

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 #1

Received and published: 14 August 2017

This is an interesting manuscript describing the efficacy of extractive electrospray ionization mass spectrometry (EESI-MS) as an online measurement technique for atmospheric chamber studies. They have used multiple online (EESI-MS and PTR-MS) and offline (ESI-MS) techniques to study the oxidation of α -pinene in the CASC chamber. They have shown that EESI-MS can be used to study SOA formed during chamber studies in almost real time (7-minute time resolution). The fact that EESI-MS is a soft ionization technique, it makes it more advantageous over the regular offline ESI-MS studies for chamber studies. They also compared MCM model results to EESI-MS

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and PTR-MS results, which showed very good correlations; it shows the potential of EESI-MS as an online measurement tool for chamber studies.

General Comments - Introduction lacks the details of other online measurement techniques (like AMS, and DART-MS) used for α -pinene oxidation products, their findings and its comparison to EESI-MS.

- More details about MCM model should be given in the SI in terms of reactions involved in the mechanism. So other laboratory trying to duplicate the work can do so easily.

- All the figures on Oxidation states of carbon against carbon number must include legends what size of the marker represents what intensity. They also should add the correct marker sizes in the inset of each figure, and if that is difficult, it should be included in SI then.

- EESI-MS studies of organic-inorganic particles: why was the study not performed on a compound that is more relevant to this study, for example, pinic acid?

- Although acids have higher sensitivity in negative ion mode, the inorganic salt has NH_4^+ ions in them, thus positive ion mode would show $[\text{M}+\text{H}]^+$ and $[\text{M}+\text{NH}_4]^+$ ions for tartaric acid. Assuming all other parameters constant, the ratio of $[\text{M}+\text{H}]^+$ to $[\text{M}+\text{NH}_4]^+$ should match the mole fraction of the tartaric acid and ammonium sulfate in the atomized solvent. This would be much better way of quantitation than just looking at the acid signal in negative ion mode. I would strongly suggest repeating this particular experiment in positive ion mode.

Specific comment: Page 1, line 30 Low visibility can also be added as an impact.

Page 2 Line 13, The line is talking about soft-ionization in general, however, the reference (Zahardis et al) is not appropriate here. The reference does talk about soft ionization techniques, but the paper is a review of soft ionization techniques for AMS instrument specifically. AMS is mostly used for online studies and not off line measurements. Since the sentence for this reference is used for very generic off-line soft

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ionization MS techniques, the reference is not valid here.

Page 2 Line 17 Once again the paragraph is talking about general ESI-MS utility in atmospheric studies. The time resolution for ESI-MS is not hours, not for all kind of studies. However, it will be hours for chamber studies, if authors are refereeing to retention times of hours with respect to chamber studies it should be specified.

Page 3 line 1 Gallimore reference should be 2017a Also, this particular reference is not published yet, thus the conclusion of this study cannot be used as the basis of claiming that EESI-MS can be used for relative quantitation.

Page 4 Line 22 Authors can probably use particle size distributions of Tartaric acid (TA) and Ammonium Sulfate particles to confirm that they are truly internally mixed. If these particles are not internally mixed they probably will show a bimodal distribution. It should be checked for all mole fractions studied, it is possible that higher concentration of ammonium sulfate will lead to a bimodal distribution.

Page 6 Line 10 Was the ESI solvent prepared 1:1 by volume or by weight. Solvent flow rate should also be provided.

Page 6 line 13-14 Authors just described ESI solvent and voltage details previous to these lines. Thus it is really ESI description, not an EESI-MS description. I would suggest adding line 16-19 that describes the particle flow rate to solvent spray before line 13-14.

Figure 1 Should show the position of three-way valve. Page 7 line 6-8 These lines are confusing. Do the authors mean the following? "Air was then pushed through the reservoir and into the EESI source at 1 L min⁻¹ and a sample spectrum was acquired." If yes, it should be corrected. If No, more clarification of the set-up is required. Page 7 line 23 Was formic acid added to the final extract before nano-ESI? If so, details should be added.

Page 7 line 25 Is 1.4kV potential difference correct? Because for EESI it is 3kV. Why

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the difference for the same solvent configuration.

Page 9 line 1 Reference and explanation should be provided for the rate constant assumption.

Page 9 line 18 References should be provided for which previous studies were used to identify the major aerosol composition.

Page 10 figure 1 Y axis should be adjusted to show the complete error bar of the first purple triangle marker at a mole fraction of 0.5. Why that particular point has so much error should be explained in the text as well.

Table 2 Once again why wasn't $[M+NH_4]^+$ seen in positive ion mode?

Page 13 line 1 The presence of $[M+H-H_2O]^+$ peak in Doezema et al studies can be explained in many ways, different instrument parameters for the two studies, different inlet, and mass analyzer voltages etc. Higher capillary Voltage used in that study could simply be due to the combination of solvent composition, solvent flow rate and capillary diameter required to get a good Taylor cone. Authors can only compare the capillary voltage if all other parameters are equal. Page 16 I would suggest moving figure S5 to the main text.

Page 16 line 14-16 If more oxidized species are present in the particle than it could possibly suggest that EESI-MS solvent is extracting some surface of the particle only rather than the entire particle as assumed in Gallimore et al 2013 and I am assuming for this study too. Many studies on oxidation of monoterpenes (Zhao et al 2016 ACP, 16, 3245; Davis et al 2015, Chem.Sci. 6, 7020; Zhao et al 2017, AMT, 10, 1373 ; Trostl et al Nature 2016, 533, 527–531) have suggested that low molecular weight compounds with high Oxidation state are present in the core of the particle and are responsible for new particle formation. Whereas, low molecular weight compounds with low Oxidation state are responsible for the growth of the particle and are usually present on the surface of the particle. Thus the lack of peaks at high m/z in EESI-MS (Figure S5)

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suggests that the solvent is extracting the surface of the particle only or at least not the entire particle. Collected particles on the filter analyzed by ESI-MS show many peaks at higher m/z , suggesting ESI is able to sample entire particle, which is expected. But, if the presence of peaks at higher m/z in ESI-MS is due to oligomers (eg $2M+H$ of pinonaldehyde) than it should be confirmed using MS/MS studies. Identifying the source of these higher m/z peaks in ESI-MS is important to identifying and understand EESI-MS extraction efficiency.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-656>, 2017.

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