

Response to Reviewer #1

We thank the reviewer for the helpful comments, which have helped improve the manuscript. Below we provide a point-by-point response to the issues raised by the reviewer. Reviewer comments are provided in *italics*, our responses follow in normal text, and modifications to the manuscript are denoted in blue.

Comment #1:

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.

Response:

As the reviewer surmises, we use the term “near-molecular level” to indicate that the EESI-TOF can provide a molecular formula but no direct structural information or isomeric separation. We have clarified this term “near-molecular level” in two places:

Abstract: “To address this gap, we present a novel, field-deployable extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF), which provides online, near-molecular (i.e., molecular formula) OA measurements at atmospherically relevant concentrations without analyte fragmentation or decomposition.”

Section 2.1: “The EESI source was developed with the specific goal to measure OA at a near-molecular level (with “near-molecular” here defined as the determination of a molecular formula, without direct structural information or isomeric separation), however it can more generally be applied to gas or combined gas/particle measurements.”

We also agree with the reviewer’s second point, namely that the possibility of isomers can complicate quantification in experimental or field measurements even if the relevant standards are available. This issue was also raised by Reviewer #2 (Comment #17). We have added the following text to section 3.2, where quantification of EESI-TOF data is considered.

“Further, for aerosol of unknown composition the possibility of multiple isomers (potentially having significantly different RRF_x) must be considered.”

Comment #2:

P7L7-8: What was the flow rate?

Response:

The flow rate is between 0.7 and 1.0 L min⁻¹, depending on the temperature of the inlet capillary. This information has been added to the manuscript.

Comment #3:

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?

Response:

Questions related to denuder performance were also raised by Reviewer #2 (Comment #8), and our response is duplicated here.

We agree with the reviewer that denuder breakthrough is problematic, as it can result in either increased detection limits or spurious particle signal. These issues were noted in the original manuscript in section 2.1 as motivation for installing the denuder and we leave the original text unchanged except that we now note that these problems can arise not only from the absence of a denuder but also from breakthrough.

We have not conducted a comprehensive, compound-by-compound assessment of the denuder. The term “most species” was instead meant to indicate that for the systems discussed in this manuscript (i.e., pure components, laboratory-generated SOA, and initial ambient measurements in Switzerland), breakthrough has not been observed. More recently, we have experienced some breakthrough issues in heavily polluted ambient locations. Characterization of these effects is ongoing and preliminary results suggest this problem can be solved without degrading performance simply by utilizing a larger denuder.

We now discuss this in section 2.1 as follows: “The denuder is very similar to that used for the CHARON-PTRMS, where it removes methanol, acetonitrile, acetaldehyde, acetone, isoprene, methylethylketone, benzene, toluene, xylene, 1,3,5-trimethylbenzene, and α -pinene with >99.9999% efficiency (Eichler et al., 2015). Our experiments show >99.95% removal for pinonic acid, and no detectable breakthrough in the chamber and field experiments presented in section 4, which were conducted at OA concentrations up to approximately $10 \mu\text{g m}^{-3}$ with the denuder not requiring regeneration for at least 2 weeks. For smog chamber experiments on wood and coal-burning emissions at higher concentrations (20 to $200 \mu\text{g m}^{-3}$, 1 experiment of 3-4 h per day) (Bertrand et al., submitted), the denuder was regenerated every 2 to 3 days, when a slower response time was observed on switching between the direct sampling and filter blank measurements. This suggests a higher capacity denuder should be used for continuous sampling under polluted conditions.”

Comment #4:

P9-10: I appreciate the discussion on pros and cons of different ESI mixtures, but was a bit surprised to read that MeOH/H₂O was used at the end for most studies. My impression from the discussion was that overall ACN/H₂O might be more suitable, especially due to the stated high background peaks in MeOH/H₂O. Please comment on this final choice.

Response:

The main consideration is that operationally the MeOH/H₂O spray is easier to stabilize and so was chosen for both the initial characterization experiments presented here and early measurement campaigns (Pospisilova, Stefenelli). With improved machining of the EESI

source and increased user experience, the ACN/H₂O mixture has become our preferred working solution for most applications (e.g., Qi) because of its lower background, as correctly identified by the reviewer. As a consequence, the set of characterization experiments performed for the MeOH/H₂O system is presently more comprehensive than that of the ACN/H₂O system, and we therefore choose to focus on MeOH/H₂O results here while noting their comparability to ACN/H₂O, rather than the reverse.

Comment #5:

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.

Response:

This issue was also raised by Reviewer #2 (Comment #2), and our response is repeated here.

Most studies describe particle-phase composition in terms of mass. Therefore, when discussing total EESI-TOF signal or relative composition, we utilize the mass flux metric. This is the quantity most closely related to mass that we can obtain given the unknown RRF_x .

However, a large part of this paper also focuses on the fundamental operation of the EESI-TOF. Here it is desirable to present results in terms of the actual quantity measured (i.e., ion flux), which in our view makes instrument operation/response most transparent. For example, although ionization efficiency and related concepts (Eq. 1 and related discussion), as well as the RRF_x , can be in principle discussed in terms of mass, these concepts and the obtained values are most clear when presented in terms of the probabilistic behavior of individual ions and molecules.

We have clarified this in the manuscript as follows (section 3.1):

“Fundamentally, the EESI-TOF measurement is in terms of the ion flux reaching the detector (Hz), as shown on the left axis of Fig. 2. However, in most studies the particle phase is described in terms of mass for both absolute and relative concentrations, making it desirable to also obtain a mass-related metric from the EESI-TOF measurements. In principle, the EESI-TOF ion signal for a molecule x can be converted to a mass concentration according to Eq. (1):”

“For reference, we show on the right axis of Fig. 3 the MF_x (in attograms (10^{-18} g) per second, $ag\ s^{-1}$) corresponding to the measured I_x ; however for the remainder of the basic characterization experiments presented herein we show instead the directly measured I_x , which is the actual quantity measured by the instrument.”

Comment #6:

P14L30 + abstract + conclusions: I find the statement of the “much smaller range” the RRF_x 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.

Response:

This issue was also raised by Reviewer #1 (Comment #6) and our response is duplicated here.

In the original manuscript, benzene was classified empirically as an outlier because its removal has a considerably larger effect on the range of SOA RRFs (60 % decrease) than does removal of either the highest RRF (1,3,5-trimethylbenzene, 40 % decrease) or the next lowest (phenol, 30 %). However, the low RRF observed for benzene is consistent with the overall observed trend, and we therefore agree it can be misleading to treat it separately. The revised text simply notes that the range of RRFs observed for SOA is lower than that for the pure compounds, while noting that the pure compounds must occupy a larger range than indicated because the RRF for benzene SOA is a factor of 3 lower than any of the pure components. As noted by Reviewer #1, this decreased RRF range for SOA is expected given that it represents the mean RRF of a complex mixture.

The revised text is as follows. “The RRF_x observed for the SOAs span a much smaller range than do the pure components, i.e. a factor 15 between benzene and 1,3,5-trimethylbenzene compared to a factor of ~30 between citric acid and dipentaerythritol (note that the range of RRF_x for pure components is an underestimate, as some pure components must have an RRF at least as low as benzene, which is itself a factor of 3 lower than citric acid). The smaller RRF_x range exhibited by the SOA experiments is expected given that each value represents the mean RRF of a complex mixture and is consistent with ambient observations, where we do not observe major composition-dependent variations in overall EESI-TOF sensitivity to bulk ambient OA (Qi et al., 2019; Stefenelli et al., 2019). However, direct calibration is clearly advisable for compounds for which absolute quantification is desired. Further, for aerosol of unknown composition the possibility of multiple isomers (potentially having significantly different RRF_x) must be considered.”

The corresponding text in the abstract and conclusions has also been modified.

Abstract: “Although the relative sensitivities to a variety of commercially available organic standards vary by more than a factor of 30, the bulk sensitivity to SOA generated from individual precursor gases varies by only a factor of 15.”

Conclusions: “The EESI-TOF sensitivity to SOA generated from a set of individual precursor gases varies within a factor of 15.”

Comment #7:

P17L3-4 + abstract + conclusions: The conclusion on the absence of matrix effects 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.

Response:

We agree that the presence and extent of matrix effects may depend on the identity of the test compound and/or the surrounding matrix. A single case study (dipentaerythritol in SOA α -pinene ozonolysis) is presented in this manuscript; investigation of a large number of systems is beyond the scope of the current work. However, we have also compared the total EESI-TOF OA signal to the detectable fraction of AMS OA (i.e., SOA and oxygenated POA) for ambient aerosol (Qi et al., 2019; Stefenelli et al., 2019), as well as laboratory-generated aerosol that is internally mixed with $(\text{NH}_4)_2\text{SO}_4$ and/or NH_4NO_3 . In general, good agreement was observed and discrepancies were explainable by the expected differences in RRF_x . Although encouraging, this does not altogether rule out matrix effects for individual OA ions. However, it does indicate that bulk OA sensitivity is likely unaffected by a soluble inorganic matrix.

The following text has been added to section 3.3:

“Although these results are obtained from a single test system, they are consistent with the general trend of matrix effects in EESI studies that are negligible or strongly suppressed relative to conventional electrospray measurements (Chen et al., 2006; Gu et al., 2007; Zhou et al., 2007; Chen et al., 2009). In addition, we find that OA signals measured by the EESI-TOF are well correlated with AMS measurements (e.g. total measurable OA, source apportionment factors, tracer ions) (Qi et al., 2019; Stefenelli et al., 2019). This suggests that EESI-TOF bulk OA measurements are likely not affected by soluble inorganic matrices typical of Central Europe (i.e., internal mixtures with NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ concentrations up to $\sim 10 \mu\text{g m}^{-3}$), although effects on individual ions cannot be ruled out.”

We have also qualified statements in the abstract and conclusions, as follows:

Abstract: “In contrast to conventional electrospray systems, the EESI-TOF response is not significantly affected by a changing OA matrix for the systems investigated.”

Conclusions: “We observe an instrument response that is linear with mass and without a detectable dependence on the composition of the OA matrix for a dipentaerythritol/ α -pinene SOA test system. Ambient measurements also suggest that bulk OA detection is not significantly affected by a changing matrix of soluble inorganic compounds.”

Comment #8:

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

Response:

The following text has been added to section 3.4: “Water can potentially decrease sensitivity by competing with the analyte for Na^+ ions (e.g. by displacing the analyte), or increase sensitivity by absorbing energy from Na^+ -adducts, thereby stabilizing them.”

References

Bertrand, A., Yuan, B., Stefenelli, G., Qi, L., Pospisilova, V., Tong, Y., Sepideh, E., Huang, R.-J., El Haddad, I., Slowik, J. G., and Prevot, A. S. H.: Characterization of fresh and aged solid fuel combustion organic aerosol by extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF), *Environ. Sci. Technol.*, submitted.

Chen, H., Venter, A., and Cooks, R. G.: Extractive electrospray ionization for direct analysis of undiluted urine, milk and other complex mixtures without sample preparation, *Chem. Commun.*, 19, 2042-2044, 10.1039/b602614a, 2006.

Chen, H., Gamez, G., and Zenobi, R.: What can we learn from ambient ionization techniques?, *J. Am. Soc. Mass Spec.*, 20, 1947-1963, 2009.

Eichler, P., Müller, M., D'Anna, B., and Wisthaler, A.: A novel inlet system for online chemical analysis of semi-volatile submicron particulate matter, *Atmos. Meas. Tech.*, 8, 1353-1360, 10.5194/amt-8-1353-2015, 2015.

Gu, H. W., Chen, H. W., Pan, Z. Z., Jackson, A. U., Talaty, N., Xi, B. W., Kissinger, C., Duda, C., Mann, D., Raftery, D., and Cooks, R. G.: Monitoring diet effects via biofluids and their implications for metabolomics studies, *Anal. Chem.*, 79, 89-97, 10.1021/ac060946c, 2007.

Qi, L., Chen, M.-D., Stefenelli, G., Pospisilova, V., Tong, Y.-D., Bertrand, A., Hueglin, C., Rigler, M., Ge, X.-L., Baltensperger, U., Prévôt, A. S. H., and Slowik, J. G.: Real-time source quantification of wintertime secondary organic aerosol in Zurich using an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF), *Atmos. Chem. Phys.*, 19, 8037-8062, 10.5194/acp-19-8037-2019, 2019.

Stefenelli, G., Lopez-Hilfiker, F. D., Pospisilova, V., Vogel, A., Hüglin, C., Baltensperger, U., Prévôt, A. S. H., and Slowik, J. G.: Source apportionment of ambient organic aerosol by online extractive electrospray ionization time-of-flight mass spectrometry (EESI-TOF), *Atmos. Chem. Phys. Discuss.*, 10.5194/acp-2019-361, 2019.

Zhou, Z. Q., Jin, M., Ding, J. H., Zhou, Y. M., Zheng, J., and Chen, H. W.: Rapid detection of atrazine and its metabolite in raw urine by extractive electrospray ionization mass spectrometry, *Metabolomics*, 3, 101-104, 10.1007/s11306-006-0050-2, 2007.