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Atmospheric Measurement Techniques Discussions

Interactive comment on "Comparison of three aerosol chemical characterization techniques utilizing PTR-ToF-MS: A study on freshly formed and aged biogenic SOA" *by* Georgios I. Gkatzelis et al.

Anonymous Referee #1

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The paper compares organic aerosol composition measurements made by three different instruments at the SAPHIR chamber. The instruments are each based on proton-transfer-reaction time-of-flight mass spectrometry, but differ in the way that aerosol is sampled, evaporated and injected into the drift tube. The work is insightful and deserves to be published after consideration of the following major and detailed comments:

A. There is virtually no discussion of nitrogen-containing ions in the measurements. Did these only constitute a minor fraction of the total signal? In PTR-MS, nitrate species

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Discussion paper

commonly fragment into a nitric acid neutral and hydrocarbon ion. To what extent is that fragmentation channel responsible for some of the incomplete detection of mass shown in Figure 1? As an aside, it is difficult to appreciate how much of the data shown in the various graphs was taken under no-NOx conditions vs. conditions with NOx present.

B. The quoted detection limits differ by 5 orders of magnitude between the three instruments. To what extent can these differences be understood in terms of the sampled mass, dilution flows, sensitivities and time responses for the different PTR-TOF-MS systems used?

C. The paper describes the aerosol sampling used in the three instruments in great detail, which is appropriate. However, there is very little detail about the PTR-TOF-MS systems used. What were the types of instruments used, why is the mass resolution so different between the three systems (Table 2) and how did the primary ion signals and calibration factors compare between the three systems?

Detailed comments:

Line 34: “predominantly” instead of “predominately”

Line 37: “carbon-oxygen bond breakage” appears to be used here and throughout the text as synonymous with process that lower the O:C ratio. However, carbon-oxygen bonds are not necessarily broken in all fragmentation processes, so I would recommend the more general “fragmentation”.

Line 88: “low-volatility VOCs” instead of “low VOCs”?

Table 2: Please add the temperature and pressure of the drift tube reactors used in these experiments. Also useful would be more details on the specific TOF-MS systems used and how these translate into the primary ion signals and sensitivities (in raw and/or normalized counts per seconds) of the three systems.

Lines 165-168: Limits of detection vary by orders of magnitude between the three

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instruments. Part of the difference (between TD and CHARON) must be related to the time response of the methods? How do the detection limits compare if the same averaging times are used? The scatter in Figure 1 appears to indicate that the precision of the measurements is similar when averaged over the same time, but perhaps the data should not be interpreted like that.

Line 168: “V/cm” instead of “V cm”

Lines 168-169: A graph showing the different distributions of primary ions in the three different instruments would be helpful.

Line 183: The mass resolution is quoted as 2500 in Table 2. Why is there such a large difference with the specifications of the mass spectrometer?

Figure 1b: the error bars and line fitted through the data points are hard to see.

Line 348: “variability” instead of “uncertainties”?

Lines 351-354: how about incomplete evaporation of the sampled OA? The upper temperature in the three instruments is quite different and some, like the CHARON, appear to be low compared to other thermal desorption measurements. For example, Figure S1 shows that an appreciable amount of OA evaporates above 150 C. How about transmission losses of OA vapors from the evaporation zone to the drift tube?

Lines 417-429: by assuming that the AMS gives the correct elemental composition of the OA (a big if), is it possible to derive stochastically what the average composition of the undetected fragments in the CHARON measurements is?

Figure 4: these graphs might be a little easier to look at, if the ACM and TD results were shown next to each other, instead of having the CHARON results in between.

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