

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 1 (<https://doi.org/10.5194/amt-2021-22-RC1>)

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 117) describes the use of a silica gel dryer to dry particles, and section 2.4 (line 150) describes their humidification to 60% RH. Can it be clarified how the 50% water content (by mass?) was determined?

Prior to injection into the flow tube, seed particles were dried using a silica gel dryer, where the RH is typically below 5%. The relative humidity of the sheath gas for the flow tube was maintained at 60%. The growth factor (ratio of wet to dry aerosol size, GF) of (dried) ammonium nitrate below 60% RH is ~1.2. In addition, SOA is slightly hygroscopic with GF typically below 1.2. Assuming that uptake of water vapour by analyte aerosol approaches equilibrium inside the flow tube, the water aerosol content may account for up to ~43%, which is consistent with our initial definition. However, as mentioned by Reviewer 2 Point 6, the sentence about water content definition is not necessary and can be confusing. Also, the droplets that are discharged from ES are now called ES droplets, particles that are injected into our EESI are called particles, and the analyte-laden droplets are the particles after reaction with the ES droplets. Thus, we removed the line 57-58 below

“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.”

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.

Kumbhani et al. (2018) reports higher EESI sensitivity towards wet particles compared to dry particles, which is suggested to be the result of water mobilizing the surface layer. If EESI extraction is limited to the surface layer, increasing the aerosol water content may improve extraction. This hypothesis was derived from semi-quantitative comparisons of results obtained using online EESI vs. offline ESI, which differ in terms of their dissolution/extraction timescales (milliseconds during EESI vs. and minutes-to-hours during ESI) or (water) concentrations. In this study, we have shown for our EESI setup that the extraction is not limited to the surface layer. In addition, we have shown previously that the response factors do not vary significantly with respect to RH for our setup (Lopez-Hilfiker et al. 2019). We have added a new discussion of our findings in relation to Kumbhani et al. (2018).

In line 251-259: “Aside from the size dependence, we did not observe any systematic RH influence on the EESI sensitivity from particle size selection (30 - 40 % RH) and SOA formation in the CLOUD chamber (20 - 60% RH) experiments. This is consistent with the findings by Lopez-Hilfiker et al. (2019), where RH does not systematically affect EESI sensitivity, but instead shows molecule-dependent effects where within an internally mixed particle ensemble the sensitivity of certain molecules may increase with RH while others decrease. The enhancement in EESI sensitivity for wet aerosol over dry aerosol was reported in a previous study (Kumbhani et al. 2018). If EESI extraction is limited to the surface of the analyte aerosol, the aerosol water content may mobilize surface species to facilitate dissolution (Kumbhani et al. 2018). However, the lack of RH dependence for our EESI setup indicates that such surface extraction limitation is absent in our study.”

We have also added information regarding the RH conditions for our experiments as reference for future studies.

In line 129-133: The high concentration of the chemical solutions ensured that sufficiently high analyte concentrations ($> 3 \mu\text{g m}^{-3}$) remain after size-selection by the AAC using the highest possible sheath flow (15 L min^{-1} at an aerodynamic diameter $D_{ae} > 150 \text{ nm}$) to produce highly monodisperse particle distributions (Tavakoli and Olfert 2014) at 30 - 40 % RH. A HEPA filter was used for the background measurements after each particle size-selection.

In line 134-136: In the second configuration (Figure S3), we investigated the size-dependent sensitivity of the EESI using biogenic SOA produced from α -pinene oxidation in the Cosmic Leaving Outdoor Droplets (CLOUD) chamber at CERN, Switzerland (Kirkby et al., 2011, Dias et al., 2017), at -50 to $-30 \text{ }^\circ\text{C}$ and 20 - 60 % RH (Simon et al., 2020).

2. Is it expected that the inorganic salt, NH_4NO_3 , would be detected as $[\text{NaNO}_3+\text{Na}]^+$? 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.

Na^+ is more electrophilic than NH_4^+ in the ion exchange and therefore bounds more strongly to the nitrate anion. In addition, NaI is present in great excess in the electrospray solution which promotes Na^+ adduct formation and suppresses other ionization pathways (e.g. $[\text{M}+\text{NH}_4]^+$ or $[\text{M}+\text{H}]^+$).

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?

Yes, our tests of using dried ammonium nitrate (without applying any humidification) indicate that NH_4NO_3 is detected predominately (> 99 %) as $[\text{NaNO}_3+\text{Na}]^+$ ions.

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 289-290 "the coagulation duration between the ES parent droplets and the analyte particles" somewhere near line 196 where the Brownian coagulation coefficient was first described to clarify what interaction is being examined here.

We refer to the Brownian coagulation as the possible mechanism that ES droplets and particles undergo during electrospray ionization. For a given Brownian coagulation coefficient, the total coagulated mass will vary with the ES droplet number concentration, analyte particle number concentration, and the time available for coagulation (i.e., residence time). After normalizing the Brownian coagulation coefficient and EESI sensitivity at 100nm as $\text{BCC}_{100\text{nm}}$ and $S_{100\text{nm}}$ in Figure 2, there is a systematic relationship between $S_{100\text{nm}}$ and $\text{BCC}_{100\text{nm}}$ for sizes below 200 nm and the slight discrepancies for sizes larger than 200 nm are clarified. We revised the discussion (line 200-216) as follows.

In line 200-216: If we assume that the detected ions from the size-selected particles in EESI are generated after coagulation and extraction between the particles and ES droplets, the normalized sensitivity $S_{100\text{nm}}$ is interpreted as the total coagulated mass. The determination of the total coagulated mass requires Brownian coagulation coefficients (BCC, computed from the particle and ES droplet sizes), number concentrations and residence time. However, the actual ES droplet size distribution could not be measured using other physical processes because these additional processes could alter the ES droplets properties and affect the electrospray ionization. Therefore, we could only calculate the BCC for different size-selected monodisperse particles assuming ES parent droplet sizes of 0.5, 1.5 or 5 μm . These three chosen ES parent droplet sizes represent the likely range of the actual ES droplet sizes, which is theoretically estimated from our ES operating parameters as summarized in Table S2, based on SI Eq. 3-6 and Figure S7. The calculated BCC values were normalized to the BCC for 100 nm monodisperse particles, denoted as $\text{BCC}_{100\text{nm}}$, as shown in Figure S6a, analogous to the normalization for $S_{100\text{nm}}$. Most normalized sensitivities (i.e. normalized total coagulated masses) correlate well with the $\text{BCC}_{100\text{nm}}$, as shown in Figure 2. 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 $S_{100\text{nm}}$ at larger particles sizes could be explained by the suggested behavior of $\text{BCC}_{100\text{nm}}$ 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 $D_p > 200\text{ nm}$ 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.

4. Line 221 – The sentence states that EESI source A provides a factor of 2 longer residence time but then the next sentence (line 223) says source B has twice the residence time as source A. Can you clarify which one has the longer residence time?

There is a typing error in line 220-222. We changed the phrase of "EESI source A" to "EESI source B": "We examined this hypothesis by using an EESI source B that provides a factor of 2 longer residence time in the electrospray ionization region."

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

There is a typing error in the caption of Figure S4. We apologize for this. We changed the word “ammonium sulfate particles” to “ammonium nitrate particles”: “Inorganic particles (NH_4NO_3) are injected into the flow tube which act as condensation sink for the low-volatility oxidation products.”

6. Figure S6, line 83, has “BCC”, not sure if this is a typo?

Yes, it is a typo; we have removed the additional “BCC”.

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 $S_{100\text{ nm}}$ 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.

The ionization efficiencies are different for levoglucosan and NH_4NO_3 for the LTOF-AMS. But $S_{100\text{ nm}}$ is calculated by normalizing the sensitivity of individual chemicals observed at different particle sizes to their respective observed sensitivity at 100nm, therefore, differences in ionization efficiencies between analytes should not affect the trend of $S_{100\text{ nm}}$.

7. It is quite nice to experimentally change the electrospray parent droplet size. The parent droplet sizes (0.7 – 5.66 μm) 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).

One of the differences between Wang et. al. (2012) and the current work is the size of the analyte droplets/particles. Wang et. al. (2012) used a dual spray setup, resulting in much larger analyte droplets ($D_p \gg 1\ \mu\text{m}$, 5-20 μm) compared to the study here ($D_p = 0.02 - 0.8\ \mu\text{m}$). While we expect the ES droplets to be similar or larger than the analyte particles in our study, the particles were shown to be overall larger than the ES droplets in Wang et. al. (2012).