

Atmos. Meas. Tech. Discuss., referee comment RC1
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Comment on amt-2021-325

Anonymous Referee #2

Referee comment on "High-frequency gaseous and particulate chemical characterization using extractive electrospray ionization mass spectrometry (Dual-Phase-EESI-TOF)" by Chuan Ping Lee et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-325-RC1>, 2021

Review of Dual-EESI, Lee et al.:

Summary:

The authors introduce a new inlet called the Dual-EESI that combines with a TOF mass spectrometer to alternately measure both gas and particle phases over the span of several minutes. Several flow tube experiments were performed and compared with CIMS measurements to show the proof of concept. They find that the EESI is more sensitive to gas phase compounds than particle phase. Future work will be to develop quantification methods for both phases. Generally, I believe this inlet will be a powerful addition to the EESI technique. But to make that true, I believe the background signal (specifically the signal due to desorption from tubing and EESI walls) needs to be better considered and characterized for sticky or semivolatile compounds (which are a focus of the manuscript). Failure to do so could lead to substantial measurement biases for such compounds. I think this will require major revisions, and perhaps an adjustment to the inlet configuration or sampling method. Once the backgrounds are properly considered, the Dual-EESI will certainly be a valuable inlet and would be appropriate for publication in AMT.

Main comments:

Line 92 and Fig. S5: This figure is used to draw the conclusion that there is essentially no difference in gas-wall interactions across the four tubing types. However, I do not think this experiment was a great way of testing that, because it did not isolate the tubing response. Instead, the measurements are combining the responses resulting from the UV lamps warming up (in the two left hand panels), the residence time distribution of the two flow tubes (especially smearing the decay in the right hand panels), and any wall interactions in the inlet/IMR of the acetate CIMS being used to sample the compounds.

Please address the following related to this comment:

-The wall interactions in the acetate CIMS could be negligible if sampling with the Eisele-type IMR at atmospheric pressure, but could be considerable if sampling in a low pressure IMR; please specify.

-I think what Fig. S5 (especially when turning UV off) does suggest is that these two particular compounds are reaching equilibrium with the wall surfaces of all tubing types on a time scale that is less than the 2-3 min decay time needed to flush out the flow tubes. So while you can't say whether there are differences between tubing types, this essentially shows that the tubing type does not matter for these two compounds when sampling this flow tube setup because the dominant wall effects are elsewhere (and obscured by the lamp warming up or the flow tubes flushing out). My guess is that the tubing wall effects are not dominant because 1) the residence time in that tubing is short, minimizing the adsorption or absorption to the wall relative the compounds that get sampled without first interacting with a wall, and 2) any compounds that desorb from the wall get diluted in the fast (2-10 liter per minute) flow, so concentrations remain relatively low. For comparison, the flow rates used in e.g. Deming et al 2019 and Pagonis et al 2017 were much slower (often 0.3 liters per min) through a meter or more of tubing, leading to much larger wall effects. I suggest you discuss these details in your manuscript in the paragraph at line 89, otherwise please explain if you have a different interpretation. Also, Palm et al. 2019 (<https://doi.org/10.5194/amt-12-5829-2019>) is another resource that may be helpful for thinking about tubing/inlet wall effects along with the Deming, Pagonis, and Liu papers.

-Lastly, this analysis applies only to the two compounds shown in Fig. S5. It's not clear whether those compounds are particularly 'sticky' or not. Could there be 'stickier' compounds that would interact more with the walls, and then show important differences as a function of tubing type? I'm not asking for a full analysis across a range of C^* values, but perhaps you could just state what the estimated C^* values are for the two compounds you show? That could help put your measurements in context with the broader measurements in the Pagonis, Deming, Liu, Palm papers.

Line 177: There are a few issues with this discussion of the camphor background percentage here. First, the 1.2-1.5% camphor signal measured at the end of the combined FP-PP-FP cycle is not the appropriate gas phase background to subtract from the amount of camphor sampled at the end of each TP mode. Again, I will suggest that you consider the framework presented in Palm et al. 2019 (<https://doi.org/10.5194/amt-12-5829-2019>). The total signal at the end of TP is the sum of the signal from compounds that are sampled directly without wall interaction plus the amount of background signal from compounds that had interacted with a surface (which depends on how much and how long a compound was sampled) and then desorbed to be sampled. That background signal is dynamic and depends on the sampling history. A more appropriate gas phase background to subtract would be that measured immediately after switching from TP to FP (after the residence time of the tubing has cleared). The concentration measured at that time will be a close approximation of the amount of background signal generated at the end of TP. For camphor in Fig. 2, it looks like the background signal could be ~10% or more of the total signal. For stickier compounds, this value could be even higher, for example it looks like ~30% of the signal for C₉H₁₂O₈ in

Fig. S18. By waiting to the end of the FP-PP-FP cycle, the background signal decays due to desorption from tubing and EESI wall surfaces while sampling clean (scrubbed) air, and is no longer relevant to the end of the prior TP. However, even the background measured shortly after switching from TP to FP is not completely accurate, because you are simultaneously changing the sources of background by switching the tubing the air is sampled through. During TP, the background can come from both the blue tubing and the EESI inner surfaces (including tubing between the blue tubing and the EESI). But when sampling FP, you cut out the background coming from the blue tubing and only sample that from the EESI (assuming the background from the walls downstream of the carbon denuder is negligible). Now, if the background coming from the blue tubing is negligible compared to the background coming from inside the EESI, then this doesn't matter and your background measurements will be close enough. But if the blue tubing is a substantial source of signal, this could be a major problem for sampling some sticky or semivolatile gases through this inlet. This could be tested by sampling a sticky compound and then injecting clean air for several seconds either upstream or downstream of the blue tubing to see if there is a difference (which would be due to background signal in the blue tubing). To summarize this lengthy comment, please carefully consider (and be explicit about) your background determination and subtraction methods, determine if the current inlet configuration and sampling method is sufficient, and make adjustments if necessary to reduce/remove these biases.

Line 326: I believe this Dual-EESI inlet will be very valuable for being able to sample gases and particles at the same time. It's not clear to me, though, that it will be as useful for deducing SVOC volatilities. I believe that to be an extremely difficult task for any instrument or combination of instruments, just given measurement uncertainties for both gas and particle measurements. This may be too much to ask for this paper, but I'm wondering if you could provide an estimate of how large the error bars will be on a calculation of the C^* value for a given compound? E.g. you could make assumptions about the relative sensitivities and measurement uncertainties for a compound in the gas vs. particle phase, and propagate the measurement uncertainties through to estimate the uncertainty on partitioning fraction or C^* . My guess is the uncertainties in C^* will be an order of magnitude or so, and will only be able to be estimated for the 2-3 or so order of magnitude range where semivolatile compounds are measurable in both phases above detection limit simultaneously. In the end, maybe it is enough to be able to say whether or not a compound is semivolatile. Any thoughts you have about the utility of the Dual-EESI in this respect would be useful to add to the manuscript, though again this is not to take away from the other very useful aspects of the Dual-EESI.

Line 317: The correlation of $R^2 = 0.115$ in Fig. S25 is quite low, so it does not seem to justify your conclusion here that higher gas relative to particle phase detection is correlated with diffusivity in air. Perhaps the estimation of diffusivity based on molecular formula (without knowledge of structure) leads to uncertainties that are too high in the diffusivity estimation? Anyway I would suggest it would be fine to leave Fig. S25 out.

Technical comments:

Fig. 1: The legend is difficult to understand. I would suggest labeling the valves and identifying which ones are open or closed for each sampling method, rather than which

sampling lines are open or closed. For instance one of the valves on the green line has to be closed during particle filter mode. Also particle filter mode is labeled as background in the legend, please make them the same to be consistent.

Fig. S6: This figure didn't copy correctly.

Line 161: Here also, be consistent with the labeling of each mode, i.e., use TP, PP, and FP instead of gas a particle, particle, and background measurement.

Line 168: Isn't EESI not expected to happen in the FP mode, when the particles have been filtered out prior to sampling?

Line 277: missing ")" at the end of "(right panel of Figure 5".

Fig. S12: The inlet should be labeled "Dual-Phase-EESI-Inlet" instead of ESI.