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Comment

# ***Interactive comment on “Light extinction by Secondary Organic Aerosol: an intercomparison of three broadband cavity spectrometers” by R. M. Varma et al.***

**R. M. Varma et al.**

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We thank the reviewers for their time and effort in evaluating our manuscript. Both reviewers seem assured of the value and timeliness of the work and interest to the community, both regarding the instrumental techniques and the unusually high refractive index found for SOA from NO<sub>3</sub> oxidation of  $\beta$ -pinene. Specific comments and concerns of the reviewers are addressed below.

**Reviewer 1:**

**One concern is the experiment that is presented as a “validation” of sorts in Fig-**

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ure 1. In this experiment ammonium sulphate aerosol is probed and Mie theory used to provide validation of IBBCEAS measurements. While any NO<sub>3</sub> absorption seems to successfully be “deconvoluted” from the remaining signal, the aerosol extinction coefficients reported are very, very low. Given the tendency for the instruments to exhibit baseline drift, I would encourage the authors to attempt this experiment at higher aerosol loading so it can be determined whether the 20-25% discrepancy between Mie model and measurements is conserved. Also, why no CE-DOAS or BB-CRDS data? The result of this experiment is obviously very important to ascertain the uncertainty in subsequent measurements, and ultimately, the refractive index reported for the SOA proxies.

The reviewer is correct to point out the limitations of using a sample with a low extinction as the basis for comparing Mie calculations to the measured extinction of the ammonium sulphate particles. Although it would be desirable to compare the measurements under conditions of higher sample extinction, it is not feasible to repeat the experiments under different conditions as the results presented here are from a one-off intercomparison campaign. What the results are intended to show is the reasonableness of the retrieved extinction values against theory, even at very low sample extinctions.

More generally, however, the comparison against Mie theory is not the only measurement of the accuracy of the approaches discussed in the paper. The agreement in the intercomparison results is itself evidence of the accuracy of the retrieved values (within the stated uncertainties); additionally, the NO<sub>3</sub> and NO<sub>2</sub> intercomparison results also indicate that the instruments accurately retrieved the overall sample extinction (that is, from gas phase absorption, and absorption and scattering from the particles), as is pointed out in the text.

BBCRDS and CE-DOAS measurements of particle extinction were not reliable on this day (15 June) and were therefore omitted. A statement to this effect will be added to Section 3.1.

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**Figure 2 – it is a pity no particle count concentration data exists for this experiment. It would provide a great opportunity to study how the refractive index evolves in time. Also, if AMS data could be added - that would be a nice improvement.**

CPC data are available for this experiment and show a very sharp rise in the particle number concentration around 09:00, followed by a rapid decrease. These data were not included in Figure 2 for a few reasons. Firstly, the aerosol extinction depends on both particle number and size, and the relationship between measured extinction and aerosol properties is better captured in the mass concentration and size shown in Fig. 2. The mode diameter exceeded 100 nm only after 12:00 and little extinction is evident before this time. Secondly, the graph is already congested (four y-axes); adding another property would obscure the relationships between the measured properties.

AMS data are analysed in detail in the Fry et al. (2009) paper and implications of their analysis of particle composition are discussed in the present work. We think that explicit treatment of the AMS data again is not warranted for this paper.

**One improvement that could be offered would be the addition of a description of how aerosol extinction was extracted from the raw data. Would be valuable to this reader from a tutorial perspective.**

The BBCRDS and CE-DOAS instruments effectively measure the total aerosol extinction in the chamber, and then subtract off the absorptions of absorbing gases. These are described in Eqs (1) and (2) and the respective instrument descriptions. The IB-BCEAS spectral analysis, based on the changes in the observed absorption strength for the O<sub>2</sub> B-band, is also described on pp. 6696-7 and Eqs (4) and (5). We reviewed the respective sections in light of this comment, but believe the analysis procedures are already written at the appropriate level and provide enough information for others to understand our approach and reproduce our experiments.

**Bottom of page 6703- authors assume uncertainty in measurements of 10%, but**

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**data in Figure 1 deviated from Mie theory by more than this. So authors may wish to expand uncertainty range or simply try measurements at higher levels of extinction for the ammonium sulfate so the performance can be better assessed.**

The uncertainty of 10% is based both on the agreement between the instruments, as well as their stated uncertainties in the context of the maximum extinction of the SOA (70–90 Mm<sup>-1</sup>) for the  $\beta$ -pinene SOA. The relative uncertainty is indeed larger in Figure 1, but those results are already close to the limits of the instrumental sensitivity and thus more susceptible to small, absolute contributions to the uncertainty (such as instrument drift). A larger relative uncertainty is therefore not surprising for Figure 1, but the stated uncertainty of 10% remains appropriate for the  $\beta$ -pinene SOA in Figures 3 and 4.

**End of page 6706 – the authors write a section about “extinction minus scattering” approaches. It is very unclear why this discussion occurs to me here. I would suggest removing this since this was not attempted in the work, and it “feels” a bit distracting to the reader.**

The reviewer is correct that extinction-minus-scattering was not attempted in this work and that this part of the discussion is not strictly necessary. Our reason for including this discussion is that this work is the first intercomparison of these types of spectrometers for aerosol studies, and their use for studying aerosol optical properties is still quite novel. Thus, readers may well be interested in their wider applicability to other aerosol types, and it was in this context that we sought to broaden the discussion to the potential utility of these spectrometers to different aerosols and the quantification of aerosol absorption, in particular.

**Page 6707 – description of broadband UV retrievals. It seems to me that use of such a method in the UV may be considerably more difficult because if any absorbing gases are present that are not accounted for in the model, aerosol extinction would be over estimated. Despite the vast knowledge that exists regard-**

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ing absorbing atmospheric gases, some trace components may be unaccounted for – and these absorbing components would mask as aerosol extinction (particularly if broadband absorption). This would cause the worst type of uncertainty in aerosol extinction – one of unknown, potentially variable quantity. In general, this section of text could easily be omitted without much value loss to the literature.

As for our response above, the aim of this section was to broaden the discussion to include the potential and limitations of the broadband spectrometers for characterising aerosol optical properties. The UV is particularly interesting in that much fewer measurements are available in this spectral region. The reviewer is correct that such measurements are more challenging at shorter wavelengths where much greater numbers of molecules absorb, and failing to account for such absorption would positively bias the retrieved extinction. That said, however, there are strategies to remove or quantify the effects of gaseous absorption, e.g., through the use of denuders on the inlet or particle filters. Potential gas phase absorption is therefore not an insurmountable obstacle to retrieving the aerosol extinction in the near-UV. We added the following sentence to address this issue: “Measures must obviously be taken to ensure that no gas phase absorption is attributed to aerosol extinction; strategies to accomplish this may include the use of a denuder, or switching between filtered and unfiltered inlet lines.”

**On page 6709 the authors conclude that organic nitrates may be responsible for the high refractive index determined. It seems to me this is perhaps a logical conclusion. Since it appears that AMS experiments were conducted simultaneously, can the authors provide any chemical speciation data to provide insights into composition? Did the aerosol composition change in time?**

Chemical composition changes are discussed in the AMS data of Fry et al. (2009), and described on p. 6703. Fry et al. (2009) show that the agreement between model and measurements indicates that the first generation of oxidation chemistry is the only significant source of nitrates and that subsequent chemistry during the run does not

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convert the nitrates to nonnitrate species. However, they did report some changes in the fractional composition of organic nitrates in particles – namely, a gradual decline over time after a maximum in particulate organic nitrate in the early stages of the experiment. This temporal change will be briefly outlined in the text: “Model results suggest that the first generation of oxidation chemistry was the only significant nitrate source in the experiment and that subsequent chemistry did not convert nitrate into non-nitrate species. After rapid initial formation of organic nitrates, the fraction of organic nitrates in the particle phase declined gradually over several hours.”

**Also, nitrated aromatics are known to absorb light in the visible portion of the spectrum (see Jacobson, M. Z. (1999), Isolating nitrated and aromatic aerosols and nitrated aromatic gases as sources of ultraviolet light absorption, J. Geophys. Res., 104(D3), 3527–3542). So in this case, is the assumption of non-absorbing aerosol discussed on page 6703 truly valid?**

Aerosols in the chamber can reasonably be assumed to be non-absorbing. Although the Jacobson (1999) paper identifies molecules absorbing in the visible, these are always substituted aromatic compounds, none of which were present during the reported experiments with biogenic precursors. The AMS data indicated carbonyls and organic nitrates were present in the particles, but these functional groups do not absorb at long visible wavelengths. We considered other likely functional groups from the oxidation products of biogenic SOA, but none absorb light above 600 nm.

**Can the authors provide additional details of the particle sizing / particle counting procedures and extraction of refractive index? A possible source of the discrepancy in refractive index (large value reported here) is an underestimation of particle concentrations. Is it possible aerosol was lost in transfer lines?**

A single vertical 0.5" i.d. stainless steel transfer line was used to sample from the chamber to the measurement container housing the aerosol instrumentation. In contrast to Teflon, static charge does not build up in a steel line. We think that SOA formed

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in the limonene and pinene experiments is not markedly lost in the transfer line, because the particles size (SMPS mode aerosol diameter, see Fry et al., 2009, Fig. 1: 50 nm < SOA <= 250 nm) is small and impact losses have not been observed in comparable SOA experiments in the chamber. The following sentence has been added to the experimental section: “A single vertical 0.5" i.d. stainless steel transfer line was used to sample from the chamber to the measurement container housing the aerosol instrumentation. In contrast to Teflon, static charge does not build up in a steel line. Particle losses during sampling are expected to be minimal because of the small particle size (< 250 nm mode diameter) and because impact losses have not been observed in comparable SOA experiments in the chamber.”

## Reviewer 2:

Major comments:

**1) In this study, it is suggested that organic nitrates are likely cause for the high SOA refractive index (Page 6709, lines 7-9). Nakayama et al. (2012) reported smaller real part of RI at 532 and 781 nm for the SOAs generated in the photooxidations of  $\alpha$ -pinene in the presence of  $\text{NO}_x$ . They reported the nitrate to organic (HRNO<sub>3</sub>/HROrg) and oxygen atom to carbon atom (O/C) ratios of the SOAs were 0.036 ± 0.006 and 0.47 ± 0.01, respectively (Table 1 of their paper). Lambe et al. (2013) recently reported that the real part of RI value at 405 (as well as 532 nm) decrease with O/C ratio for SOAs generated in the photooxidations of  $\alpha$ -pinene in the absence of  $\text{NO}_x$  (Fig. 6 of their paper). I think it will be valuable if the authors can add the HRNO<sub>3</sub>/HROrg and O/C ratio for the SOAs generated in this work and compared with their results.**

We thank the reviewer for drawing these relevant papers to our attention; these will be added to the text and Table. We reported the organic nitrate composition as a fraction of the total mass (p.6703) based on the Fry et al. results. The  $\text{NO}_3$  oxidation chemistry prevalent during our experiments resulted in a large fraction of organic nitrate of 40-

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45% (corresponding to HRNO<sub>3</sub>/HROrg of 0.66 to 0.82 at the extinction maximum), which suggests that the oxidation regime in our experiments is distinctly different from other studies and at least partly responsible for the higher refractive indices in our study. This difference is largely addressed in the discussion already by referring to the HC/NO<sub>x</sub> ratio.

**2) The mass of SOA in Fig. 2 seems to show non-negligible generations of SOAs from around 9:00 before the additions of ozone at 10:30. It might be nice if the authors would add possible explanations.**

We checked the times and quantities of additions based on measured O<sub>3</sub> concentrations to resolve this discrepancy. Experiments were indeed started in a clean chamber, but the limonene oxidation and particle formation started with the addition of ozone at 08:50, and not 10:30 as originally stated in the text. The time of the second O<sub>3</sub> addition is correct (ca. 14:30) and the caption to Figure 2 will be amended accordingly. The text in Sect 3.1 will be modified slightly to indicate the time of the oxidant addition: “Limonene was introduced in two stages: in the first stage, 10 ppbv of limonene was added to the chamber followed by the addition of NO<sub>2</sub> and O<sub>3</sub> before 9:00”.

**3) It is important to show the reliability of the calculations of real part of RI. It would be better if the authors could add temporal variations of mass (or total volume/surface) concentration and mode (or average/mean) diameter of SOAs in Fig.3(a) and 4(a).**

The SMPS mode diameter will be added to the Figures 3a and 4a.

Minor comments:

**1) Page 6693, lines 13-14: How was the interval of zero air measurement?**

Reference ring-down times  $\tau_0(\lambda)$  were acquired whilst flushing the cavity with dry synthetic air at the start, the end and at least once during a SAPHIR experiment. Any differences in these  $\tau_0(\lambda)$  measurements due to, for example degradation in the cavity's

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alignment caused by temperature variations, tended to produce a spurious broadband contribution to the measured spectrum which was fitted by the unstructured  $\varepsilon_{con}(\lambda)$  absorption term in equation 1. Such instrument artefacts produced uncertainties of typically  $< 5 \text{ Mm}^{-1}$  on the aerosol extinction measured by BBCRDS (this is the figure quoted on page 6693 line 22). The following sentence was added: “Reference ring-down times  $\tau_0(\lambda)$  were acquired at the start, end, and at least once during a SAPHIR experiment, and  $L_f$  was based on fits to the known water vapour content of the chamber (Shillings et al., 2011).”

## 2) Page 6693, eq. (1) and page 6696, eq. (3): How did authors determine the $L_f$ and $L_s$ values?

$L_f = 1.05$  for the BBCRDS instrument was determined from fitting the water vapour absorption structure in the wavelength range 652 – 665 nm in BBCRDS spectra acquired when sampling aerosol-free air of known humidity from the SAPHIR chamber. The humidity reference was taken from the SAPHIR chamber’s own humidity sensor, and the water vapour absorption cross sections used to fit the BBCRDS spectra were calculated making appropriate allowances for multi-exponential ring-down decays caused by the BBCRDS instrument linewidth under-resolving individual, strong, rotation-vibrational lines in water vapour’s spectrum (e.g. Shillings et al., 2011). This has been clarified with minor comment (1) above.

Shillings, A. J. L., Ball, S. M., Barber, M. J., Tennyson, J., and Jones, R. L.: An upper limit for water dimer absorption in the 750 nm spectral region and a revised water line list, *Atmos. Chem. Phys.*, 11, 4273–4287, doi:10.5194/acp-11-4273-2011, 2011.

## 2) Page 6694, line 9: 400 m => 400 micro meters?

400  $\mu\text{m}$  is the correct dimension. This will be corrected in the text.

## 3) Page 6695, line 14-17: How did authors measure wavelength dependence of $L_0$ values?

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The spectral dependence of  $L_0$  has been described in Meinen et al. 2010 and Dorn et al. 2013. The LED spectrum with applied optical filters is narrow compared to the mirror reflectivity for the mirrors used here. In the spectral evaluation range, the mirror reflectivity and thus the light path vary insignificantly (less than the measurement accuracy). Thus for the presented results any variation in the light path within the analysed spectral range was ignored. This has been made explicit in the text: “In the spectral evaluation range, the mirror reflectivity and thus the light path vary insignificantly and any variation in the light path within the analysed spectral range was ignored.”

**4) Page 6723, Table 5 One of the Kim (2010) should be Kim (2012). Nakayama et al (2012) also reported the RI values at 532 and 781 nm for SOAs generated from ozonolysis and photooxidation of  $\alpha$ -pinene.**

This reference will be changed and the Nakayama and Lambe references added to the Table.

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Interactive comment on Atmos. Meas. Tech. Discuss., 6, 6685, 2013.

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