Atmospheric Measurement Techniques Discussions

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Comment on amt-2021-22

Anonymous Referee #2

Referee comment on "Effects of aerosol size and coating thickness on the molecular detection using extractive electrospray ionization" by Chuan Ping Lee et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-22-RC1, 2021

Review: Lee et al., "Effects of Aerosol Size and Coating Thickness on the Molecular Detection using Extractive Electrospray Ionization"

Lee et al. present a characterization study of extractive electrospray ionization (EESI) of particles which is a topic of great interest given increased use of EESI to examine particles and their components. This EESI study of coated and uncoated particles of varied particle diameters is highly valuable given the range of results from existing EESI studies in the literature. The variety of methods of particle generation and compositions lends insight into the mechanism of extraction over a range of conditions that are greatly informative to the EESI community. The experimental techniques are robust and well-described and the paper is well written. The authors have clearly taken care in their experimental techniques, one example being the use of a size selection method that does not suffer from multiply charged particles.

Data are presented to show that Brownian coagulation between the analyte particles and the electrospray (ES) droplets can explain the reported increase in sensitivity for small particles because of increased time for coagulation for those smaller diameters. Brownian coagulation coefficients are shown to play a dominant role in controlling the sensitivity of EESI for SOA particles formed from pinene ozonolysis. A variety of particle compositions are shown to be fully extracted but with size dependence.

Main comments and questions are listed below:

1. The introduction mentions that the analyte particles contain <50% water. The experimental (section 2.3, line 118) describes the use of a silica gel dryer to dry particles, and section 2.4 (line 154) describes their humidification to 60% RH. Can it be clarified how the 50% water content (by mass?) was determined?

Continuing the idea of particulate water content, this seems to be a large amount of water such that the particles are likely to have much greater internal mobility than dry, solid particles (even though many particles cannot be completely dried). The presence of particulate water could have a significant effect on their timeframe for solubility or coalescence within the ES droplets. Since results are contrasted with a comparison paper, Kumbhani et al. 2018, which reports a seemingly large effect of the presence of water in their particles during EESI analysis, it is important to clarify this. It is not clear if all the particles generated in Lee et al. have this much water, but if so this could be a further difference between results here and in the comparison papers that may be worth noting.

2. Is it expected that the inorganic salt, NH_4NO_3, would be detected as $[NaNO_3+Na]^+$? It seems strange that no ammonium ions or ammoniated adducts are detected. If there is ion exchange from NH_4NO_3 particles with the NaI that is added to the electrospray solution, this is consistent with full extraction of analyte particles by the electrospray droplets. But related to the question above, if the NH_4NO_3 was initially dried to lower than 50% water content, do the authors believe this ion exchange would still occur?

3. I'm afraid I did not follow at first what the Brownian coagulation was referring to, although it is an insightful calculation. May I suggest that the authors use the same or similar wording used in the conclusion earlier on in the manuscript? Namely, include the description from line 276-277 "the coagulation duration between the ES parent droplets and the analyte particles" somewhere near line 198 where the Brownian coagulation coefficient was first described to clarify what interaction is being examined here.

4. Line 216 – The sentence states that EESI source A provides a factor of 2 longer residence time but then the next sentence (line 217) says source B has twice the residence time as source A. Can you clarify which one has the longer residence time?

5. Figure S4 mentions the use of ammonium sulfate particles being coated with pinene oxidation products. Should this be ammonium nitrate?

6. Figure S6, line 83, has "BCC", not sure if this is a typo? Also in Figure S6, the last sentence of the caption says that the mass concentrations for levoglucosan and NH_4NO_3 were measured by an LTOF-MS. Perhaps it would not change the trend of $S_{100\ nm}$ values in Fig. S6, but are there ionization efficiencies that affect the mass concentrations of levoglucosan and NH_4NO_3? There is limited description of how AMS signals were characterized in the main text and supplementary information.

7. It is quite nice to experimentally change the electrospray parent droplet size. The parent droplet sizes (0.7 – 5.66 um) seem larger than in the papers the authors compare with but I'm not sure this is always true. For example, Wang et al. (2012) points out that the ESI droplets are usually smaller than sample droplets and that this size is important in examining the mechanism. Could this be another difference between your studies and comparison papers (the conclusion does not refer back to this difference in drawing on

comparisons).