Atmos. Meas. Tech. Discuss., 8, C3633–C3643, 2015
www.atmos-meas-tech-discuss.net/8/C3633/2015/

Atmospheric Measurement Techniques
Discussions
Open Access

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

S. Carbone et al.

carbone@if.usp.br

Received and published: 28 October 2015

We thank the referees for the valuable comments concerning this manuscript. We have addressed all of the comments and the manuscript text has been revised based on our responses to comments. The language has been thoroughly checked. We will be glad to answer to any further question.

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.

Reply: We appreciate the supportive comments about our experiment design and results. We have proofed the manuscript to our best ability, making changes to the language structure, to address the issues of being “at times poorly written”.

1- There is very little discussion on what types of fragments that are detected in SP-AMS 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?

Reply: This is an important point; we appreciate the reviewer for bringing it up. We have added to the supplemental information (Table S2) a comprehensive list containing all the metal-containing ions and their respective metal-containing fragments which we might expect to observe during our laboratory experiments. 20 metal-containing ions containing oxygen and nitrogen in the form of metallic salts (nitrites, nitrates and nitrides) and oxides were positively identified in our laboratory mass spectra. Most of these ions could only be detected when the metals solutions were at their highest concentration levels, suggesting that their concentrations were a small fraction of the total ion signal detected for a given metal sample. The three exceptions were MnNO+, FeNO+ and NiNO+ which were observed at several steps of the laboratory RIE experiments. Unfortunately, the quantification of these ions was complicated by overlap with the tail of the ion signals from the surface ionized ions, Rb85, Sr86 and Sr88. Thus, while it is possible that the observed large discrepancies in the RIE_meas/RIE_theory ratios (i.e., « 1) for Mn, Fe, and Ni may be due in part to the formation, and lack of quantification, of these products, we currently do not have a conclusive explanation. The following was added to the text.

"A comprehensive list containing all the metal-containing ions and their respective fragments, which we might expect to observe during our laboratory experiments, was added to the supplemental information (Table S2). From this list, 20 metal-containing ions containing oxygen and nitrogen in the form of metallic salts (nitrites, nitrates and nitrides) and oxides were positively identified in our laboratory mass spectra. Most of these ions could only be detected when the metals solutions were at their highest concentration levels, suggesting that their concentrations were a small fraction of the total ion signal detected for a given metal sample. The three exceptions were the fragments, MnNO+, FeNO+, NiNO+ that were observed at several steps of the RIE laboratory experiments. While we were unable to quantify these metal complex ions, it is possible that some of the difference in the RIE ratios observed for Mn, Fe and Ni was due to formation of these side products."

2- 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?

Reply: Most metallic oxides (from the metals investigated in this study) will vaporize at the rBC vaporization temperature (4000 °C). However, metal oxides were not the focus of this work and we do not yet know the SP-AMS detection sensitivity for these compounds.

3- 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.

Reply: This work is focused on attempting to quantify the detection of trace metals on rBC particles in the SP-AMS using electron-impact ionization. Thermal surface ionization (TSI) is an interference to the EI signal. While we have attempted to explain why we observe some metals with larger than expected relative ionization efficiencies (RIEmeas) compared with rBC ion signals due to likely TSI mechanisms, we are not attempting to quantify or compare TSI-generated ions based on different chemical forms of the metals. As described in section 3.1.5 we explained that most trace metals were detected in their metallic ion form, rather than as either metallic salts or oxides. While we appreciate the reviewers concern, we currently do not have enough expertise or experimental evidence to include an expanded discussion on this topic in the paper.

4- Please discuss if there are other disadvantages by using TSI. For example in terms of peak shape.

Reply: Yes. The disadvantage of TSI, especially in terms of ions generated per molecule and peak shape are discussed in the text (L.206).

“In general, this type of ionization is undesirable because (1) it produces ions with a significantly different efficiency (typically orders of magnitude higher) than standard electron-impact (EI) ionization and (2) it produces ions with different energies associated than the ones produced by the EI ionization. In practice, TSI may cause a distortion in the ion peak shape detected by the instrument, further complicating the mass quantification process by the SP-AMS.”

5- 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.

Reply: The original rBC RIE relative to nitrate reported in the manuscript was wrong, the right value is 0.56, it is now corrected in the text. However, a ratio of 2 is still present between the RIE_theory (1.28) and RIE_measured (0.56). One possible explanation is the CE. Willis et al., (2014) measured the CE of bare RB particles and estimated a value of 0.6 for irregularly shaped particles. The irregular shape leads to divergence in the particle beam width, such that particles at the edges of the particle beam do not intersect the laser beam. Coated RB particles result in more spherical particles, which exhibit narrower particle beams with better laser beam overlap (Cross et al., 2010; Onasch et al., 2012; Willis et al., 2014). In this laboratory study, RB was coated by metals, however in very small content. Therefore, it is likely that these particles exhibited a CE more similar to bare RB. An additional issue that may affect the rBC RIE relative to nitrate include different potential ionization efficiencies between the laser vaporizer and the tungsten vaporizer, which is discussed in more detail by Lee et al. (2015). In particular, the two vaporizers (1) generate neutral plumes in different regions of the ion chamber and (2) generate neutral plumes with different molecular velocities, both of which could lead to different ionization efficiencies. Since the temperature of the tungsten vaporizer is typically operated at 600 °C and the carbon vaporizers from rBC materials at ∼4000 °C, these different materials will have different kinetic energies during evaporation and the carbon clusters may spend less time in the ionization chamber, leading to lower ionization efficiencies. Despite these apparent discrepancies between the ionization efficiencies from the laser vaporizer (rBC) and tungsten vaporizer (nitrate), we expect the ionization efficiencies of metal and rBC generated from vaporization in the laser vaporizer to be more similar with respect to (1) neutral plume location and (2) neutral velocities. Furthermore, by measuring metal ionization efficiencies relative to rBC (i.e., RIEmeas), the absolute collection efficiencies for rBC particles in the SP-AMS laser vaporizer is not required.

“The RIErBC,nitrate may be affected by different potential ionization efficiencies between the laser vaporizer and the tungsten vaporizer, which is discussed in more detail by Lee et al. (2015). In particular, the two vaporizers (1) generate neutral plumes in different regions of the ion chamber and (2) generate neutral plumes with different molecular velocities, both of which could lead to different ionization efficiencies. Since the temperature of the tungsten vaporizer is typically operated at 600 °C and the carbon vaporizers from rBC materials at ∼4000 °C, these different materials will have different kinetic energies during evaporation and the carbon clusters may spend less time in the ionization chamber, leading to lower ionization efficiencies. Despite these apparent discrepancies between the ionization efficiencies from the laser vaporizer (rBC) and tungsten vaporizer (nitrate), we expect the ionization efficiencies of metal and rBC generated from vaporization in the laser vaporizer to be more similar with respect to (1) neutral plume location and (2) neutral velocities. Willis et al., (2014) measured the CE of bare RB particles and estimated a value of 0.6 for irregularly shaped particles. The irregular shape leads to divergence in the particle beam width, such that particles at the edges of the particle beam do not intersect the laser beam. Coated RB particles result in more spherical particles, which exhibit narrower particle beams with better laser beam overlap (Cross et al., 2010; Onasch et al., 2012; Willis et al., 2014). In this laboratory study, RB was coated by metals, however in very small content. Therefore, it is likely that these particles exhibited a CE more similar to bare RB. However, by measuring metal ionization efficiencies relative to rBC (i.e., RIEmeas), the absolute collection efficiencies for rBC particles in the SP-AMS laser vaporizer is not required."

6- 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?

Reply: Unfortunately, there were no single particle measurements capable of measuring the mixing states of the emitted particles. Based on the volume size distributions

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

measured by ELPI (Fig. 3, Happonen et al. 2013) there was only one mode in the size range of the SP-AMS suggesting that rBC and metals are internally mixed in the same size range. However, it is possible that not all of the particles contain rBC material (i.e., not all particles are soot particles). If the latter case is true, then the SP-AMS sensitivity drops as the rBC mass fraction decreases due to more of the metals residing on non-rBC particles. This is the most likely explanation for the observations shown in Figure 8. An explanation was added to the text.

"Although, the volume size distributions measured by ELPI (Fig. 3, Happonen et al. 2013) indicated that only one mode was present in the size range of the SP-AMS, suggesting that rBC and metals were internally mixed in the same size range, it is possible that not all of the particles contained rBC material (i.e., not all particles are soot particles). If the latter case is true, then the SP-AMS sensitivity drops as the rBC mass fraction decreases due to more of the metals residing on non-rBC particles."

Minor comments and questions: 7- 5739 – r21 change to "field experiment"

Reply: OK.

8- 5742 – r15 b "All generated particle contained rBC". Please motivate whether this is a good assumption

Reply: The main assumption here is that the ratio between the mass of each dissolved metal and the suspended RB particles was the same in the size-selected, dry particles as in the atomized solution. For this assumption to hold, all of the atomized solution droplets would need to contain a rBC particle. Towards this goal, we used only trace amounts of metals and high RB mass concentrations in the solution in an attempt to ensure that all of the metal was associated with RB particles. While we did not definitively test the validity of this assumption, the linearity of the measured metal ion signals relative to the calculated metal mass loadings (Figure S3) and the comparisons of the RIEmeas vs RIEtheory (discussed in section 3.1.5) provides indirect support. We have modified the text to state this more clearly.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

9- 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

Reply: Correct. By using a mobility-mass measured effective density, we do not need to assume spherical particles. The text was slightly modified to make this point.

“Based on this assumption, the number concentration of particles measured by the CPC was converted into rBC mass assuming monodisperse particles (300 nm, mobility diameter, dm) with an effective density (the mass is divided by the volume of a sphere with the same mobility diameter dm) of RB (900 kg m-3) (Onasch et al., 2012).”

10- 5746 – r4 Write out TSI first time it is used in R&D section

Reply: OK.

11- 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.

Reply: Since the SP-AMS was operated with both the laser and tungsten vaporizers, we expect ion signals derived from refractory material vaporized only by the laser to go to zero at low laser power or when the laser was turned off. The only consistent ions signals observed during the laboratory experiments under these conditions included ammonium and nitrate. We believe that the nitrate comes from the stock metal solutions and the ammonia likely comes from the filtered sample air. The sentence was rewritten to explain about the presence of ammonium nitrate while the laser power was still very low.

“The only exceptions were nitrate and ammonium. The presence of those ions under the condition of very low laser power, suggested the presence of ammonium nitrate salt (10% of the rBC signal), derived from the nitrate in the stock metal solutions and trace ammonia in the filtered sample air, which was vaporized by the tungsten vaporizer.”

12- 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.

Reply: Yes, most likely it occurred from impurity. The sentence was clarified.

“Because this metal was not present in the solutions used in this experiment, it was likely due to contamination.”

13- 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.

Reply: Unfortunately no filter measurements were performed in parallel with the SP-AMS during the laboratory experiments. It would have been possible to do the filter measurements, however, the sampling time needed for the filters would have probably been close to 24 hours that is much longer than the time needed just for the SP-AMS measurements. As we made all of the standard solutions using the same analytical method, we do not believe that we could have messed up the generation of the standard solutions for Mn, Fe, and Ni, but not for the other metals, though human error is always a possibility. Thus, we believe that another reason likely exists, though we do not know what it is. Currently, we do not believe that metal oxides would form from the stock and standard solutions; however, we have some evidence for metallic salts with the nitrate in the stock solutions (i.e., MnNO+, FeNO+, and NiNO+). We do not know of a reason why these metal complexes appeared form, whereas others did not. Since we were unable to quantify these compounds, we do not know if they actually account for the apparent losses of the metals in our experiments. As we have not addressed

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

the issues of metal complexes in this initial work, it is possible that metal complexes may have formed for some of the metals (e.g., Mn, Fe, and Ni), such that they might vaporize at higher than expected temperatures. As explained earlier, vaporizing at significantly different temperatures may alter their individual ionization efficiencies (due to different velocities/times in the ion chamber). Other vaporization and/or ionization issues we have not thought of may also be at play. We have added/modified the following in the text:

"The transition metals Mn, Fe and Ni presented the lowest ratio and highest deviation from unity (0.36, 0.47 and 0.28, respectively). We currently do not have a conclusive explanation for this discrepancy. Losses may have occurred at three stages: (1) losses in the atomizer, where the mass ratio of the metal to rBC was not kept constant despite our best efforts, (2) formation of side products, such as metallic oxides or salts, which were not quantified during the RIE experiments, and (3) losses in the laser vaporizer due to the high temperature required to evaporate certain metals or metal-containing compounds."

14- 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 sample." Why would the salt and oxide formation lead to underestimation of metals?

Reply: SP-AMS detected metals in the atomic, salt and oxide forms, however only the metallic atomic forms were studied and quantified through the method described in this manuscript. The metallic oxides and salts may have different RIE values relative to the atomic form. While the ICP-MS methodology reports the sum of metal concentration in all those above mentioned forms.

15- 5750 – r26 and 5752-r1 The two statements seems contradictory: "Moreover, the SPAMS 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.”

Reply: The paragraph was rewritten and the contradiction was removed.

16- Table 2: include estimated vaporization temperatures

Reply: They were added to Table 2.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/8/C3633/2015/amtd-8-C3633-2015-supplement.pdf

---

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