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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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Dear authors, Regarding surface ionization: As is already stated in your AMTD manuscript (Carbone et al., 2014), thermal ionization will depend on the ionization potential of the analyte atom or molecule, the temperature of the system, and the electron work function of the material from which the analyte atom or molecule is vaporized (Heumann et al., 1995). Therefore, one might hypothesize that SP-AMS thermal ionization could be significantly different for atmospheric samples than for the samples considered here. Since metals such as iron may be often measured in the atmosphere as metals (e.g. from industrial sources and/or abrasive processes) or light-absorbing dust, the RIEs measured for metal salts mixed with Regal Black (RB) might be signif-

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icantly different to those observed in the atmosphere. In particular, the work function would be different due to the particle surface being different from RB, and the ionization temperature might change since the metal surface would itself be heated rapidly by the SP-AMS laser. If additional discussion on whether these effects would make a significant or negligible difference to the observed metal RIEs, this might be very helpful for the interpretation of future SP-AMS results. Perhaps the Saha equation with an estimate of the relevant work functions (e.g. Heumann et al. 1995; Sodha et al., 1975) could be used? Or, more directly, the thermal ionization of pure-metal nanoparticles could be measured as described in Section 2.3.3?

Reply: Thank you for your suggestions. Regal Black consists of an oxidized surface analyte (http://www.cabotcorp.com/solutions). It has been shown that the work function of commercially available furnace blacks increases with increasing acidity of the surface (Fabish and Hair, 1977). Because, in this laboratory experiment, the metals were dissolved in nitric acid, Regal black work function was probably higher than highly oriented pyrolytic graphite (HOPG, 4.6 eV). However, it is likely that in ambient measurements, for example from industrial sources, rBC work function is also slightly higher than HOPG. Industrial sources might have more organics, such as acids attached to rBC, which will also increase rBC work function towards Regal Black value. Concerning the RIE values, in fact, the RIE of pure metallic salts will be different than pure metals. Note that in this study, the RIE of metallic salts were not determined in the laboratory study. Although the determination of thermal ionization of pure-metal nanoparticles is important to understand which processes control the ionization, it was not the main objective of this study. No doubt, that is an important topic for future research studies. We have included the following discussion to the section 3.1.4 in response to your comments.

“The probability for TSI is described by the Saha-Langmuir equation (Zandberg and Ionov, 1971). Emission of positive ions is favored when the ionization potential of the desorbing atom or molecule is similar in magnitude or lower than the work function of

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the surface. In this experiment, assuming the particle surface consists of RB (a carbon black material), its work function might be similar to highly oriented pyrolytic graphite (HPOG), which has a work function value of 4.6 eV (Shiraishi et al., 2001). In fact, the RB work function might actually be larger than that of HPOG as RB is advertised by its manufacturer as an oxidized carbon black and the work functions of commercially available carbon blacks increase with increasing acidity and oxidation of the surface (Fabish and Hair, 1977). In this laboratory study, nitric acid was present inside the stock metal solutions, which could have further increased the work function of RB. A relatively high work function value for RB ($\sim$5.1 eV) would be in agreement with our observations of multiple metals undergoing TSI in the SP-AMS. The key comparison in this case is the number of ions generated by TSI, estimated from the Saha-Langmuir equation, compared with the number of ions generated by EI for a given metal, which is estimated using the theorectical approach described in section 2.3.2. In ambient measurements, the work function of rBC particles is probably also higher than that of HOPG. For example, combustion processes, such as from industrial sources, may emit organic compounds, such as hydrocarbons and acids, which attached to the co-generated rBC particles. Ago et al. (1999) showed that the presence of additional surface functional groups containing oxygen increased the work function of carbon nanotubes. Thus, ambient rBC particles likely have a work function that may be closer to that of Regal Black than HOPG. Under these conditions, TSI may be a significant inteference to the ability of SP-AMS to quantify these trace metals on ambient rBC particles."

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