We thank the reviewers for their comments. The original comments are in normal font type. Our point-by-point responses are shown below in **bold** *and italics*. Manuscript changes are shown in blue and *italics*.

Reviewer 2 (*https://doi.org/10.5194/amt-2021-22-RC2*)

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:

1. Line 197: 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.

As requested, we added EESI source B in line 195-197: "*The* $S_{100\ nm}$ *for different types of analyte particles decreases by up to 3 orders of magnitude as the volumetric geometric mean diameter increases from 30 to 300 nm, and some of them start to reach a plateau at larger sizes for experiments using EESI source A and* ***B****."*

2. Line 217: 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.

There is a typing error in the figure and we apologize for this. We corrected the typing error of the interaction region distance denoted in Figure S1 where EESI source A should have 0.5 mm and EESI source B should have 1 mm, instead of the other way round. At the same time, we also corrected the typing mistake in line 220-222 as mentioned by Reviewer 1 at Point 4. After corrections of these 2 typing mistakes, the conclusion is supported by the data.

3. Lines 210-216: 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.

We clarified our interpretation of the coagulation coefficient in Line 210-216. In combination with the correction of the typing error described above (in 2), the conclusions are supported by the data:

"*Smaller particle sizes that have higher BCC are collected more efficiently and thus contribute a higher percentage of their total mass for extraction. Furthermore, the plateaus of* $S_{100\ nm}$ *at larger particles sizes could be explained by the suggested behavior of* $BCC_{100\ nm}$ *when the size of the particle is similar to the actual ES droplet size or partly to the estimated ES parent droplet size in our study. The high deviation of size-dependent sensitivity (~50 %) for* D_p *> 200 nm is likely due to the variation of the actual ES droplet size distribution in different calibration runs, which can deviate from the estimated ES parent droplet size. Knowledge of the actual ES droplet size distribution is needed to further explain the variabilities but are beyond the scope of the current study.***"**

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.

The reviewer meant that one normalized sensitivity for the estimated ES parent droplet size of 5.66 μm in Figure S6c plateaus at the smallest diameter and it could be the opposite of what the Brownian coagulation coefficient calculation suggests. Please note that the ES droplet sizes meant by the Reviewer is an estimated ES parent droplet size using scaling laws (without accounting for the micrometer precision of the ESI capillary position) which we used as a theoretical reference to account for the possible variability range of our ES parameter settings. As this is an estimated ES parent droplet, it might not directly represent the actual ES droplet size that undergoes coagulation with the size-selected particle. For example, if there will be a slight change (± 5 % from 0.5 mm distance, i.e. ±25 μm) of the ESI capillary position, the actual ES droplet size could be smaller or larger than the estimated ES parent droplet size (5.66 μm) in the case of more or less time for evaporation, respectively.

To vary the actual ES droplet size in our experiments, we changed the ES capillary diameter (by a factor of 2), the ES capillary flow (a factor of 10) and ES voltages (20 %) as shown in Table S2. Such range of ES parameter settings should result in different actual ES droplet sizes that result in different normalized sensitivity behaviors. Despite all of these different normalized sensitivities, our whole experimental data demonstrates good correlation of BCC_{100nm} and S_{100nm} for sizes smaller than 200 nm and the normalized sensitivity plateaus when the particle sizes could be similar to the actual ES droplet size, as suggested by $BCC_{100\ nm}$. As a result, we clarified the possible discrepancies in line 212-215: "*The high deviation of size-dependent sensitivity (~50 %) for D_p > 200 nm is likely due to the variation of the actual ES droplet size distribution in different calibration runs, which can deviate from the estimated ES parent droplet size. Knowledge of the actual ES droplet size distribution is needed to further explain the variabilities but are beyond the scope of the current study.****"***

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.

In order to generate enough particles for size-selection, the nebulization solution concentration was increased for size-selected standard calibrations conducted at larger sizes. It is possible that this led to small changes in the relative particle composition in the two-component mixtures. In addition, the ionization process (e.g. during droplet evaporation) and ion chemistry during the extraction process of EESI may also vary for different chemical species, especially so when comparing sugar/alcohol molecules (levoglucosan and sucrose) with an inorganic salt (NH_4NO_3). These differences on top of the prevailing size-dependent sensitivity merit systematic exploration in future studies (a step further), such as different chemical composition ratio at the same total coagulated mass, ES droplet and particle size distributions. This concern is admittedly under-constrained in the current study, as reflected in our manuscript changes above and below.

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 droplet size in Figure S6. Therefore, it does not make sense to attribute the scatter in the data to ES droplet size. Or maybe you are saying that you have no idea what the droplet size is in any experiment. If that is the case, then state that.

We did not measure (ultrasonically, optically or electrically) the actual electrospray droplets size, as doing so may affect the properties of electrospray droplets and the electrospray ionization. Thus, we agree with the reviewer that we do not have full control on the actual ES droplet size. Our approach was to perform theoretical calculations over a range of ES parent droplet sizes that is plausible according to a range of our ES operating parameters. As detailed in our response above, the theoretical calculation and experimental observation generally agree regarding the EESI sensitivity

dependence on the particle size. Therefore, we are confident that the actual size of ES droplet is an important parameter to explain the sensitivity behavior of plateau and scatter for larger particles. We have added a clarification regarding the ES droplet sizes as described above.

4. Line 221: 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.

The typing error in line 220-222 was pointed out Reviewer 1 and we changed the phrase of "EESI source A" to "EESI source B": "*We examined this hypothesis by using an EESI source B which provides a factor of 2 longer residence time in the electrospray ionization region.****"***

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.

We corrected the errors in source labeling (A vs. B) in the main text and the supplementary information, and the implication of residence time should support the observed sensitivity dependence. A longer residence time for coagulation in EESI source B enables a higher extraction fraction of the particle and thus exhibits a less steep sensitivity size dependence.

5. 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.

This conclusion is supported by our analysis as explained in our responses to Point 1-4 above.

Minor comments:

6. Lines 57-58: 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.

We removed the sentence about water content definition as it is not very necessary. Now, the droplets that are discharged from ES are called as ES droplets, particles that are injected into our EESI are called particles, and the analyte-laden droplets are the particles after reaction with ES droplets. Thus, we removed the line 57-58

"Due to the lower water content of our analyte droplet in all our experiments (< 50%) than a typically known water content of droplet (> 90 %), we refer to our analyte droplets as analyte particles here hereafter."

and changed to

"*For clarity, we refer to our neutral analyte droplets as "particles" prior to their interaction with ES droplets and as "analyte-laden droplets" afterwards.****"***

7. Line 65: 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.

We think that this comment is referring to Line 64-66: "Using other techniques such as Dual- phase Doppler anemometer, Wang et al. suggested that the extraction happens via fragmentation of the analyte and ES droplets (Wang et al., 2012)", which describes the fragmentation of analyte droplets following droplet-droplet collision. Note that Wang et al., 2012 employed a dual-spray setup, where analytes are introduced as droplets with sizes similar to or larger than that of the ES droplets. We added a clarification to the main text in line 65-67: "*...Wang et al. suggested that the extraction happens via fragmentation of the analyte droplets and ES droplets as the result of droplet-droplet collisions (Wang et al., 2012).****"***

8. Line 132: 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.

We removed sentence in line 132-133 because it was already mentioned in the caption of Figure 1. The SI figures are now in the correct order as referred in the text.

9. 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.

We mean that our main conclusions are not dependent on whether we have core-shell vs. single-phase particle morphologies. Assuming that extraction is limited to the particle surface, then either the core-shell or homogenous single-phase morphologies should result in the reduction of the NH_4NO_3 core signal as the organic coating thickness increases, but in different ways, whether due to the limited extraction "depth" or decreases in the NH_4NO_3 mass as a fraction of the coated particles, respectively. Because we did not observe reduction in the NH_4NO_3 signal during coating experiments, surface extraction limitations do not appear to be present, and thus our main conclusion should hold for either morphology. We added a clarification to this as follows:

Line 271-275: "*If extraction were limited by the particle surface, the EESI signal for NH_4NO_3, i.e. $[NaNO_3+Na]^+$, should decrease similar to the size-dependent sensitivity (Figure 2) that is exhibited by the source A. If the coated particles were of core-shell morphology, then the extraction of the NH_4NO_3 core would be limited by the thickness of the organic coating and the ES extraction depth. If the coated particles were of homogeneous inorganic-organic mixture, then the detected NH_4NO_3 signal would decrease in proportion to the decreasing NH_4NO_3 mass fraction.****"***

10. 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.

We added "(Figure 2)" in line 180 before "(Figure 3a)" to keep the order.

11. Line 284: What do you mean by dissolution period?

We rephrased the line 282-285 that consists of dissolution period for clarity.

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

We added the word "initially" and changed the order of TOF and Orbitrap in the Figure 2 caption: ***"****Blue and yellow markers indicate EESI source A and B which were initially developed for TOF and Orbitrap mass analyzers, respectively.****"***

13. 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.

The reviewer is correct, the key difference between EESI Source A and B is distance between ESI capillary and the ion transfer capillary. Even though we did not use the Orbitrap in this study with source B, we decided to keep the schematic of the two sources separated to contextualize their design differences.

14. 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.

We added HEPA filter in the description of the experiments in line 132-133: ***"****A HEPA filter was used for the background measurements after each analyte particles size-selection.****"***

For simplification, we removed the channel that bypasses the denuder, corrected, and labelled the EESI in the Figure S2. However, Figure S4 remained the same because the bypass channel was required to observe the steady-state of the gas and particle composition for each step of coating as mentioned in the Section 2.4.

15. 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.

We updated the Figure S6 for the same range of x- and y-axes and its caption as requested.

16. 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.

We have corrected the Source labels in Table S2 and combined the mixed particles into one row as mixed nebulization solution shown below.

Index no.	**EESI Source Designs**	**ES voltage (kV)**	**ES pressure (mbar)**	**ES capillary inner diameter (um)**	**ES solution**	**Nebulization solution**	**ES Flow, Q (nl min^{-1})**
Levo1 + AN1	A	2.6	200	50	H_2O:ACN (50:50 v/v)	Mixed	354
Levo2 + AN2	A	2.9	800	100	H_2O:ACN (50:50 v/v)	Mixed	22655
Levo3	A	2.95	200 - 400	75	H_2O:ACN (50:50 v/v)	Single	1792-3584
Levo4	A	2.88	200 - 400	75	H_2O	Single	1309-2617
AN3	A	2.95	200 - 400	75	H_2O:ACN (50:50 v/v)	Single	1792-3584
AN4 + Suc1	A	2.9	600	75	H_2O:ACN (50:50 v/v)	Mixed	5375
AN5	A	2.9	600	75	H_2O:ACN (50:50 v/v)	Single	5375
Levo5	B	2.8	120 - 250	75	H_2O:ACN (50:50 v/v)	Single	1075-2240
Levo6	B	3	120 - 250	75	H_2O:ACN (50:50 v/v)	Single	1075-2240
Levo7	B	3	120 - 250	75	H_2O:ACN (50:50 v/v)	Single	1075-2240
Levo8	B	2.9	120 - 250	75	H_2O:ACN (50:50 v/v)	Single	1075-2240
Levo9	B	2.9	120 - 250	75	H_2O:ACN (50:50 v/v)	Single	1075-2240

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

Figure S8 was referred in line 233-235 and is related to Figure 3 and Figure S9. The purpose of Figure S8 is to show the overview the EESI-TOF measurements and particle size distribution properties for consecutive SOA formation events in a very well-controlled chamber (CLOUD chamber at CERN). The shaded regions in Figure S8 denote the stage of the SOA formation where the size-dependent sensitivity of EESI is observed. These shaded regions were shown separately for of each SOA formation event in Figure S9. Thus, Figure S8 is related to Figure S9.

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

Figure S12 is referenced in line 279.

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

We checked the texts and corrected typographical errors.