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Comment on amt-2021-325

Anonymous Referee #1

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-RC2>, 2021

Review of Lee et al. Dual EESI

This manuscript presents a novel mass spectrometric technique for studying gas- and particle-phase organic compounds with a single electrospray (ESI) ion source. The instrument operates by alternately sampling from three distinct channels: a direct inlet, an inlet where gas-phase compounds are denuded, and an inlet where particles are filtered and gas-phase compounds are denuded. These three channels allow the authors to separate ESI background, from gas- and particle-phase signal by difference.

The technique works, is useful for studying the atmosphere, and is appropriate for AMT. My suggested revisions are below.

My main criticism is that this is a SESI + EESI instrument, and not a dual-EESI. These acronyms each correspond to distinct ionization pathways, and each have extensive literature describing the factors that affect their sensitivity. I think the authors will be best served by connecting their technique with the existing literature by calling this "dual ESI", "S/EESI", or anything that conveys that the method aims to separate EESI signal from SESI signal.

The novelty of this work is that the authors are bringing together two established techniques (SESI+EESI) in a single ion source. There are already SESI techniques for studying organic gases in the atmosphere that go beyond "technically possible", and the authors cite one example (Zhao et al 2017). That work already demonstrated linear SESI response for organics in the atmosphere, and even characterized the strong humidity dependence of SESI sensitivity.

Overall, I feel that there are significant details missing from this paper, covered in the additional comments below. The most critical area in need of discussion is the slow response time of the instrument to the gas-phase analytes, and how this response time affects the background subtraction. The authors largely avoid addressing this by sticking to raw time series instead of showing background-subtracted data, and since the background subtraction is central to the technique more detail is needed.

70: What was the ESI working solution? Looks like AcN:Water and NaI dopant, and I'm guessing the solvent ratio is 1:1, but this needs to be added to methods

158: $[M+H]^+$ ions for PTR-MS

169: EESI only occurs if there are soluble particles present to be intercepted by the ESI drops. So in the FP channel, only ESI is occurring, since there are no gas- or particle phase analytes. In the PP channel signal is due to both ESI and EESI. In the TP channel signal is ESI + EESI + SESI

178: The FP measurements surrounding the TP measurement are very uneven, due to the slow response time of the camphor gas. The subtraction of FP from TP is critical for determining gas-phase signal later in the paper, and so the authors must discuss how they defined average FP signal for slow-responding gases.

Fig 3: Should y-axis read "Relative Signal" instead of "Relative Gas Concentration"?

Fig 3: There is clear and consistent structure to the residuals of gas-phase (SESI) sensitivity, and the authors must address this. I do not agree that this is a linear response for gas-phase analytes.

Fig 6: I am unable to follow the significance of including the deprotonation ionization pathway from the nitrate CIMS. Are these data points all from a single experiment? Or did the authors run separate experiments with difference conditions in the Nitrate CIMS IMR? If it's all one experiment, then some acids are being detected as both $[M+NO_3]^-$ and $[M-H]^-$ by the nitrate CIMS (e.g. $C_9H_{12}O_5$, $C_9H_{14}O_5$, and $C_9H_{16}O_5$). Those two nitrate CIMS peaks would correspond to a single SESI peak $[M+Na]^+$; so the authors should be summing the two nitrate CIMS signals in order to plot against the SESI signal, and not plotting the nitrate CIMS ionization mechanisms separately. There is no discussion in the text to help the reader understand the significance of the two ionization schemes, and the authors must add clarification.

302: There is no discussion of how the saturation concentration for Figure 7 is calculated.

Is it based on the attributed molecular formula? What conclusion am I supposed to draw from the C* trend?

Figure 7: are those actually arbitrary units? Or is that signal? The authors confidently discuss signal ratios, so I think this is signal, but that's not clear.

Figure S6 did not render legibly in my pdf