

## ***Interactive comment on “An Extractive Electro spray Ionization Time-of-Flight Mass Spectrometer (EESI-TOF) for online measurement of atmospheric aerosol particles” by Felipe D. Lopez-Hilfiker et al.***

**Anonymous Referee #1**

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In their manuscript, Lopez-Hilfiker et al. present the development and characterization of an extractive ESI interface coupled to a TOF-MS. In contrast to previous EESI-MS developments, they demonstrate their setup to have suitable performance, especially regarding detection limits, to allow for real world applications and some proof-of-concept results from deployments at a smog chamber, an aircraft and ambient ground-based measurements are included in the paper as well. There is most certainly a need for better online characterization of particle chemical composition and the described EESI-TOF is a commendable step forward. The paper is generally well written, the

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instrument characterization was done in a comprehensive and mostly convincing fashion and the proof-of-concept results provide interesting first insights. I recommend the paper for publication after addressing the following issues.

- The term “near-molecular level” is used a few times. I assume this refers to MS measuring masses only instead of really individual compounds, but the term should be explained in the paper. A word of caution regarding quantitative results from mass measurements vs. fully resolved (chromatography) measurements might be justified as well.
- P7L7-8: What was the flow rate?
- P5L9-10: What does “most species” mean? Which species are not removed and could this pose a problem? Related, could 0.x % denuder breakthrough distort results for volatile species with high gas-phase and very low particle phase concentrations?
- P9-10: I appreciate the discussion on pros and cons of different ESI mixtures, but was a bit surprised to read that MeOH/H<sub>2</sub>O was used at the end for most studies. My impression from the discussion was that overall ACN/H<sub>2</sub>O might more suitable, especially due to the stated high background peaks in MeOH/H<sub>2</sub>O. Please comment on this final choice.
- P13L1-6: Is the usage of mass flux for some and ion flux for most other results really justified? It adds some complexity and the advantage of using mass flux in ag/s is not fully clear to me.
- P14L30 + abstract +conclusions: I find the statement of the “much smaller range” the RRF<sub>x</sub> spans for SOA as compared to pure components a bit misleading. Given it represents a mean value for a very complex mixture, it is not surprising it varies less than individual compounds. Even more, with Benzene included (its exclusion seems quite arbitrary), the difference to the studied pure model compounds becomes smaller.
- P17L3-4 + abstract +conclusions: The conclusion on the absence of matrix effects

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seems to be based on dipentaerythritol experiments only. The insensitivity of this single compound to the specific particle matrix studied cannot, however, be generalized. From conventional ESI it is well known that some species are more susceptible to matrix effects than others. In addition, the organic matrix in these experiments is certainly not representative to the full range of real world particle matrices (both organic and inorganic). I would recommend more caution here. A general absence of any particle matrix effects can only be demonstrated by detailed comparisons with GC/LC-MS based quantification.

- P18L2-5: Can you comment on possible mechanisms of water vapor interference?

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