

Interactive comment on “Characterization of trace metals with the SP-AMS: detection and quantification” by S. Carbone et al.

Anonymous Referee #1

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The manuscript by Carbone et al. “Characterization of trace metals with the SP-AMS: detection and quantification” takes the first few steps towards SP-AMS real-time quantification of metals internally mixed with black carbon aerosol particles in the atmosphere. The authors use a novel technique to fabricate internally mixed metal/carbon black particles that are generated by nebulization in which metal salt solutions are mixed with carbon black nanoparticles suspended in water. The results are sound and the experimental design is nicely planned. However, the paper is at times poorly written and should be proof read by a native English speaker. I list a number of points below that needs answers and actions. After the MS has been revised accordingly, the paper merits publication in AMT.

There is very little discussion on what types of fragments that are detected in SP-AMS
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for each metal in the lab-study. Are all ions atomic or are ions containing one or more oxygen atoms detected? Any metal ions that contain nitrogen and oxygen from the nitrate ions in the solution? Does this vary between the metals? Most importantly if there are differences in this aspect, can it explain the differences in sensitivity between some of the metals?

Oxides commonly have a lower vapor pressure compared to the corresponding metal and metal salt. This means they may vaporize at a higher temperature. Will this affect the sensitivity of the instrument? Thermal Surface Ionization will depend on the vaporization temperature of each metal, this means that salts or oxides may result in different degree of TSI for the same element if they are vaporized at different temperatures. Please expand on this in the manuscript.

Please discuss if there are other disadvantages by using TSI. For example in terms of peak shape. The RIE_{measured} of rBC relative to nitrate is 0.25. From the IE cross section of C3 in Naghma et al. (2013) one could calculate RIE_{theory} of C3. The calculated RIE_{theory} is much higher than RIE_{measured}

What is the reason for this discrepancy? This question has bearings for the quantification of the metals as this factor may provide an additional uncertainty into the interpretation of RIE_{measured} for the metals. For example, if collection efficiency (CE) is the reason for the discrepancies in RIE for C3, the method implies that the CE is similar for metals and C3? Is this a good approximation (compare with DOS/DEHS measurements by Willis et al. 2014)? Please expand on this in the paper.

It is shown in fig 8 that the SP-AMS sensitivity drops as the rBC mass fraction decreases. To fully understand this, we need to understand the mixing state and size distributions of metal and rBC. For example as the rBC fraction drops, the probability to form externally mixed non rBC containing metal particles increases. Particles with no or low rBC fraction may also be smaller, and may therefore not focus very well in the SP-AMS and miss the laser. What knowledge on the mixing state can be gathered

from co-located instruments?

Minor comments and questions:

5739 – r21 change to “field experiment”

5742 – r15 b “All generated particle contained rBC”. Please motivate whether this is a good assumption

5742 – r15 c “all particles were spherical”. Do they need to be spherical if the quoted density is an effective density? Please expand in the manuscript

5746 – r4 Write out TSI first time it is used in R&D section

5746 – r1 “This fact suggested the presence of particles without rBC that were vaporized by the tungsten vaporizer.” How can the comparison with laser off be used to determine if the ammonium nitrate was in separate particles or as a coating on rBC particles? Please explain. . .

5746 – r15 “Because this metal was not present in the solutions used in this experiment, it was likely originated in the ceramics of the filament or contamination.” Why would it be in the ceramics of the filament if it occurred in the difference spectrum? Is it more likely an impurity.

5747 –r21-25 Losses: where there any filter measurements carried out in parallel? If no, would it be possible to do or is the concentration too low? I assume losses in nebulizer could be quantified that way. (2) “formation of side products, such as metallic oxides.” Where would these form? (3) “losses in the laser vaporizer due to the high temperature required to evaporate certain metals” I believe this is already accounted for as the rBC particles (that gives the reference) are heated to even higher temperature.

5750 –r23 “In addition, the clear evidence of oxides and metallic salts formation (Figs. 7 and 8) in periods of high rBC loads may lead to an underestimation of the metals by the SP-AMS while the ICP-MS method determines the total metal content in the

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sample.” Why would the salt and oxide formation lead to underestimation of metals?

5750 – r26 and 5752-r1 The two statements seems contradictory: “Moreover, the SP-AMS instrument is limited to measure only soot-containing aerosol particles.” and “This is indication that pure metals or metal compounds may absorb effectively laser light at 1064 nm and evaporate.”

Table 2: include estimated vaporization temperatures

References: Naghma, R., & Antony, B. (2013). Electron impact ionization cross-section of C₂, C₃, Si₂, Si₃, SiC, SiC₂ and Si₂C. *Molecular Physics*, 111(2), 269-275.

Willis, M. D., Lee, A. K. Y., Onasch, T. B., Fortner, E. C., Williams, L. R., Lambe, A. T., ... & Abbatt, J. P. D. (2014). Collection efficiency of the Soot-Particle Aerosol Mass Spectrometer (SP-AMS) for internally mixed particulate black carbon. *Atmospheric Measurement Techniques*, 7(12), 4507-4516.

Interactive comment on *Atmos. Meas. Tech. Discuss.*, 8, 5735, 2015.

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