

Interactive comment on “Atmospheric sulphuric acid and neutral cluster measurements using CI-API-TOF” by T. Jokinen et al.

Anonymous Referee #3

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REFeree #3 REPORT

A. SUMMARY

This paper presents the first field measurements of a CI-API-TOF allowing, in principle, the analysis of neutral sulphuric acid (SA) molecules and clusters entering the instrument. It is an important advance in instrumentation and should be published in ACP after addressing the issues raised below.

B. OVERALL COMMENT

There are many poorly-written sentences throughout the manuscript, eg.

p.31992 "Both two API-TOF instruments were first run without chargers to be able to

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get them respond to one another."

"two" is redundant; "correspond" not "respond"... Better to say something like:

""Both API-TOF instruments were first run without chargers to calibrate their relative signal response."

The entire manuscript should be carefully read and the grammar corrected.

C. REPORT

Page 31984

Title: The title is rather misleading because the paper shows only measurements of the SA monomer and no neutral cluster measurements - only clusters that were originally charged.

I.7: Two-hour averaging is far too long for most field measurements, due to SA variability. It would be better to quote a sensitivity for shorter integration times - say 10 min.

I.7: What does this sentence add to the abstract?: "Signals from sulphuric acid clusters up to tetramer accompanied by ammonia were also obtained but these were found to result from naturally charged clusters formed by ion induced clustering in the atmosphere during nucleation".

Page 31985

I.19: Sipila et al (2010) indicate that neutral nucleation of sulphuric acid can proceed fast enough to account for atmospheric boundary layer observations but Kirkby et al (2011) disagree, showing that a ternary vapour is required. The text is ambiguous and misleading at present. It should be corrected.

Page 31988

I.14: This entire paragraph is poorly written and hard to understand. It should be

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clarified, eg. what do the following sentences mean?:

"The limit of detection (LOD) for sulphuric acid monomer is defined as three times the standard deviation added to the mean value of the background signal."

and

"The LOD is probably due to the utilization of the TOF mass spectrometer, in which all mass channels are integrated simultaneously thus improving the statistics."

I.14: "high signal-to-noise" not "low signal-to-noise".

I.17: "...background." not "...background signal."

I.17: What is the source of the background? Is it electronic noise? State it.

p.31989

Section 2.4: What T stability is required? This can be expressed as Δ_M / Δ_T so the reader can see how sensitive the APiTOF is to temperature drifts.

Section 2.4: How easy is it to calibrate the instrument in a complex background environment where known mass peaks are weak or confused? Explain in text.

p. 31990

I.11 There is no - or extremely weak - evidence for the tetramer in Fig.2, despite a 2 hour integration time. This should be stated in the text.

I.17: "In case of the trimer and tetramer these other compounds are already predominant, but the sulphuric acid signals can still be dependably separated." This is not true for the tetramer and should be removed.

I.21: "Fluorinated compounds are one possibility that may originate from the PTFE-tubing used to carry sheath flow to the inlet." If this is true then please explain why did the authors not use stainless steel tubing.

I.27: "This peak has a strong diurnal cycle (Fig. 3) and therefore the signal is likely to origin from atmosphere (C₈H₉O₁₀N₂-) rather than the instrument's surfaces." The sampling probe presumably also has a diurnal temperature cycle so this seems a weak argument. Please explain.

p.31991

I.27: "Using integer mass only (Fig. 3), one could say that neutral sulphuric acid clusters are present at all times since the CI-API-TOF cluster signal exceeds the signal estimated to result from naturally charged ions." This is a meaningless observation since the integer mass is dominated by contaminants - not SA clusters. In fact the CI-API-TOF clusters generally lie *below* the API-TOF clusters during the nucleation bursts (figs.3 and 4).

p.31992

I.10: "In all cases the expected ion contribution to the signal is, within measurement accuracy, equal to the signal from the CI-API-TOF." This means the error bars in Fig.4 must very large since, for example, the trimer in the CI-API-TOF is a factor 4 smaller than the API-TOF. It is remarkable that the authors consider Fig.4 is acceptable without error bars. It impossible to judge the significance of the measurements without them. Please put error bars on Fig.4.

p.31993

I.16: "Other possibility is that in the ambient atmosphere the oxidised organics rapidly condense on dimers forming compounds that can not be detected using nitrate ion based chemical ionization." Please present the evidence that leads to your speculation that oxidised organics condense on SA dimers.

p.31994

I.2: "Furthermore, most of the observed masses followed a similar diurnal cycle as sulphuric acid, possibly indicating photochemical production pathways and therefore

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the diurnal behaviour could not have been straightforwardly used for concluding the composition." What does this sentence mean? Please write it more clearly.

I.9: I assume the high naturally charged fraction (1-2%) reflects the low charging efficiency from the CI section. Is this correct? Please state the charging efficiency (= charged monomer / neutral monomer) due to the CI section.

I.14: Do the authors allow that there may be close to 100% ion-mediated nucleation, as proposed by Yu and Turco? If so does this disagree with your earlier observations that IIN is very small (1-10%)? Please explain.

I.19: "assuming...and no overlapping peaks in the spectra." But there *are* overlapping peaks for all clusters, so this is a meaningless detection limit.

p.3199

Fig.1: "The average ratio between the two data sets is 3.78." The average ratio between the two data sets in the figure is close to 1. Please explain.

Fig.1: Are the high CIMS values below $1E5$ CI-API_TOF due to noise in the CIMS? If so, this is an advantage of the CI-API_TOF and should be stated in the text.

p.3200

Fig.2: Are these data from the CI-API-TOF or the API-TOF? Please state in the label.

p.3201

Fig.3: This figure is terrible. It is completely illegible. Please fix it.

p.3202

Fig.4: Errors bars are required.

Fig.4: Why have the colours been switched between Figs. 3 and 4? Please use consistent colours. Please also use different markers and lines so the different lines can be better distinguished.

Fig.4: The tetramer signal (CI-API_i-TOF signal and ASPI_i-TOF) should be shown as an upper limit but not as a direct measurement. It is over-stating the data to claim this is a real measurement of the tetramer signal.

Fig.4: Was there any evidence that the CI charger generated additional background? That is, did the background in the CI-API_i-TOF at the SA peaks (97, 195, 293, 391, 408) appear **larger** than for the API_i-TOF? Please state this in the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 31983, 2011.

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