of a purely scattering substance or of a substance with constant absorption throughout the measured spectrum.

We have revised the paragraph starting on line 26 of page 6488 (it contains the sentence at lines 5-6 on page 6489) as follows:

"The extinctions obtained from polydisperse Fullerene soot, Aquadag, and 2-CB are ~1.5 times larger at 300 nm than 700 nm. Unlike the other compounds tested, polydisperse cinnamaldehyde has a strongly curved spectrum where extinction at 300 nm is 7.5 times larger than at 700 nm (Fig. 9, right panel). The shape of this spectrum is suggestive, especially since cinnamaldehyde has a molecular structure consistent with expectations for a BrC compound. The characteristic trait of BrC is strongly enhanced absorption in the UV spectral range. Given the variable sources of BrC and the differing photochemical fates of the diverse chemical compounds that are likely to contribute to BrC (e.g., Lee et al. (2014); Laskin et al. (2015)), there is no widely adopted standard BrC surrogate. Both 2-CB and cinnamaldehyde were tested here specifically to try to identify a possible BrC surrogate (based on Scheme 1 in Lee et al. [2014]). Of the two, cinnamaldehyde exhibits the curvature that might arise from enhanced UV absorption (assuming that absorption contributes a significant fraction to the extinction at the lower UV wavelengths). For the rest of this discussion, we will treat cinnamaldehyde as a BrC surrogate compound."

The discussion about the extinction following a power law should be erased or modified (pages 6489 – 6490). For BrC it is the absorption which has been observed to follow an inverse power law relationship with wavelength, the extinction will not necessarily follow an inverse power relationship. Even with a theoretically perfect power law behaviour of the absorption and scattering, the extinction will not follow an inverse power law (see Figure below where first I forced the absorption and scattering coefficients to have an Ångström exponent of 6.3 and 2, respectively. The extinction coefficient plotted is the sum of the abortion and scattering. Finally, I fitted power laws to all traces and a polynomial to the extinction. It is clear from the residual that the polynomial fit is a better fit to the extinction.)

We agree with Referee #3 on this point, which is the one we were trying to make. The Ångström exponent was introduced in 1929 for extinction/optical depth (Moosmüller and Chakrabarty, 2011) and is still used to describe extinction in the literature. The polynomial discussion was included to show other mathematical descriptions may be preferable. We have modified this discussion as follows:

page 6489, line 26:

"As discussed in the introduction, historically the extinction spectrum has been described with an inverse power law relationship with wavelength as in Eq. (1) (Ångström, 1929; Moosmüller and Chakrabarty, 2011)."

page 6490, line 7:

"Absolute α_{ext} differences between the 450,530 nm pair and a SpEx-enabled 300,530 nm pair were small for the BC surrogates (0.00 to 0.18) but significant for the BrC surrogate (cinnamaldehyde, 0.79). This result supports prior studies (e.g., Eck et al. (1999); Schuster et al. (2006)) indicating that for some aerosols mathematical descriptions other than power laws may better describe the spectral shape of α_{ext}."

page 6490, line 17:

"Power laws are typically used when decades of data are spanned in log-log space over the relevant intervals in x and y."

page 6490, line 21:

"This curvature is why α_{ext} is sensitive to the choice of wavelength pairs used in its calculation. In all cases polynomials provided a better fit to the data than power law functions."

The authors should add a paragraph on how they handled multiple charge particles in the size selected measurements. With 80 lpm flow they probably had very high concentration solutions in there atomizer, this will cause size distributions with large mode diameters and when choosing 200nm many multiple charge particles will go through. In other words, the size selection measurements will not be monodisperse and they might not be comparing measurements of the same size.

We have added the following sentence, immediately following the sentence that ends on line 28 of page 6482:

"For these size-selected tests, we did not correct the size distributions for multiply charged particles as all compounds selected at the same size using the same flow rates will have similar percentages of multiply charged species resulting in a similar size distribution for all cases."

Other comments:

Is the Xenon lamp temperature controlled? From Fig. S1 it seems critical to have a temperature control as any temperature change might cause a wavelength drift in the output spectrum and hence a wrong calculation of the extinction coefficient.

The xenon lamp is not temperature controlled, now noted in the sentence starting on line 12 on page 6480:

"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."

We account for the small drift from one spectrum to the next, by averaging the reference spectra immediately prior to and after each sample spectrum (see sentence on lines 14-17 of page 6480).

Did the authors check for stability of the lamp throughout a long time period? What's the intensity variation in say an 1h, 5h or 24h period?

We examined the intensity variation over long periods both in the laboratory and in the field where we collected data around the clock. Over a 24 hr period the drift in intensity could be quite large (dropping with decreasing temperatures overnight in Colorado by ~50% before increasing again with temperature the next day). This was not solely due to lamp stability, but also involved factors related to the temperature of the optical cell and the tightness of the screws holding the optics in proper alignment (in the mobile laboratory vibrations while driving loosened the screws). These observations during the Colorado field deployment have motivated instrument upgrades that are underway to improve thermal and mechanical stability of the instrument. Nonetheless, on the short time scales used for acquiring spectra, using our averaging approach for the reference spectra, we obtained reproducible extinction spectra both in the lab and in the field (as will be shown in a manuscript in preparation from the Colorado field campaign).

Why was there a 1nm offset found in the absorption spectrum of NO2? Did the authors do a calibration with a mercury lamp?

The offset was evident in the comparison of our measured NO_2 spectra with the calculated values from the cross-sections. We did not perform any calibrations of the spectrometer.

Do the authors have measurements of NO2 at lower concentrations than 5ppm? Can the authors show that the SpEx measured different concentrations of NO2 at more relevant atmospheric concentrations and that the measured concentration of NO2 is similar to that measured to the NO2 instrument?

We performed a series of 4 tests using the 5 ppm calibration standard and dilutions of 1 ppm, 250 ppb, and 100 ppb. The following two sentences were added to the text:

on 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)."

on page 6484, line 10:

"Similar results were obtained in all four tests, only the 5 ppm results are shown here."

For the 600 and 900 nm PSL measurements, the authors mention the best fit was found using slightly larger diameters. I'm guessing these measurements were done using a DMA, so if in the DMA the diameters were chosen to be 600 and 900 nm, why the difference? Regardless of the manufacturer specifications the DMA will transmit the chosen diameter.

We did not use a DMA for the PSL tests as they are manufactured to be monodisperse. We initially referred to 900 nm PSLs in the text for parallel construction with the 200 nm and 600 nm tests, but they were in fact 903 nm ± 9 nm (see page 6485 line 2). Per the recommendation of Referee #2, we have amended our language and replace 900 nm with 903 nm throughout the manuscript.

The authors should compare there PSL results to values in the literature. Chartier and Greenslade 2012, Miles et al. 2010 and Washenfelder et al. 2013 have good summaries of the values available.

We have added the following sentences to the text:

page 6484 line 20:

"The wavelength dependence of the refractive index (Fig. 4, top panel) is consistent with results reported by Washenfelder et al. (2013) and references therein."

page 6484 line 22:

"The 600 nm PSL spectra also agree well with that shown in Chartier (2010)."

And the following has been added to the list of references:

"Chartier, R. T., Aerosol extinction measurements with a new multipass aerosol differential optical absorption spectrometer (A-DOAS): Laboratory validation and initial ambient measurements, M.S. Thesis, University of New Hampshire, Durham, NH, September, 2010."

Page 6485 line 25: "in Fig. 5b good agreement is found..." Can the authors give percent difference to give a quantitative number to the 'good agreement'?

That sentence now reads:

"However, in Fig. 5b good agreement (typically within 15%) is found with the measured spectra from SpEx at each instrument's specific wavelengths."

In Fig. 5 why is there a difference between the CAPS and the nephelometer at 450nm?

I do not know why there was a difference between CAPS and the nephelometer at 450 nm. For a purely scattering substance they ought to be the same, but they were not.

Page 6486 line 17-18: "SpEx data were averaged over 5nm. . ." why do the authors need to average over 5nm? what is the wavelength resolution?

We have revised the text to include the wavelength resolution (page 6478 line 19):

"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."

We averaged the SpEx data over 5 nm to minimize differences that might arise from any mismatch in the exact wavelength window between the CAPS PMex spectral resolution and SpEx.

What agreement do the authors get if they do the same analysis done in Fig.6 with only the purely scattering substances and the nephelometer?

We have added a plot to the supplementary information equivalent to Fig. 6 for the nephelometer and appended a sentence to page 6486 line 23:

"A similar comparison between SpEx extinction and scattering measured by the TSI nephelometer for the purely scattering aerosol tests shows similarly good agreement (Fig. S3) with slopes near unity and r^2 values of 0.94-0.95."

Can the authors give single scattering albedo for the absorbing substances they measured at the nephelometer wavelengths? These values can be useful to other authors using them as proxies.

Following the sentence noted above (page 6486, appended to line 23) we have added:

"Single scattering albedo values calculated from the nephelometer and SpEx data shown in Fig. S3 are given in Table S3."

Page 6487 line 25: "for Luberon natural Red, there is surprisingly little difference be- tween the PM1 and PM2.5 spectra." Maybe it is due that there are not many particles above 1µm? The authors can check the size distribution from the APS

We were careful to confirm the sizes generated by the wrist shaker and are confident that our size distributions are correct.

References

Chartier, R. T. and Greenslade, M. E.: Initial investigation of the wavelength depen- dence of optical properties measured with a new multi-pass Aerosol Extinction Differ- ential Optical Absorption Spectrometer (AE-DOAS), Atmos. Meas. Tech., 5, 709–721, doi:710.5194/amt-5195-5709-2012, 2012.

Miles, R. E. H., Rudic, S., Orr-Ewing, A. J., and Reid, J. P.: Influence of uncertainties in the diameter and refractive index of calibration polystyrene beads on the retrieval of aerosol optical properties using Cavity Ring Down Spectroscopy, J. Phys. Chem. A, 114, 7077–7084, 2010.

Washenfelder, R.A., Flores, J.M., Brock, C.A., Brown, S.S., and Rudich, Y., Broadband measurements of aerosol extinction in the ultraviolet spectral region, Atmos. Meas. Tech., 6, 861-877, doi:10.5194/amt-6-861-2013, 2013.

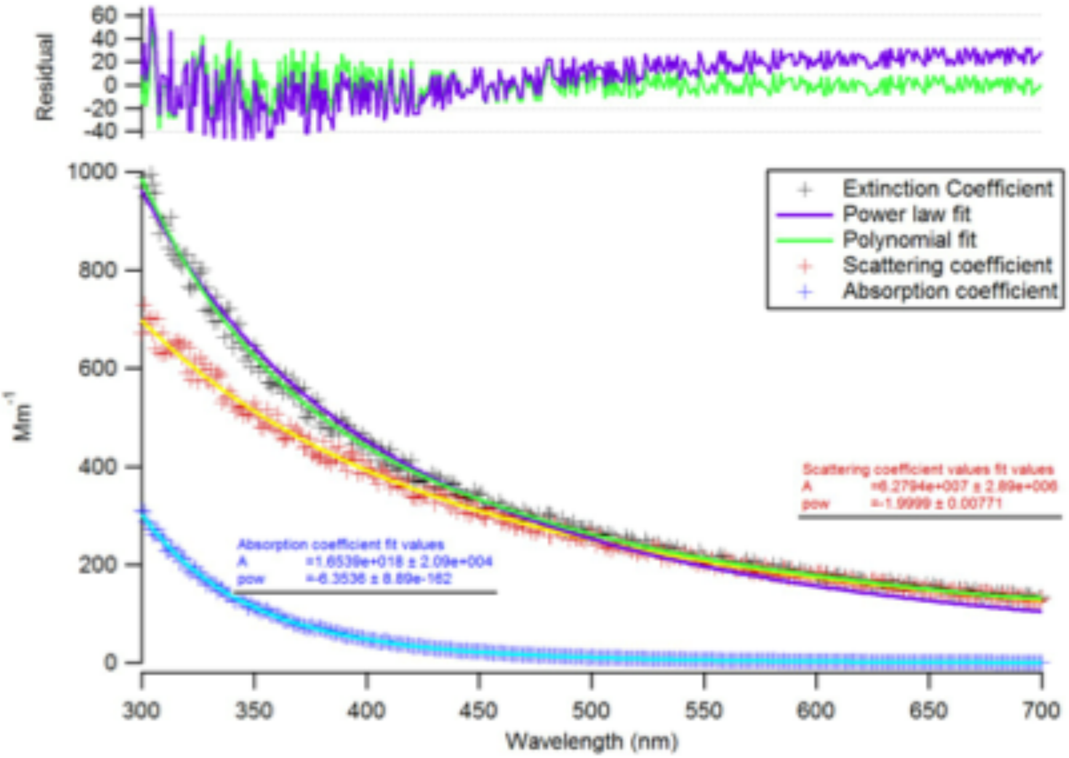
Residual
60
40
20
0
-20
-40
1000
800
600
400
200
0
Mm⁻¹
Extinction Coefficient
Power law fit
Polynomial fit
Scattering coefficient
Absorption coefficient
Scattering coefficient values fit values
A =6.2794e+007 ± 2.89e+006
pow =-1.9999 ± 0.00771
Absorption coefficient fit values
A =1.6539e+018 ± 2.09e+004
pow =-6.3536 ± 8.89e-162
300
350
400
450
500
550
600
650
700
Wavelength (nm)

Fig. 1.