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Atmospheric Measurement Techniques Discussions

Interactive comment on "Effect of secondary organic aerosol coating thickness on the real-time detection and characterization of biomass burning soot by two particle mass spectrometers" *by* Adam T. Ahern et al.

J. C. Corbin (Referee)

joel.corbin@psi.ch

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The manuscript "Effect of secondary organic aerosol coating thickness on the real-time detection and characterization of biomass burning soot by two particle mass spectrometers", by A. Ahern et al. presents an environmental-chamber based study of two commercially-available aerosol mass spectrometers, the SP-AMS and the LAAPTOF, using soot produced by a wood burning.

The aerosols sampled were thoroughly characterized, the measurements are presented in detail, and the results are thoroughly discussed and interpreted. The study

was exceptionally well designed and used a realistic sample, birch-bark soot from a wood stove, ensuring that soot microstructure and impurity content were representative of an atmospheric aerosol. Moreover, the results for the SP-AMS are not at all what would have been predicted from previous understanding. The measurements therefore represent a very valuable contribution to our understanding of both SP-AMS and include useful data for the LAAPTOF.

Although I think the study and manuscript are excellent, I still have a number of comments. The bulk of these relate to Fig. 9, which I think contains the manuscript's main message, and which I think should be improved to make a direct estimate of the overlap of the particle beam with the laser beam.

In the following I will write p1.5-10 to refer to lines 5 to 10 on page 1.

1 General comments

1.1 LAAPTOF

Clearly, the major focus of the analysis was the SP-AMS rather than the LAAPTOF. While there is, of course, no reason why equal amounts of text should be devoted to each instrument, the paper reads as though it is an SP-AMS paper with a few LAAPTOF comments included. The obvious suggestion is that the LAAPTOF results move into another manuscript. Whether or not the authors accept this suggestion, it would also be nice to see more statistics on the LAAPTOF performance. Examples:

1.1.1

Fig. 7 could include LAAPTOF "EC" signals, and possibly more,

1.1.2

To what degree is Fig. 8 representative? Could error bars be added, if all particles looked like these? Or clustering be performed to illustrate whether or not all particles looked like these? Likely, future LAAPTOF studies from the community will perform clustering analyses on both source and ambient data sets using the recently-published software (Reitz et al., 2016).

1.1.3

The dominance of CO+ was noted in Section 3.4, but what about the NO+ ion visible in Fig. 8, which is of equal intensity to CO+ in that spectrum? Where did the N come from?

1.2 Discussion

There is some discussion within the section titled Experimental Methods that would fit better in Results and Discussion. Specifically: p5.12-17, p7.3-20, p7.38-45, Section 2.4.

1.3 Conclusions

Perhaps the conclusions are missing a comment on which aspect of the SP-AMS needs to be revised to address the quantification issues reported here? My impression is that this would be the far-from-homogeneous laser beam that the particle beam sees.

1.4 Terms

At various points the terms “soot”, “rBC”, and “black carbon” were used, as well as “BBA”. For example, in the abstract the SP-AMS sensitivity is first described relative to rBC and then later to black carbon. As another example, in the introduction I wasn’t sure if BBA meant only soot from BB, or only efficient combustion (certain stages of biomass burning don’t produce soot), etc. On p3.5 it is stated that particles contained “BBA, rBC, and SOA”, so I’m confused about what BBA is. Isn’t rBC a subset of BBA? Maybe this should read “rBC, SOA, and ash”?

Similarly, the term SOA was used sometimes while OM was used at other times. I personally prefer OM, which can refer to both the particulate phase SOA and the category of ions observed in the mass spec, as the authors did on p3.5-6.

If the authors retain the pairs of terms rBC and BBA, and SOA and OM, then a table defining abbreviations might be worthwhile.

2 Formulation of SP-AMS sensitivity to size and shape

2.1 Definition of E_s and E_z

E_s has been defined as a shape-dependent collection efficiency in the present manuscript, which is slightly different to the usage suggested in the main text of Onasch et al. (2012).

The definition of E_s in Onasch2012 was subtly changed from its original meaning of collection efficiency due to particle shape. Onasch2012 actually defined $E_{s,\mathrm{new}}$ as *the fraction of particles lost due to particle beam divergence causing particles to miss the vaporizer* in the main text, and I think this change allows a clearer description of the

present results.

However, in Table 1 of Onasch2012, E_s was defined as "size and shape related collection efficiency", which is more similar to previous definitions of E_s ($E_{s,\mathrm{old}}$ = shape-related collection efficiency), not fully consistent with the first quoted definition, and overlaps with the definition of E_L *(the fraction of particles lost during transit through the inlet and aerodynamic lens)*. A similar point has been made implicitly by the authors, who specifically wrote *SP-AMS IR-beam particle collection efficiency* when directly relevant.

To avoid confusion in this comment, I will define E_z similarly to $E_{s,\mathrm{new}}$, but specifying E_z as the collection efficiency of the SP-AMS laser vaporizer, for particles exiting the aerodynamic lens. Since E_z is obviously a function of aerodynamic diameter d_a, one may equivalently define it as $E_z(d_a)$, "the aerodynamic-size dependent collection efficiency of the laser, for a perfect lens". If $E_z(d_a) = 1$, a plot of SP-AMS response versus d_a would mimic the transmission efficiency graphs for E_L shown in Liu et al. (2007; e.g. their Figs. 9 and 10). Conversely, the SP-AMS response if $E_z(d_a) = 1$ would be flat after correction for lens transmission, by definition.

2.2 Specific comments on shape and transmission issues

I think that changing from the current E_s to E_z as defined and discussed above, would improve this manuscript for the following reasons. These comments relate to the x-axes of Fig. 9.

2.2.1 Changes in χ

A major reason why a shape-based definition of E_s can be misleading is that no realistic experiment ever measures particles of equivalent $d_{\text{vol.-equiv.}}$ but different shape (χ_v),

which is the only scenario where E_s is directly meaningful.

Rather, as in the present study, most experiments measure soot as it is coated, so $d_{\text{vol.-equiv.}}$ increases while χ decreases. So a plot of either one of these variables is difficult to interpret, especially for different initial particles (Figs. 9a,e,d,h in the manuscript).

2.2.2 Lower limit of E_L

Liu et al. (2007) have shown that the transmission efficiency of the AMS lens, E_L, can drop off from unity for aerodynamic diameters <150 nm and >400 nm. Although the studied particles were labelled as 143, 187, and 220 nm in Fig. 9 (initial mobility diameters), all of these particles had $d_{va} < 150$ nm, as seen in Fig. 9G, and could have been outside of the E_L=1 range at $t = 0$.

As the authors likely know, a constant d_{va} for all d_m is the expected behaviour, as shown theoretically by DeCarlo et al. (2004; their Eq. 57) and in the laboratory by Slowik et al. (2004; their Fig. 4) as well as the present study (Fig. 9G).

To clarify Fig. 9 and strengthen its message, I would suggest (i) changing the mobiilty-diameter labels in Fig. 9A to initial-mass labels (femtograms), and (ii) measuring $E_L(d_a)$, to establish the range of d_a where E_z is the main factor controlling the signals in Fig. 9. Since the implicit goal of Fig. 9 is to explore whether or not E_z reaches a plateau for some range of d_{va}, it would be a great improvement to be able to rule out the effects of E_L.

2.2.3 χ subpanel in Fig 9

On a related note, I would suggest removing the χ from Fig. 9 because (i) it is an approximate calculation (specifically, the approximation is $\chi_v \approx \chi_t$) whereas all other

measurements in Fig. 9 are not, and (ii) I don't think it adds more to the plot than the d_{va}, which by virtue of being a measured quantity already includes χ_v.

3 Expected C_3^+ signals as a function of coating

Figure 9 and its discussion imply that the C_3^+ signal (y-axis of Fig. 9) was expected to level off with increasing coating, as was observed by Willis et al. (2014). Of course, I agree – it would be extremely strange if this signal did not level off, since the SP2 literature makes it very clear that the evaporation/sublimation of an OM-coated rBC particle is a two-step process; first OM evaporates then rBC sublimates.

The manuscript currently concludes that the signal does not level off, and I am inclined to agree with this conclusion, but it is such a surprising conclusion in the context of the SP2 and AMS literature that it would be worth clarifying two things: first, the issue of E_L as noted in comment 2.2.2 above, second, normalizing each soot size to the actual mass of soot within the particle (instead of the initial C_3^+ signal as was done). The first point would remove a potentially important bias from Fig. 9G. The second point would allow the 3 selected mobility sizes to represent repeat experiments.

To expand on the second point, the expected signal of C_3^+ is directly related to the true rBC mass concentration. One could rewrite Eq. 1 in Willis et al. (2014) as:

$$\mathrm{C_{rBC,SP\text{-}AMS}} = \frac{I_{\mathrm{C_3^+}}/f_{\mathrm{C_3^+}}}{\mathrm{Q}\cdot\mathrm{IE_{rBC}}\cdot\mathrm{E}_z(d_{va})\cdot\mathrm{E}_L(d_{va})} \tag{1}$$

where $I_{\mathrm{C_3^+}}$ is the observed C_3^+ signal, $f_{\mathrm{C_3^+}}$ is the fraction of rBC signal observed as C_3^+, Q is the SP-AMS flow rate, and $\mathrm{IE_{rBC}}$ is the ionization efficiency of rBC. The other two terms, E_z and E_L were defined above, and are the only terms that should be a function of coating here, since they are both functions of d_{va}.

If E_L is measured and $\mathrm{IE_{rBC}}$ is inferred as done by Willis et al. (2014), then $E_z(d_{va})$ could be reported directly by replacing $\mathrm{C_{rBC,SP\text{-}AMS}}$ with $\mathrm{C_{rBC,SP2}}$ above, and rearranging. Unless I am mistaken, this $E_z(d_{va})$ would be a universally applicable correction factor for the SP-AMS in laser-only mode.

If E_L cannot be measured for some reason, one could plot the right hand side of

$$\mathrm{E}_z(d_{va})\cdot\mathrm{E}_L(d_{va}) = \frac{I_{\mathrm{C_3^+}}/f_{\mathrm{C_3^+}}}{\mathrm{Q}\cdot\mathrm{IE_{rBC}}\cdot\mathrm{C_{rBC,SP2}}} \tag{2}$$

against d_a and at least overlay a literature curve for E_L, which would clarify the current Fig. 9G since the reader could then interpret the lower and upper limits of d_a with extra caution. (In case it's not clear, I'm focussing on Fig. 9G since that is the subpanel which should be generalizable to other studies.)

Extending this reasoning to determine the difference of E_z for potassium vs. rBC would not necessarily require knowledge of $\mathrm{IE_K}$ (Drewnick et al., 2006) but only the assumption that $\mathrm{IE_K}$ is constant. Perhaps filter-based quantification of K would help.

4 Other comments

4.1 Endless increase in K sensitivity

The apparently endless increase in sensitivity to K should be further discussed, especially with respect to Willis et al. (2014)'s results where the collection efficiency for organics (not K) coated on regal black (not nascent soot) appeared to level off with coating mass ratios of $\sim$3.

Could the increase in sensitivity to potassium have been related to its being surface

ionized from organics rather than BC? (I'm envisioning a potassium salt crystal attached to a BC particle.) Both surface and material would matter during surface ionization. Some mention of the Saha equation or Carbone et al. (2015)'s work might also be relevant here (e.g. p12.24). This or some other physico-chemical effect, rather than particle beam focussing into the laser, might explain the apparently continuous increase in sensitivity. (I am only suggesting a brief discussion of this.)

Note also Ghazi and Olfert's (2015) data where particle sphericity at OM-to-rBC mass ratios of 5 are reported. (So as not to contradict the d_{va} discussion above, I mean to suggest that sphericity should be the point at which whatever interactions causing the increased sensitivity to K reach their limit; nothing to do with E_z.)

4.2 Figure 7

[a] How confident are you that interference from OM ions is not an issue in the quantification of these C_x^+ ions?

[b] When C_9^+ was not observed unless particles were coated, was the expected C_9^+ signal well above the detection limit? (i.e., can you exclude improved absolute signals as an explanation for the appearance of these higher-x C_x^+ ions?)

4.3 LAAPTOF quantification

4.3.1 linear response

After the positive comments about the linear response of the LAAPTOF in the abstract, I was surprised by the complexity of Fig. 12. The response to 187 nm particles was linear, while the response to the other 2 sizes was definitely not! I do not think Figure 12 can be fairly described as "linear" and I would say that this word does not belong

in the abstract nor conclusions, except with a strong caveat. Also, how many particles were used for this graph? Are statistical errors negligible (error bars)?

4.3.2 complex SOA

p19.25: "despite the complex nature of the SOA coating"

Comment 1: is alpha pinene SOA complex from the perspective of 193 nm LDI? From what perspective? I would suggest that it is rather chemically homogeneous in terms of intramolecular structure.

Comment 2: Jeong et al. (2011) and Healy et al. (2013) found a good correlation between OM signals in SP-LDI-MS and reference measurements, contrary to laboratory studies suggesting a high sensitivity to impurities, so it seems that complex OM mixtures are more-easily rather than less-easily quantified. This might be discussed here. Citations to these two papers are also missing from p7.11.

4.3.3 charring

The word "charring" is used at p20.6,21; p21,4 to describe the formation of C_1^+ from OM during LDI. My feeling is that charring is associated with combustion and combustion timescales, and that a word like "decomposition" brings to mind the rapid molecular reactions that are likely involved in LDI.

4.3.4 variability

p20.13: "Despite the variability in the soot core composition..."

As commented in the General section, it would be nice to see quantitative information on how the authors observed this variability and on exactly what varies (relative K,

absence/presence of species, etc).

Second, how was variability in particle composition differentiated from variability in LAAPTOF performance?

Third, shot-to-shot variability is mentioned on p20.8, but how significant is this? How was it observed? And can it not also be invoked at p19.23 to explain the poor linear regression?

5 Minor comments

5.1 p2.37

Here I would say “compositional” rather than “chemical” information.

5.2 p3.3 and p17.9

p3.3 and p17.9 mention a “laser beam waist” without defining “waist”. I understand it to mean the effective beam area as the beam is viewed from the perspective of an incoming particle? I’m not sure if the definition of “waist” matches this.

5.3 p3.11,42

Here the phrases “conventional aerosol mass spectrometer” and “normal operation” are ambiguous since the AMS has not yet been defined, and since this paper also discusses LDI-SP-MS.

5.4 p3.13-15

Please reword these lines to allow for the caveat that the AMS can also see potassium, e.g. Drewnick et al. (2006), though not so well as the SP-AMS.

5.5 p3.36

I’d suggest giving “sequential vaporization” an expository sentence, here or later, given its central importance to your message.

I’d also suggest changing “only the vapors” to “the neutral vapors.”

5.6 p4.9

Please provide the wavelength, laser fluence, and expected/designed/estimated aerodynamic size transmission range of the LAAPTOF in the Experimental section.

5.7 p5.1

Another essential difference between spark-generated EC (which should not be called soot, as it is a very different material) and flame-generated soot is the microstructure of the carbon, which causes it to have, for example, different optical properties (Gysel et al., 2012) and so would interact differently with 193 nm and 1064 nm light.

5.8 p5.16

Both biomass-burning and engine-exhaust soot may be fractal-like, if the combustion conditions are of the right efficiency. So why would biomass-burning particles have a

higher surface area than engine exhaust soot? I would actually expect a lower specific surface area due to slightly larger primary particles.

5.9 p5.24

"electrical mobility" $->$ "mobility"

5.10 Figure 2

The last sentence in the legend could be clarified by mentioning d_{va} only.

5.11 p9.12 – σ

I wasn't clear where this effective beam width σ was from (Willis et al. 2014?). Also, it should depend on the absolute laser power of an SP-AMS, which is not a controlled variable at present.

5.12 p9.33

There is a publication using the SPLAT from PNNL which discussed this broadening in detail (in terms of line widths), and might be worth citing here.

5.13 Section 2.4

It would be here helpful to state the mass of BC for comparison to the mass of OM. Also, instead of assuming a density of OM for Schwarz's coatings, it would be clearer to compare volumes since the present experimental results could be converted to volume.

(The latter is not intended as a request.)

5.14 p11.11

The caveat "by mobility" is not needed (or?).

5.15 p12.1

The fragmentation table is mentioned here as though it is highly complicated, perhaps you could alter the text to emphasize that only CO_2^+ and C_1^+ are inferred from a frag table in this case (or?), to strengthen your point.

5.16 p12.14

Please mention that C2H3O+ also represents other anhydrosugars (Lee et al. 2010)

5.17 p13.14

f_{44} wasn't mentioned before. Also, if laser-off measurements are generally available, the ratio of OM with laser on to off would be very interesting.

5.18 p13.17

Fullerenes are not rBC!

C60 sublimates at 600 C – it's not refractory.

A citation to the HRTEM literature would be relevant here.

5.19 p13.25

"particle mobility" $->$ "size", since not just mobility size is used.

5.20 p17.1-8

I'm not clear on what was actually done here. Was the beam-width probe repeatedly moved into its central position throughout the coating experiment? It sounds like it was held constant, but that seems unlikely.

5.21 p17.19

Referring to the extensive discussion above, "depends on particle size and shape" should be changed to a well-defined size, d_{va}.

5.22 Figure 9a

The selected soot sizes are given in "soot core" sizes. Since the SP2 measures only soot cores, I had thought volume-equivalent SP2 information was being given initially, but actually these are mobility sizes (I think). Given the confusion between d_{ve}, d_{va}, and d_m in this manuscript I would suggest changing to m_p in femtograms here; which is also important to know the coating mass ratio for comparison to the x axis.

5.23 Figure 9 legend

The sentence including "SP-AMS:SP2" seems to be a relic of an older draft.

5.24 p19.14

"even with a high SOA:rBC mass ratio $>$ 9"

Could you provide some context, e.g. citation to a paper like Ghazi and Olfert's?

5.25 p21.21

In the conclusions, the authors cite Lee et al. (2016) as an example of how the present manuscript can help to improve the quantitative interpretation of SP-AMS measurements – I would suggest citing all of the other relevant SP-AMS papers here (which can be found via the citations to Onasch et al. (2012)).

It might also be worth mentioning, somewhere, that some atmospheric studies found a good correlation between SP-AMS-estimated and reference rBC concentrations. This good correlation could be interpreted as implying a constant rBC size distribution for those studies.

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