

# ***Interactive comment on “Online molecular characterisation of organic aerosols in an atmospheric chamber using Extractive Electrospray Ionisation Mass Spectrometry” by Peter J. Gallimore et al.***

**Anonymous Referee #2**

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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  $\alpha$ -pinene with O<sub>3</sub>. 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  $\alpha$ -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

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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.

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.
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

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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.

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.

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