

## ***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 #2 for their constructive comments and questions, which have helped us to improve the clarity of the manuscript. Our responses to specific comments and changes to the manuscript are detailed below:

1. Page 5227, Lines 13-25: There are several differences in the set-ups at the ARI and UofT facilities and it would be helpful to tabulate those (in addition to the quantities listed in the text currently, also include in this table the operating flowrates of the DMAs).

A table of experimental parameters, summarized in lines 13-25, has been added to

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section 2.1.

2. Page 5228, Lines 6-7: It is mentioned that contributions from doubly-charged particles were characterized using a SMPS. I'm assuming that the particles from the first DMA were neutralized in the SMPS and the size distributions were then measured. How was this data used to account for the contribution of doubly-charged particles in the subsequent analysis? Given that the measurements are mostly made in terms of particle mass and with particles in the size range of 200-400 nm, the contribution of doubly charged particles cannot be ignored here.

Particles from the DMA were neutralized in the SMPS and the size distributions were measured. This data was used to determine appropriate solution concentrations to be used in the atomizer so that doubly charged particles contributed less than 10% to the total particle mass exiting the DMA. In cases where doubly charged particles accounted for greater than 10% of the particle mass, the SMPS size distributions were integrated to correct the CPC counts and the SP-AMS signals.

3. Figure 2: What are the “bare” particle sizes associated with the data shown in Figure 2?

The ‘bare’ particles associated with Figure 2 are 200 and 300 nm in mobility diameter. An explicit statement of this has been added to the figure caption.

4. Figure 2a: The one data point from ARI beyond  $R_{Org/RB}$  of 3 seems to suggest that  $RIE_{rBC}$  could be decreasing beyond  $R_{Org/RB}$  of 3 and there is significant uncertainty in the data of UofT. It is not clear that the sensitivity is saturated beyond  $R_{Org/RB}$  of 3.

We acknowledge the large uncertainty in the  $RIE_{rBC,app}$  measurements, and that there may be finer scale variations occurring that the error in our measurement do not allow us to observe. A third set of measurements (Figure S2) provides  $RIE_{rBC,app}$  values over a wider range of  $R_{Org/RB}$  from an ARI SP-AMS (this data was not included in Figure 2 because particle mass measurements were not available during this particular

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experiment). These data also suggest a saturation beyond  $R_{\text{Org}/\text{RB}} \sim 3$ .

5. Figure 2b: Why is the data from ARI not included for  $\text{RIE}_{\text{organics}}$  for  $\text{RIE}_{\text{rBC,app}} > 2$ ?

ARI experiments at high coating thicknesses were difficult to interpret due to homogeneous nucleation of BES, and were not included in Figure 2 for this reason. This issue is further discussed in response to question 6.

6. Page 5232, Line 20: Homogeneously nucleated organic particles are mentioned as a possibility in these experiments. Do the CPC (and SMPS) measurements indicate this possibility? Also, would there be sufficient mass in these particles to affect your measurements?

CPC and SMPS measurements were used to determine when homogeneous nucleation of BES was a large issue. These measurements were used to determine which data were appropriate to include in Figure 2 (ie, with minimal or no nucleation occurring). Nucleation is an issue for two reasons: (1) large amounts of small particles can aggregate to form particles large enough to enter the SP-AMS and effect the measurements of organic loading (this could be observed at small particle sizes in pToF data in extreme cases), and (2) nucleated particles increase the total CPC concentrations that are used to determine the known amount of particle mass loadings used in RIE calculations. Nucleation is mentioned as a possibility in the remaining data because it is difficult to rule out completely when some particle loss and particle formation may be occurring in the condenser. We have made a concerted effort to minimize this impact of this issue on the final data shown in Figure 2.

7. Figure 2: "The error bars are standard deviations of 2 to 3 measurements". A standard deviation from two measurements is generally not acceptable. A more accurate representation of uncertainty should be estimated from error propagation analysis.

The error bars shown in Figure 2 have been changed to reflect the propagation of the error in mass based ionization efficiency ( $\text{mIE}_{\text{app}}$ ) measurements used to determine

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the  $\text{RIE}_{\text{app}}$  values. This error analysis provides similar results to that used previously, giving relative errors in the range of 10-20% on  $\text{RIE}_{\text{app}}$  values.

8. Page 5237, Lines 24-29: In comparing the  $f_{\text{RB}}$  values obtained with the SP-AMS with the Mass-Analyzer, how are the SP-AMS measurements corrected at different core sizes for CE and sensitivity?

The SP-AMS measurements for different rBC-core sizes are corrected using the upward trend in  $\text{RIE}_{\text{app}}$  for rBC and NR-PM with increasing coating thickness. This trend was fit to a sigmoid relationship (Figure 2) so that the appropriate  $\text{RIE}_{\text{app}}$  value could be obtained when  $f_{\text{RB}}$  is known from mass analyzer measurements. The measured  $\text{RIE}_{\text{app}}$  in this case is the product of the  $\text{RIE}_{\text{rBC}}$  and CE, where  $\text{RIE}_{\text{rBC}}$  is the maximum ratio of the ions detected for rBC material sampled ( $\text{mIE}_{\text{rBC}}$ ), assuming all rBC particles vaporize in the laser beam, to the ions detected for ammonium nitrate ( $\text{mIE}_{\text{NO}_3}$ ). The CE factor, which is unity or less, is a measure of the missed rBC ion signal due to poor overlap between the particle beam and the laser beam vaporizer; that is, to account for rBC particles that miss the laser beam and are not vaporized. This is currently described on P5238/L11-13, but this paragraph has been reorganized for greater clarity:

"To further assess the ability of the SP-AMS to quantify the mixing state of rBC-containing particles the mass fraction of Regal Black ( $f_{\text{RB}} = \text{mass}_{\text{RB}}/(\text{mass}_{\text{BES}} + \text{mass}_{\text{RB}})$ ) in BES coated particles of various rBC core sizes (40 to 300 nm) was measured with the SP-AMS and compared to  $f_{\text{RB}}$  obtained from particle mass measurements. Figure 6 demonstrates that  $f_{\text{RB}}$  values derived from the SP-AMS agree well with  $f_{\text{RB}}$  values from particle mass measurements when SP-AMS values are corrected for CE. The measured  $\text{RIE}_{\text{app}}$  in this case is the product of the  $\text{RIE}_{\text{rBC}}$  and CE, where  $\text{RIE}_{\text{rBC}}$  is the maximum ratio of the ions detected for rBC material sampled ( $\text{mIE}_{\text{rBC}}$ ), assuming all rBC particles vaporize in the laser beam, to the ions detected for ammonium nitrate ( $\text{mIE}_{\text{NO}_3}$ ). The CE factor, which is unity or less, is a measure of the missed rBC ion signal due to poor overlap between the particle beam and the laser beam

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vaporizer; that is, to account for rBC particles that miss the laser beam and are not vaporized. To obtain the corrected values, the upward trend in  $RIE_{app}$  measured for rBC and NR-PM with increasing coating thickness (Figure 2) was fit to a sigmoid relationship to obtain the appropriate  $RIE_{app}$  values for a given coating thickness (determined by mass analyzer measurements for different rBC-core sizes). SP-AMS values derived using the  $RIE_{rBC}$  for uncoated Regal Black and  $RIE_{Org}$  typically used for organics (i.e., 0.2 and 1.4, respectively) can underestimate fRB by up to ~50% and data in Figure 6 exhibit a pronounced non-linear relationship. For the specific case of BES, if the  $RIE_{Org}$  value is higher than the recommended value of 1.4, the underestimation would be less than that depicted in Figure 6. When the changes in CE with particle coating are taken into account the relationship in Figure 6 shows excellent linearity ( $R^2 = 0.98$ , slope =  $1.01 \pm 0.05$ )."

9. Page 5238, Lines 13-15: The correction of SP-AMS data requires knowledge of the  $RIE_{app}$  and CE with coating thickness. As coating thickness is usually an unknown, is it feasible to make these corrections for ambient/atmospheric measurements?

The issue of how to determine CE (or  $RIE_{app} = CE \cdot RIE$ ) for rBC-containing ambient particles is of particular importance for further use of the SP-AMS. The driving factor for collection efficiency (CE) in the SP-AMS is the particle beam divergence, which is due to particle size (smaller particles diverge more) and shape (i.e., non-spherical particles diverge more). While both of these issues are related to the coating state, they are not fully defined by the coating state. In this work, a liquid organic species was used such that increasing coating generated larger, more spherical particles with less divergent particle beams. However, ambient organic species may not produce coatings in the same manner so that the relationship between coating state and CE observed here might not be directly applicable. From this perspective, beam width probe (BWP) measurements will be the most direct method for measuring the CE in situ. One goal of this manuscript is to emphasize the utility of BWP measurements to aid in determining CE by its relation to beam width. Future development of the SP-AMS technique will

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relate collection efficiency to beam width through laboratory measurements (like those described here) and ambient measurements. The goal of using BWP measurements to determine CE is now more explicitly stated in section 3.5 and in the article's summary.

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

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