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Comment

Interactive comment on “Collection efficiency of the Soot-Particle Aerosol Mass Spectrometer (SP-AMS) for internally mixed particulate black carbon” by M. D. Willis et.al.

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We thank Referee #1 for their thoughtful reading of the manuscript and their many helpful comments. Our responses to specific comments and the corresponding changes to the manuscript are detailed below:

P5225/L17: In addition to Bond et al. (2013) I recommend citing Lack et al. (2014) in mentioning different techniques used. See reference below. (Lack et al., 2014)

This reference has been added.

P5225/L24: Instead of “new” I recommend, “recently developed.” “New” implies to me
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that this is the first reporting of this instrument. Also, I personally don't think that it is necessary to mention that it uses the SP2 laser system. The SP-AMS simply uses a particular Near-IR laser.

This sentence has been reworded as follows: "The Soot-Particle Aerosol Mass Spectrometer (SP-AMS) is a recently developed instrument that combines a near-infrared laser system for volatilization of rBC with the Aerodyne High-Resolution Time-of-Flight AMS (DeCarlo et al., 2006) to quantify non-refractory particulate matter (NR-PM) (Onasch et al., 2012)".

P5226/L7: Although it is true that freshly emitted rBC tends to be smaller than Regal Black particles, by referring to the spherule sizes I find that this gives a somewhat misleading picture.

The reference to the spherule size has been removed so that this sentence now reads as follows: "...freshly emitted particulate black carbon tends to be smaller and less compact..."

P5229/L4: "V-ToF" should be defined.

This sentence has been reworded for clarity as follows: "Three SP-AMS instruments were used in this study (UofT SN 215-121, ARI SN 215-039 and 215-130), all of which are Time-of-Flight mass spectrometers operated in V-mode with both the tungsten vapourizer (~600°C) and the laser vapourizer simultaneously, unless otherwise noted".

P5229/L4: The tungsten vaporizer should be mentioned earlier in this section. As written, this seems to assume the reader is quite familiar with possible differences in SP-AMS operation conditions.

Two sentences have been added earlier in this section to introduce the operating modes of the SP-AMS, as follows: "SP-AMS instruments contain both the traditional tungsten vapourizer and the IR-laser vapourizer, and can be operated with the both tungsten and IR-laser vapourizers on or with only the tungsten vapourizer on. In order

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to operate with the IR-laser vapourizer only, the tungsten vapourizer must be removed because its lowest possible temperature is $\sim 200^{\circ}\text{C}$ due to heating by the filament.”

P5229/L16: I find the sentence beginning “The signals arising. . .” to be a bit difficult to understand, and suggest rephrasing and/or elaborate.

The discussion of refractory CO_x^+ species has been rephrased as follows: “Signals from refractory oxygen containing species can arise during the vapourization of rBC and can contribute to signals at CO^+ and CO_2^+ (Corbin et al., 2013; Onasch et al., 2012). The signals arising from CO^+ and CO_2^+ were not included in the organic loading if it accounted for greater than 10% of the total organic signal, since the appropriate chemical fragmentation of these species arising from Regal Black was not quantified in this work.”

P5229/L21: It is not clear what “was carried with each SP-AMS instrument” means.

This should read “was carried out with each SP-AMS instrument”. This error has been corrected.

P5231/L23: I was of the impression that particle bounce can also be an important issue, and that $E_b = 1$ is only true for certain particle types. Can this be clarified?

It is certainly correct that $E_b=1$ is only true for particular particle types when considering the tungsten vapourizer; however, here we refer to the laser vapourizer where particle bounce is not important for collection efficiency.

P5231/L26: I am having some difficulty understanding how the $mIE_{\text{rBC,app}}$ values were determined “for a range of coating thicknesses” when the next section indicates that the apparent sensitivity of the instrument to rBC depends on the amount of coating. Clarification of this section is needed.

The reference to “a range of coating thicknesses” in section 3.1.1 (P5232/L1) has been removed from this section, since the discussion of $mIE_{\text{rBC,app}}$ values determined from coated particles is more appropriately left for section 3.1.2. The true mIE_{rBC} should

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not depend on coating (particle morphology and beam divergence); however, the measured value of $mIE_{rBC,app}$ does certainly depend on coating ($mIE_{rBC,app} = CE * mIE_{rBC}$). mIE_{rBC} is defined as the maximum number of ions detected for a measured sample of rBC particulate mass, assuming that all of the particles fully vaporize in the laser beam. The CE factor accounts for particles that either (a) miss the laser vaporizer and are not vaporized or (b) particles that skim the laser beam and are not fully vaporized. Without the a priori knowledge that all rBC particles fully vaporize, only the product $CE * mIE_{rBC}$, the apparent RIE ($RIE_{rBC,app}$), can be determined.

Fig. 2: Why is only the UofT data fit and not the ARI data?

The fit to the UofT data is shown because it is used to correct the data shown in Figure 6, which consists entirely of data from the UofT instrument. An explicit statement of this has been added to the caption for Figure 2.

P5232/L23: The authors mention earlier that particle number concentration measurements are made to identify when homogeneous nucleation was a problem. Here, they note that such particles cannot be neglected. Although it may be true that they cannot be neglected, it would seem that the authors might have sufficient information available to let them know when this is a problem (or at least a bigger problem).

The particle number concentration measurements were used to determine when homogeneous nucleation of BES was a significant issue. Data displayed in Figure 2 comes from experiments in which the particle number concentration measurements indicated that nucleation was not a large problem. The possibility of nucleation in the remaining data is mentioned because nucleation cannot be completely ruled out from our measurements.

P5233: It would have been nice had the authors turned off the laser to determine the RIE for the organics (BES) from the tungsten vaporizer alone. This would have helped to understand the larger RIEs here. C'est la vie.

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Measuring the RIE for BES from the tungsten vapourizer alone would certainly be valuable for understanding the larger RIE values observed here. It should be noted that attempting to measure RIE_{BES} using BES coated rBC particles on the tungsten vapourizer could be complicated by particle bounce for uneven coatings ($E_b < 1$). A better approach would be to measure the RIE_{BES} with pure organic particles. The differing response to NR-PM with the laser and tungsten vapourizers will be a focus of future development of the SP-AMS.

Fig. 2/P5233: One thing not really discussed is why the fractional increase in the apparent RIE is greater for Org than for rBC. Granted, the differences are not huge, but they are nonetheless noticeable. It would be useful if the authors could comment on this. One thought is that it is related to the dual laser/tungsten vaporizer operation. The Org are vaporized by both, but the rBC only by the laser. Further, that the Org apparent RIE increases at all is somewhat surprising, since presumably those particles not vaporized by the laser are vaporized on the tungsten vaporizer. Perhaps this is telling something about differences in the RIE between particles vaporized by the tungsten vs. laser vaporizer? Of course, it could also be related to particle shape and beam divergence when the particles are only thinly coated, which would also influence the organics. I think that much of this is hinted at, but could be more clearly stated.

Possible reasons for large and increasing values of $RIE_{Org,app}$ are discussed in the second paragraph of section 3.1.2 (P5232/L24). Clarification that this discussion refers to both the concepts of larger than expected $RIE_{Org,app}$ values and the increasing trend with coating thickness has been added to this paragraph. It is certainly possible that since BES volatilizes from both vapourizers, its signal is further enhanced compared to the rBC signal. Further work is required to fully understand the differing response to rBC and NR-PM in the SP-AMS.

The relevant paragraph has been modified as follows: “Under thicker coating conditions, the observed $RIE_{Org,app}$ values are significantly higher than 2 and increase with coating thickness. Reasons for this may be due to differences between the laser

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and tungsten vaporizers and may include; (1) an enhanced ionization efficiency for gas phase molecules generated in the laser vapourizer due to their position relative to the filament; (2) an improved ion extraction efficiency of ions originating from neutral gas-phase molecules vapourized at the laser vapourizer, due to their position in the ion chamber; or (3) a collection efficiency on the tungsten vapourizer of less than one ($E_b < 1$) for organics on rBC particles. The fact that an $RIE_{Org,app} > 2$ for thinly coated particles is observed not only with dual vapourizers, but also with the laser vapourizer alone may suggest an enhanced sensitivity to species volatilized from the laser vapourizer. In addition, the fractional increase in $RIE_{Org,app}$ is larger than that of $RIE_{rBC,app}$ which may indicate the relevance of possibility (3), above, since organic species are volatilized from both vapourizers in this instrumental configuration. Further work is required to fully understand the differing responses to rBC and NR-PM in the SP-AMS.”

P5234/L17: The authors state: “A decreasing signal transmission with a BWP centered in the particle beam is indicative of particle beam narrowing.” Isn’t this additionally complicated by non-unity E_s values for the uncoated particles?

This is perhaps more clearly stated as follows: “With a BWP centered in the particle beam, a lower signal transmission will indicate a narrower beam since a larger fraction of particles are blocked by the BWP wire.” The signal transmission, at any BWP position, is determined by comparing the signal at that position to the signal obtained from the same unblocked beam (normalized to particle number concentration). Uncoated particles certainly have non-unity E_s values, but by comparing the blocked and unblocked signals for the same particle beam some comparison can be made between different types of particle beams.

Fig. 4a/P5235: I’m having some difficulty separating the results with the BWP centered in the particle beam versus positioned outside of the particle beam from this single figure. The associated text indicates that both are shown on this one figure. Can this be clarified?

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The figure caption has been modified to clarify how these two sets of data were obtained: “(a) $mIE_{rBC,app}$ as a function of the signal transmission when the BWP wire is positioned the center of the particle beam. The two sets of data were collected sequentially for each coating thickness by positioning the BWP wire outside the particle beam to measure $mIE_{rBC,app}$ and then moving the wire into the center of the beam to measure the associated signal transmission. Colours indicate organic coating thickness estimated from SP-AMS measurements of rBC and NR-PM.” A reference to this explanation was also added to the text associated with this figure.

Fig. 4b/P5235: That the rBC and organic signal co-vary with an approximately 1-1 relationship is an important result, given that Onasch et al. (2012, Fig. 6b) observed very different dependencies of the organic and rBC signal on laser power, and that by blocking the beam the authors are forcing the particles to pass through outer regions of the laser beam that, presumably, have lower power due to the Gaussian beam shape. I suggest that this is emphasized. Ahh, I see that it is mentioned in more detail later in the manuscript (p5237).

A reference to the later discussion was added to the end of section 3.2 for clarity.

P5237/L1: It is certainly true that a simple comparison between beam widths would not quantitatively provide information on the collection efficiency. However, it should be relatively straightforward to expand to 2 dimensions to account for the asymmetry of the laser geometry.

This approach can certainly be applied in principle to estimate the overlap between the particle and laser beams. Due, in part, to the uncertainty in the upper limit of laser beam width the authors believe that a more widely applicable approach would be to develop a relationship between particle beam width and CE using laboratory and ambient data from a number of SP-AMS instruments. This is the subject of future work and is discussed below.

P5238/L7: “Standard” should be defined. Or perhaps just stated more explicitly as

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“using the RIE_{rBC} for uncoated Regal Black and the and RIE_{Org} typically used for organics.”

This sentence has been reworded as follows: “SP-AMS values using the RIE_{rBC} for uncoated Regal Black and RIE_{Org} typically used for organics (i.e., 0.2 and 1.4, respectively) can. . .”

P5238/L18: It is not only when instrumental sensitivity is well known that the Regal Black fraction can be well estimated, but when the coating state is already known so that the appropriate CE (or RIE_{app}) can be applied. Without such a priori knowledge of the coating state, the correct CE to use would not be known. This has important implications for laboratory experiments, but more importantly for ambient measurements. One question is whether some sort of recursive analysis methodology could be applied, where an initial estimate of the coating-to-core ratio could be determined from the raw data, which is then used to estimate the appropriate CE to use. A new coating-to-core ratio could then be estimated, along with a new CE and so on until convergence is reached. But, perhaps no convergence would ever be reached. Something for the authors to, perhaps, consider in future studies.

It is certainly true that instrumental sensitivity (mIE) and CE (i.e., particle beam divergence due to particle size/morphology/coating state) must both be well known and L18/P5238 has been reworded to emphasize this. The issue of how to determine the appropriate CE for ambient particles with an unknown coating state is very important. One goal of this manuscript is to emphasize the utility of a beam width probe to aid in determining the in situ collection efficiency through its relation to the measured particle beam width. This is especially important since the CE is a function of particle size and shape, both of which are affected, but not fully defined, by the particle's coating state. Since organic species found in ambient particles tend not to have the properties of BES (e.g., they might be semi-solid or solid, rather than liquid), using the coating-to-core ratio to determine CE may not be sufficient since it may not account fully for particle morphology (e.g., non-uniform coatings generated by coagulation or by the

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condensation of solid or semi-solid NR-PM). The goal of using BWP measurements to determine CE is now more explicitly stated in section 3.5 and in the summary.

P5238/L25: Which should be that. This has been corrected.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 5223, 2014.

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