

Responses to Reviewer #2 – “Online molecular characterisation of organic aerosols in an atmospheric chamber using Extractive Electrospray Ionisation Mass Spectrometry” by P.J. Gallimore et al.

Reviewer comments are in blue text, author responses are in black text.

This manuscript (acp-2017-656) reports the application of extractive electrospray ionisation mass spectrometry (EESI-MS) to the analysis of chamber aerosol produced by reaction of the monoterpene α -pinene with O₃. Gas phase reactants and products were monitored with proton transfer reaction mass spectrometry (PTR-MS), whereas particle phase products were monitored with EESI-MS with time resolution on the order of 7 min. The time dependence of the MS signals for α -pinene (by PTR-MS) and pinonic acid, pinic acid, and OH-pinonic acid (by EESI-MS) correlated well with predictions from the Master Chemical Mechanism (MCM). The signal intensity of reaction products correlated approximately linearly in log-log space with MCM predictions. Additionally, EESI-MS of test particles containing tartaric acid and ammonium sulfate in known relative molar ratios resulted in a linear signal with increasing mass concentration across all organic-inorganic molar ratios down to 1:1.

This manuscript is well written and the experiments appear to be carefully performed. The figures are well constructed and easy to interpret. This manuscript is within the scope of Atmospheric Chemistry and Physics and will be suitable for publication once the comments below are satisfactorily addressed.

We thank the reviewer for the positive appraisal of the manuscript and respond to the comments below.

Comments:

1. One area where this manuscript could be significantly strengthened is in clarifying how much of the EESI-MS signal may arise from gas phase molecules. The chamber contains both organic particles and semivolatile compounds that are going to be present in both the gas phase and the particle phase. It appears the authors use a charcoal denuder to remove the gas phase before sampling into the EESI-MS. However, the authors provide no figure or discussion that quantifies how much, if any, of the EESI-MS signal may arise from gas phase products. The authors should discuss this in the revised manuscript. Resolving whether signal arises from gas or particle could be easily tested by placing a filter to remove the particles before the EESI-MS inlet and monitoring the resulting signal. Note that even if the charcoal denuder removes much of the gas phase, it is possible that compounds that were in the particle phase may partition back to the gas phase during the residence time in the 10 L reservoir. This is an important point, as the authors are comparing their EESI-MS results, which are assumed to be entirely particle phase, to MCM predictions, which is a gas phase model.

We agree that this is an insightful additional test and followed the reviewer's suggestion of performing additional experiments using a filter. The manuscript has been modified in the following places:

Page 7, lines 15-17: “An optional High Efficiency Particle Air (HEPA) filter (HEPA CAP, Whatman) was used to test the possible contribution of gas phase species to the observed MS signal.”

Page 19 line 24-page 20 line 15: “The semi-volatile nature of SOA means that both gas- and particle-phase species will be present in the chamber. We examined whether gas-phase species contribute to our observed EESI(-)-MS signal under the “medium” reaction conditions by removing particles from the sample flow using a HEPA filter (Figure 1). With particles filtered out, none of the species listed in Table 2 could be detected above levels observed for the solvent blanks. This was also the case even if the charcoal denuder in Figure 1, intended to remove gas-phase species, was bypassed.

The aerosol mass loading in the chamber ($\sim 300 \mu\text{g m}^{-3}$) would strongly bias most of the compounds in Table 2 towards the particle phase. For instance, the most abundant ion, pinic acid, has a vapour pressure $\sim 2 \mu\text{g m}^{-3}$ at 294 K (Bilde and Pandis, 2001), so $> 99\%$ would be expected to reside in the particle phase based on an absorptive partitioning argument (Pankow, 1994). This might explain the lack of detected species in the present SOA system. However, a number of studies have detected gas-phase species using an electrospray source, e.g. (Horan et al., 2012; Wu et al., 2000; Zhao et al., 2017). The ion source design and operating parameters appear important in determining the ionisation efficiency and mechanism (uptake into droplets or gas-phase chemical ionisation). Future work to simultaneously detect semi-volatile species in both phases, and understand the relative efficiencies of gas- and particle-phase ionisation, is therefore merited.”

Abstract (page 1, lines 19-20): “Under our experimental conditions, EESI-MS signals arise only from particle-phase analytes.”

Conclusions (page 26, line 25-27): “Our limited tests with this EESI-MS configuration show that the signal arising is a result of droplet-particle collisions, with negligible contribution from gas-phase analytes.”

2. When the authors examine relative quantification in the mixed organic-inorganic system, they observe that down to a 1:1 organic:inorganic mole fraction the MS signal intensity scales linearly with organic aerosol mass concentration (Fig. 2). The authors also suggest (page 10, line 20) that suppression of signal may be occurring, but that it is small. It is unclear why the authors did not continue this experiment to higher inorganic aerosol (lower organic aerosol) mole fractions to confirm this suggestion. More discussion is required on this point.

We have added the following discussion to emphasise the purpose of Figure 2 (page 10, lines 21-23): “Specifically, we establish the potential impact of inorganic seed particles on the relative quantification of organic acids (detected as $[\text{M-H}]^-$) in the chamber experiments which follow.” $5 \mu\text{g m}^{-3}$ ammonium sulfate seed particles were added to the chamber, and this corresponded to small fractions of the aerosol mass during MS analysis. These conditions are covered by Figure 2.

We agree that considering a wider parameter space (including particle composition) in future is desirable to extend the applicability, and understand potential limitations of, the EESI-MS technique.

3. The authors should include in the revised manuscript the values for the low mass cut-offs on their mass analysers. As illustrated in Fig. S4 and visualised in Fig. 3, the EESI-MS and PTR-MS spectra appear very different. However, it is not entirely clear if this is due wholly to the different compositions in the gas and particle phase or due to the mass ranges that can be studied with each instrument. The PTR-MS spectrum contains a large number of ions below 100 m/z whereas the EESI-MS spectra do not, but it is not clear in the discussion whether the Orbitrap would necessarily be able to analyse effectively below 100 m/z .

The mass ranges for the mass analysers are already stated in the methods section (page 8, line 12: m/z 100-500 for EESI-MS; page 9 line 9: m/z 10-500 for PTR-MS). We have added the following emphasis in the discussion (page 12, lines 14-15): “The low mass thresholds of the EESI-MS and PTR-MS mass analysers were m/z 100 and 10 respectively in this study.”

References

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