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Atmospheric Measurement Techniques
Discussions

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

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We thank the referee 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 manuscript evaluates a detection and quantification of metals by deploying an SPAMS instrument. Relative ionization efficiency was found for several trace metals by performing laboratory experiments and compared to the RIE derived from theoretical calculations. Appropriate detection limits of specific metals were also derived, which, along with RIE, enabled the quantification of metal concentrations in ambient aerosol. Since a presence of the trace metals can affect human health, but their levels and ef-

fects are still purely understood, this study fills the gap and enhances the quasi real time SP-AMS potential in evaluating and quantifying pollution episodes in urban environment and assessing the risks to human population. Therefore, I recommend this study for publishing in AMT after revisions listed below are made:

1- My major concern is with the quantification of metals in ambient samples, which is the main outcome of this paper, so merits more detailed evaluation and discussion. As for now, Figure 8 gives an impression that LD/quantification of metals depends on rBC, while LD calculations described in paragraph 3.2.4 did not account for this fact. I would strongly recommend evaluating the influence of rBC concentration on LD's of the metals and their quantification. Say, by identifying a threshold value for rBC in order to quantify metals in ambient samples or give more comprehensive discussion on conditions required. Lines 27-28 page 5751 and 1-4 page 5752 raise a doubt on proper quantification in ambient samples, however, conclusions state opposite 'A method for the detection and quantification of the trace elements with the SP-AMS was presented'. You either present the method for quantification with all explanations and evaluated uncertainties or this is just another study towards the quantification, but it cannot be both.

Reply: This study consists of quantifying trace metals on soot-containing particles. In fact, it does not attempt to quantify trace metals in all ambient particles. That is, this method is suitable only to quantify co-emitted trace metals and soot aerosol particles, such as in combustion processes. The manuscript text was reformulated to make that point clear. Concerning a minimum amount of soot, when this component is low, the metals are most likely not associated with soot particles and are not detected via the laser vaporizer in the SP-AMS. As such, to identify a minimum amount of soot material is probably not the right approach to be used. It does not matter how much soot material would exist if the metals were not associated with these particle types. Thus, if we assume that trace metals and soot were co-emitted, for instance in a combustion process, and if the trace metals condense on the soot, if soot is present, then the minimum amount of soot necessary to detect the metals will be equal or larger than the detection limit of soot. Regarding the presented limits of detection, those are relevant only for when the metals are on soot aerosol particles. The sensitivity section was reformulated and the discussion above was added to the manuscript.

"3.2.4 Sensitivity The presence of rBC in the aerosol particles is essential to detect trace metals with the SP-AMS laser vaporizer. Metals associated with the rBC will be evaporated with the 1064 nm wavelength laser and detected. This fact was verified with the measurements at the heating station, by a clear dependence of the metals (sum of all the metals) on the rBC concentrations, i.e. the larger the rBC mass loadings, the larger the SP-AMS measured metals concentrations (Fig. 9). The different ratios between metals and rBC during the measurements were likely caused by the different conditions during the combustion (e.g., effective fuel spraying, high temperature, optimal air-to-fuel ratio) and the different combinations of fuels used. Because of the strong dependence of trace metals on rBC particles one could expect that the sensitivity will also depend on the rBC mass loading present in the aerosol. In fact, the SP-AMS sensitivity drops as the rBC mass fraction decreases. That is, when the latter is low, the trace metal mass loadings are most likely not associated with rBC particles, trace metals will reside on non-rBC particles, and are not detected via the laser vaporizer in the SP-AMS. As such, it does not matter how much rBC material would exist if the trace metals were not associated with these particle types. Thus, if we assume that trace metals and rBC are co-emitted, for instance in a combustion process, and if the trace metals exist on the rBC particle, if rBC is present, then the minimum amount of rBC necessary to detect the metals will be equal or larger than the detection limit of rBC. One method to investigate the sensitivity of the SP-AMS for trace metals is to estimate the limit of detection (LD). LD was calculated by using three times the standard deviation of the metal concentration during a period when filtered air was measured (DeCarlo et al., 2006). The LD values were obtained as an average of two minute measurements in one hour of filtered air sampling during the experiment in the heating station. The LD values for metals varied between 10 (Sr+) and 117 (Mn+) ng

m-3, Table 2. During the same period, the LD of rBC was 13 ng m-3. The latter was smaller than the value reported by Onasch et al. (2012) due to the different averaging time employed (one minute), but consistent with the Allan variance analysis. The presented limits of detection are relevant only for when the metals are on rBC aerosol particles."

Specific comments: 2- Use consistent abbreviation for Regal black, it is RB in the abstract and rBC in the rest of the manuscript. BTW explanation for rBC abbreviation is absent from the text, so I just assumed that it is Regal black.

Reply: RB (Regal black, REGAL 400R pigment black, Cabot Corp) is the commercial name of the chemical compound used to calibrate the SP-AMS with respect to refractory black carbon content. Because RB presents similar fragmentation pattern as the soot, it is used as a surrogate (Onasch et al., 2012). Refractory black carbon (rBC) is the terminology used to define laser-light absorbing refractory black carbon. This explanation was given in the 2.1.1 section, where the SP-AMS was described. In order to clarify the difference between the two terminologies an explanation was added to the text in the section 2.2.

"The RB chemical ion signal measured by the SP-AMS is called rBC and is the sum of the C1+ to C5+ carbon cluster ions."

3- Lines 23-25, page 5736: The first sentence of Introduction combines the real metal sources (combustion and industrial sources) with the metal carriers (sea salt, dust), it should be separated.

Reply: The sentence was rewritten and metal sources and carriers were separated.

"Trace metals are found in atmospheric aerosol particles from various combustion processes, such as vehicular emissions and industrial sources (Gao et al., 2002; Mbengue et al., 2014), and mechanical processes, such as wind-derived soil dust and sea-salt (Pacyna 1998; Allen et al., 2001)."

4- Was RH of aerosol flow measured? as 25 cm diffusion dryer might not be enough to dry nebulised particles.

Reply: Yes, RH was measured and was below 60% during the whole experiment.

5- Lines 11-13, page 5740: This sentence is not clear

Reply: The sentence was rewritten.

"The quantification experiments occurred in several steps, including a blank and eight varying solution concentrations for each metal. In the blank step, only the RB was atomized and measured (2.4 x10-5 kg of RB in 0.2 L of deionized water, concentration of 1.2 x10-4 kg L-1, this concentration was kept constant throughout the experiment). During this step, the RB sample was tested for the detection of each of the 13 metals of interest, before the addition of any metal, to rule out potential contamination. From the metals evaluated in this study, only Na exhibited a measureable background concentration (less than 0.1%). The other metals were not detected, indicating background concentrations of metals in the original RB below the limit of detection. In the following steps, a given standard metal solution was added to the RB solution gradually (1 x10-3 L per step), increasing the metal content. As a result, the amount of each metal in the atomized solution varied between zero and 8 x10-8 kg. SP-AMS measurements were done at every step."

6- Lines 22-25, page 5740: Add some discussion on how relevant rBC is to the ambient measurements in addition to its suitability for SP-AMS.

Reply: The following sentences were added to the manuscript.

"In ambient measurements, the detection of metals in aerosol particles containing rBC is important as they are generated and co-emitted by many different combustion sources and both components are important for local, regional and global climate and pollution issues and both exhibit adverse impacts to human health (Ramanathan and Carmichael 2008, Dockery 2001)."

7- Line 15 page 5741: acid as well?

Reply: Yes, nitric acid was present, in very small amount, in the metal standards. This compound was added to the sentence in the manuscript.

8- Line 22 and 24 page 5741, correct "species"

Reply: OK. They were corrected.

9- Lines 17-19 page 5743: it requires more information – vaporiser and filaments are off, so what is causing the TSI? Laser? It should be written.

Reply: The hypothesis was that with tungsten vaporizer and filament off the metals would be ionized on the hot rBC surface. That information was added to the text.

"The SP-AMS was operated with the laser vaporizer on, but with the tungsten vaporizer turned off and the EI filament current set to zero. Under these conditions, the soot particles are still heated to vaporization temperatures (~4000 °C) via absorption of the laser vaporizer power, but measured ions must be generated by mechanisms other than EI ionization, such as TSI. Under these experimental conditions, we sampled RB particles coated with a mixture of all 13 metals; the results obtained in this experiment will be discussed in the results section."

10- Figure 3. Figure caption is not clear, what is rBC fraction relative to the rBC, and why Rb fraction relative to rBC is equal 1, which would mean no rBC in the particle and, I assume it was not the case here, therefore, caption needs clarification.

Reply: The text in the caption was clarified. Figure 3 corresponds to the fraction of metals signal (Hz) relative to the highest rBC signal (Hz) as a function of the laser diode current (LDC). The fraction value of 1 is possible because it was calculated in signal (Hz), not in mass. That means Rubidium and rBC presented similar values in Hz. We found it more illustrative to the reader to present the information this way, otherwise rBC would be isolated on the top and the metals at the bottom of the figure. We added a sentence in the text to clarify that.

11- Figure S2: word ‘vaporiser’ is missing after ‘Tungsten’ as filaments can also be made of tungsten.

Reply: OK, the word was added.

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