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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF" *by* T. Jokinen et al.

T. Jokinen et al.

tuija.jokinen@helsinki.fi

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Referee #3 We thank the referee for the critical comments to the manuscript.

Specific comments:

1. Title: This method allows one to measure neutral sulphuric acid clusters with concentration 3.6e4 or more. Evidence of these clusters was not found due to the low cluster concentration (below LOD) or poor charging efficient.

2. LOD: The referee is absolutely right pointing out that 2-hour averaging is far too long for field measurements. We have calculated a new LOD with better time resolution of 15 minutes, LOD = 3,60e4 for the monomer, and clarified the definition of LOD. P. 31984 l. 7.

3. This sentence is essential because we have cluster signals similar to Zhao et al. (2010) but our data do not prove the existence of neutral clusters.

4. More detailed description is now provided in the introduction. P. 31985 l. 21.

5. a) P. 31988 the last paragraph is almost completely rewritten. b) Low signal-to-noise has been corrected to high signal-to-noise. c) LOD is defined as 3 x standard deviation of the background, this is now corrected and d) the source of the background is now stated in the text as following: Most of the background results from the electronic noise, minor contribution can result from particles with very high m/z (>3000 Th) having time-of-flight longer than the reciprocal of the pulsing frequency (12 000 Hz).

6. Section 2.4; a) The CI-APi-TOF was kept inside a temperature controlled room throughout the campaign and only the tip of the sampling tube was actually placed outside. We have not yet studied how outside temperature fluctuations would affect our data. b) Mass calibration is easy since a constant flow of nitric acid is ionized to produce reagent ions that we always dominant in the spectrum. This has been clarified in the text, p. 31989 l. 21.

7. P. 31990 l. 11 and 17, We fixed the sentence to clarify that sulphuric acid tetramer signal needs longer integration time to be reliably separated from overlapping peaks next to it.

8. P. 31990 l. 21. The authors know that Teflon originated mass peaks are visible in the spectrum e.g. m/z 113 but we had no previous indication of fluorinated compounds at m/z 195. Next time we will consider using different materials as stainless steel to carry the sheath flow.

9. P. 31990 l 27; The instrument is kept inside a temperature controlled container and the authors feel that a stable signal is more likely to originate from the instrument surfaces than a signal with a clear diurnal pattern. Of course it cannot be completely excluded that some contaminants may have diurnal patterns as well. In that case

the contaminant should originate from wall of the sample tube that is exposed to the outside temperature variations.

10. P. 31991 l. 27; This is an essential statement and we wished to keep it as is. If you look at publication by Zhao et al. (2010) they used integer mass to evidence the existence of neutral sulphuric acid clusters. Our data is not evidencing that the conclusions by Zhao et al. were not valid, but we want to point out that without the high mass resolution significant artefacts can result.

11. P. 31992 l.10; To figure 4 we added error bars to clarify measurement accuracy.

12. P. 31993 l. 16 while no publication can be sited the authors feel is not wildly speculative to make this assumption and that's why we want it to stay in the manuscript.

13. P. 31994 l. 2; The sentence is rewritten.

14. P. 31993 l. 9; Nitrate ion concentration in the ion reaction region is estimated to be <1·106 molec cm-3 (Kurtén et al., 2011). Reaction rate coefficient is in the order 1·10-9 and the reaction time is in the order of 0.1 s. This results in a charging probability in the order of 10-4. A concentration of 107 molec cm-3 of sulphuric acid monomer together with 0.01 transmission efficiency and a sample flow of 10 cc s-1 results in a signal 10 cps at the detector as indicated in figure 4.

15. P. 31994 l. 14; Our data do not provide information on the relative roles of ion mediated, ion induced and neutral nucleation.

16. P. 31994 l. 19; We clarified the sentence in the conclusions.

17. Figure 1, we have multiplied the CI-APi-TOF data by 3.78 already. The figure caption has been modified to more reflect this fact.

18. Figure 1, The high CIMS values below 105 are due to the greater sensitivity of the CIMS.

19. Figure 2, This is CI-APi-TOF measurements and it has now been stated in the

figure caption.

20. Figure 3, This is an ACPD formatting issue that hopefully will be corrected in the final publication.

21. Figure 4; This has been addressed and the colours have been switched to be consistent.

22. Figure 4; We had no evidence that the CI-inlet generated additional background.

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