Comment on amt-2021-22
Anonymous Referee #1

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-RC2, 2021

This paper presents a series of carefully planned and executed experiments to explore the sensitivity of the EESI source as a function of particle size and composition, as well as EESI operating conditions. It represents a useful contribution to our understanding of the EESI, especially as it is becoming more commonly used in the measurement of ambient aerosol particles. However, some of the conclusions are not supported by the data and this needs to be corrected before publication.

Specific comments:

Discussion of the trend in normalized sensitivity on pages 5 and 6:

Line 196: Why do you state that the sensitivity reaches a plateau only for EESI Source A? The one set of data for EESI Source B shows a clear plateau.

Line 204: What are you referring to as a longer period for coagulation? Do you mean the difference in length of interaction region in Source A and in Source B? If so, please state this more clearly. Source A has a 1 mm interaction region and Source B has 0.5 mm, so Source A has the longer period for coagulation. By your argument, Source A should have less of a size dependent sensitivity. The data in Figure 2 shows exactly the opposite. The blue points (Source A) have, taken as a whole, a steeper slope than the red points (Source B). Please draw a conclusion that it is supported by the data.

Lines 206-211: None of these conclusions about plateaus or deviations are supported by the data. First, rephrase the sentence on lines 206 to 208 to make it clear that it is the calculation that suggests the sensitivity plateaus when the particles are close in size to the ES droplets. The data does not suggest this at all. In Figure S6, the data for the largest ES droplets plateaus at the smallest diameter, exactly the opposite of what the calculations suggest. In addition, the sensitivity changes for two components of a single particle, e.g., levo and NO3 or sucrose and NO3, are very different on the sensitivity vs size graphs. For example, NO3 plateaus at ~ 250 nm and turns back up while levo from the same particles does not plateau at all. Sucrose plateaus at ~ 300 nm while NO3 from the same particles does not plateau at all. I don’t think you can draw any conclusions about particle size/droplet size relationships from the data. For the claim about the high deviation in the data above 100 nm, there is no discernible pattern as a function of ES
Discussion of residence time on page 6:

Line 218: This statement that Source B has twice the residence time of Source A is not consistent with the schematic in Figure S1 and directly contradicts the preceding sentence. Residence time is not the explanation for the shallower sensitivity dependence of Source B. In addition, this (incorrect) residence time argument was already made in the previous paragraph and there is no need to repeat it here. Please remove this discussion.

Update the abstract:

Lines 25-26: This sentence needs to be updated once you have revised the discussion sections. You do not demonstrate that the sensitivity dependence varies with ES droplet size or with residence time.

Minor comments:

Lines 58-59: This sentence about water content is confusing – are the ES droplets really >90% water if you are using 50:50 H2O:ACN for the solution? You could just say you are going to call the analyte droplets particles to avoid confusion with the ES droplets. No need to invoke water content.

Line 64: What do you mean by “fragmentation of the analyte”? Isn’t the point of EESI that it does not fragment the analyte so that you get molecular information.

Line 135: The figures should be in the same order in the SI as you call them out in the text. Here you have S5 before S3 or S4.

Line 160: What do you mean by depending on conditions? What conditions and how do you know what morphology you have? You also say that the morphology will not affect your conclusions, “as discussed below” but you do not discuss morphology at all in Section 3.2. Please add a sentence or two about morphology to the discussion in Section 3.2.

Line 181: The figures should be in the same order as they are called out in the text. Here you have Figure 3a before Figure 2.

Line 269: What do you mean by dissolution period?

Figure 2 caption: In the text, Source A and B are the TOF and Orbitrap, respectively. Please correct.

Figure S1: Is the only difference between Source A and Source B the length of the gap between the ESI capillary and the transfer tube? Since you don’t do any experiments with the Orbitrap, why show the schematic of it? I would move the inset for Source B to part A of the figure and delete part b of the figure.

Figure S2: In the schematic, you show a denuder and a HEPA filter, but you do not mention the use of the HEPA filter in the description of the experiments. You also don’t mention bypassing the denuder as is shown in the schematic. Maybe you could simplify the red part of the schematic to match the text. Is the red arrow next to the HEPA filter in Figures S2 and S4 going in the wrong direction? Finally, please label the EESI.

Figure S6: Use the same symbols in 6d as in 6c for the same particles. In the caption,
delete the extra “BCC” after the second sentence. Move the sentence about what A and B denote after the sentence describing panels b-d. It would be much easier to compare the data in these four panels if you use the same range on the x and y-axes.

Table S2: You have reversed the Source labels A and B. Please correct. Why do you have two separate rows for experiments with mixed particles? For example Levo7 and AN2 are the same experiment, so just use one row.

Figure S8: What is the point of this figure? How is Figure S8 related to S9? I think you could skip S8.

Figure S12: This figure is not referenced in the main text. I think you could skip it.

Typographical errors:

- There are many, many typographical errors (missing words, random extra words, misspellings, etc.). The authors should proofread much more carefully before submitting an article.