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Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Wavelength and NO_x dependent complex refractive index of SOAs generated from the photooxidation of toluene" *by* T. Nakayama et al.

Anonymous Referee #1

Received and published: 31 July 2012

The manuscript by Nakayama et al. investigates the optical properties, specifically the complex refractive index, of the SOA formed by the photooxidation of toluene under different (high) levels of NOx and the SOA formed by the photooxidation of 1,3,5-trimethylbenzene in the presence of NOx using a photoacoustic spectrometer at 405, 532, and 781 nm and a cavity ring-down spectroscopy at 532 nm. The study shows there's only slight absorption at 405 nm for the Toluene-SOA and no absorption in any wavelength for the 1,3,5-TMB-SOA. The study also shows that absorption increases with higher NOx concentrations .They explain their results by the increase in the nitrate to organics ratio in a H-ToF-AMS and correlate this to the hypotheses that nitrated aromatic compounds in the particle phase are likely to be the major contributors to

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the absorption in the UV. The study shows the influence anthropogenic emissions can have on SOA and how nitro-aromatic compounds affect both the real and imaginary components of the complex refractive index.

I would like to mention it is a shame the authors did not use (or show) their 355 nm CRD in this study. I believe the study is relevant and an important contribution to the gap of knowledge concerning optical properties of SOA; however, I have some concerns which should be address before I recommend the manuscript for publication.

1) The authors mention on page 14560 and in the conclusions that ÂÍThe imaginary part of the RI value (k) for the toluene-SOAs was found to increase steeply to shorter wavelengths at 405 nm, while the real part of the RI (n) gradually increases to shorter wavelengthsÂÍ, I disagree with this conclusion. On Fig. 5 the authors show the result from their previous publication (open circles) to justify this; however, the error bars on the k value are large and the result from Zhong and Jang (2011) does not show a ÂÍsteepÂÍ jump in the absorption. Moreover, the real part may also show a ÂÍsteepÂÍ jump, as two of the three values retrieved jump from values around n = 1.45 to n > 1.6. This change in n is quite large and not a gradual step. The author should explain these changes in the components of the RI.

2) In page 14569 the authors mention that ÂÍThe bulk absorption per soluble carbon can be compared with the particulate absorption coefficients using the following relationship, assuming that the particles are small relative to the wavelengthÂÍ and use the relationship to calculate the mass absorption cross section; however, the size of the particles is in the same range as the wavelength (one of the reasons the authors used Mie theory to calculate the RI). How can the authors justified using this relationship? The authors need to give a stronger justification for the whole analysis presented in the "Atmospheric implications" section.

3) The error analysis in the text is not clear and should be expanded. The authors mention in page 14556 that there is at least a 6% error associated with the calibration,

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since they use a TSI SMPS there is a 10% error in the concentration count, there is a further error in the mean diameter, but the error bars in Fig. 3 – specially for 532 and 781 nm – do not seem to reflect the cumulative error in the measurements. Moreover, the authors do not seem to incorporate the errors investigated by Miles et al. 2010 for CRDS refractive index retrievals. It is also not clear to me how the error in the RI retrieved for 781nm can be smaller than for 532 and 405 nm; specially, because the Qext values are quite small.

4) Equation 2 on page 14559. f(Dp) – the normalized surface area weighted size distribution function – does this refer to the measured size distribution from the SMPS normalized to the total area? Weighted to what? It should be made clear on the text from where you get this size distribution as it is crucial to your retrieval algorithm. Technical corrections:

In Table 2 and throughout the text write out the k values. For example, it is clearer to have k=0.0018 than k = 1.8 and in an above parenthesis (x 1000) – which should actually be (Ãů 1000) – and it will also clarify to how many significant figures the k values can be retrieved. p 14553, 21: change ÂĺwasÂĺ to ÂĺwereÂĺ p 14554, 4: add Âĺ, Âĺ after closing parenthesis p 14554, 22: change ÂĺandÂĺ to Âĺin theÂĺ p 14555, 5: change ÂĺandÂĺ to Âĺin theÂĺ p 14556, 7: delete ÂĺaÂĺ between ÂĺaddingÂĺ and ÂĺpurifiedÂĺ P 14559, 2 and 7: delete “the” before “Mie theory” p 14568, 9: change ÂĺFig. 8Âĺ to ÂĺFig. 9Âĺ p 14568, 17: delete ÂĺtheÂĺ before ÂĺMexicoÂĺand change ÂĺcityÂĺ to ÂĺCityÂĺ p 14568, 18: delete ÂĺtheÂĺ after ÂĺreportedÂĺ p 14570, 6-7: Rephrase: ÂĺIn addition, the MAC values for combustion-OA may several times larger than those for the toluene-SOAs as discussed aboveÂĺ As it is written in is not clear what you mean.

Reference: Miles, R. E. H., S. Rudic, A. J. Orr-Ewing, and J. P. Reid (2010), 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(26), 7077-7084.

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It would have been great if the authors uses (or show) their 355 nm CRD in this study. Such results may provided much needed additional information.

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