Atmospheric Measurement Techniques Discussions

Atmos. Meas. Tech. Discuss., referee comment RC1
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Comment on amt-2021-125

Anonymous Referee #1

Referee comment on "Constraining the response factors of an extractive electrospray ionization mass spectrometer for near-molecular aerosol speciation" by Dongyu S. Wang et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-125-RC1, 2021

This manuscript describes an effort to estimate the sensitivity of an extractive electrospray ionization TOF-MS to multifunctional organic compounds produced from the oxidation of 1,3,5-trimethylbenzene, d-limonene and o-cresol. The authors use the semi-quantitative response of a Vocus-PTR instrument to the same compounds (or molecular formulas) measured in the gas phase to estimate the sensitivity of the EESI-ToF-MS to those molecular formulas in the particle phase. The authors find a very wide range in EESI response factors, largely driven by molecular size/volume and degree of oxidation or functionalization. Further, comparison of summed EESI signals with total organic content from an aerosol mass spectrometer indicates promise for bulk quantification.
This is an interesting analysis that I believe should be published in AMT, given that the following comments and suggestions can be adequately addressed.

Major Comments:

(1) As the authors state in their abstract, these results demonstrate that some level of quantification with the EESI-ToF-MS is possible without standards; however, this analysis includes a series of logical leaps that lead to significant uncertainty in resulting EESI response factors. The authors state that the Vocus-PTR -based EESI response factors range from 10^3 to 10^6 ions/s/ppb, with an geometric mean of 10^4.5 ions/s/ppb. For a given EESI RF for a specific compound, what is the associated uncertainty? (e.g., determined by propagating the uncertainty in calculated k_MH applied to Vocus data, described in L125-127 to become "more uncertain" as parameterizations are applied to more oxygenated species, through to the resultant EESI response factor). Related to this, how are the error bars in Figure 3a generated?

(2) Estimation of EESI response factors for specific molecular formulas in this work hinges

on quantification of Vocus signals using k_MH calculated according to Sekimoto et al., 2017 (in addition to assumptions about gas-particle partitioning). Under the fIMR conditions given in L 135-136 (i.e., 59 Td), is Vocus sensitivity linear with k_MH for compounds that can be calibrated? At 59 Td, water clusters should dominate the reagent ion distribution over H3O+, potentially producing a regime where sensitivity is not linear with k_MH. The authors should show that their sensitivity is linear with k_MH (as an SI figure), thus demonstrating that they can apply k_MH for these unknown compounds. If the Vocus sensitivity is not linear with k_MH under these conditions, the authors should demonstrate how this impacts their use of Vocus signals to constrain EESI response.

(3) A statement prominent in the conclusions section is that the EESI-ToF-MS responds quantitatively to organic aerosol concentrations even with significant inorganic aerosol present. This seems a rather important conclusion of this paper, but the exact origin of this conclusion is somewhat unclear. Please make explcit whether this conclusions arises directly from the linear relationship between summed EESI signals and AMS OA, or some other specific result.

(4) This manuscript contains a large number of symbols and acronyms. A glossary of terms might be useful as an appendix to this paper so the reader can reference it easily.

Specific Comments:

L21: Inorganic coating or inorganic seed particles?

L48: The authors may also wish to cite https://pubs.acs.org/doi/10.1021/acsearthspacechem.9b00312 in this context

L70: What additional differences can be contributed by "operators" beyond the instrument parameters already listed?

L85-101: Please state clearly whether the seed aerosol was polydisperse or monodisperse

L180-185 (an in conclusions): Can these different factors contributing to EESI RF_x be separated? Some discussion on how these could be separated, if at all, would be useful here.

L39-391: Both larger molecules/higher molar volume and higher solubility in water are somewhat opposing features. Is it clear from this analysis which features are dominant?

L481: "law of averages" -- please be more specific