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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Total sulphate vs. sulphuric acid monomer in nucleation studies" *by* K. Neitola et al.

Anonymous Referee #2

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General comments:

This paper presents measurements of sulfuric acid monomer compared to total sulfate (gas+particle), and concludes that the measured sulfuric acid monomer is about two orders of magnitude lower in concentration compared to sulfate. The monomer measurements were performed using two different chemical ionization mass spectrometers (CIMS), whereas the total sulfate was measured using a MARGA instrument. The MARGA total sulfate data agree with calculated estimates of sulfuric acid concentrations based on temperature. Next, the authors use these instruments in flow tube experiments to explore particle production and the impacts of this 2-orders-of-magnitude discrepancy on observations of particle formation. The authors hypothesize that this discrepancy between the measured sulfuric acid monomer and total sulfate appears to

be related to contaminants in the flow tube. This is an interesting study that highlights the potential importance of trace contaminants on observations of nucleation. It would be suitable for publication in ACP once the authors have successfully addressed my concerns, described below.

Specific comments

1. The grammar in this manuscript is so poor (in my view) as to be distracting. In some sections, every sentence has small errors. Larger errors make it difficult to understand what the authors are trying to say. This article should have been reviewed for grammatical and descriptive errors before submission, and I could not accept this without a thorough review and correction of these errors. I will try to put some of these at the end of this review, but in no way will this be a complete list.

2. In my view, the most interesting results are those from the saturator itself (Figure 3). It is more difficult for me to understand the purpose of the nucleation experiments. No reason for performing these experiments is mentioned in the introduction, and it is not until Section 3, Results and Discussion, that we see an overview of the study and an explanation for why these nucleation experiments are presented. According to the authors, the purpose is to compare their results with previous studies. My recommendation is to put a paragraph similar to this (p2596, ln16) in the introduction (p25790).

3. If the purpose of the nucleation experiments is to compare the results with previous studies, this could be extremely difficult due to the fact that nucleation rates are not actually being measured in this study. As stated on p25800, ln 7, the residence times in this flow tube were so long that by particles had grown to 8 nm when detected at the outlet. As Sipila et al showed, this will greatly affect both the power dependence on sulfuric acid as well as nucleation thresholds.

4. Also, except for the comparison to the Brus et al study (Figure 10), no other comparisons are made. Likely, it was because it would be difficult due to the above-mentioned problem with nucleation rates (Item 3). This study would be a lot more useful to readers

if you can place it in context by comparing results to prior studies.

5. If Items 3 and 4 are not consistent with the authors' intentions, it would be good to have a clear explanation as to the value of the results in Figures 6 and 7.

6. Since contaminants are a likely source of the discrepancy between sulfuric monomer and sulfate, it's important to state exactly how the purified air is generated for the saturator and flow tube experiments. What, exactly, is the "carbon capsule" shown in Figures 1 and 2? How do you know that any residual amines or ammonia have been removed from this air? Hanson et al. used a weak phosphoric acid denuder to scrub bases from their air supply. Was something similar done?

7. Section 3.5 provides important insights into the possible source of this discrepancy between sulfuric monomer and sulfate. It may in fact be the most important section, since possible contaminants in the flows provide an explanation for these observations. The authors just refer to the supplemental information and state that the results and a discussion are provided there, but I see very little discussion there about the effects of contaminants. Since 100ppt is about 2.5x10ˆ9 molecule cmˆ3, or about the reported concentrations of the sulfuric acid monomer, that and other contaminants are sufficient to neutralize the acid. Please provide a summary of the results of your "extensive measurements" in the main article so the reader can better interpret these results. For example, if dirty air was used then it could fully explain most of these results . . . and of course make them inconsequential since most nucleation experimenters go through great lengths to characterize and eliminate contaminants.

Technical corrections

abstract, ln12: the online technique did not detect sulfuric acid concentrations, but sulfate.

p25788, ln23: This paragraph starts off by introducing new particle formation, but then describes impacts of larger particles. Nanoparticle growth provides the link between

new particle formation and climate impacts, at it should be stated here.

p25789, ln6: change "done" to "made" . . . I will suggest other places in this paragraph that language can be improved but I don't want to do this for every paragraph. In several areas there is incorrect placement of an article in front of a noun (either absent or it's there and shouldn't be). A native English speaker can easily correct this.

ln9: change "solved" to "found"

ln17: remove "the" from in front of nucleation

ln19: change "have" to "has"

ln22: In this list of recent lab studies of nucleation, the recent work from David Hanson's group(1) should be presented.

p25793, ln20: please explain what a 2x100 cm log chamber is. Is it two sections of 100cm long tube? Or something with a diameter of 2 cm? In general, the description of this flow tube is very confusing. For example, I have no idea of what this is (ln24): ". . . with one hole in 5 cm Teflon connector between the 100 cm pieces." Does this refer to the fact that you have 2 pieces of 100 cm tubing? Updating Figure 2 to reflect this would be all you need to do.

p25794, ln14: Don't the two CIMS also differ in the type of mass spectrometer used? Also please define what a "differentially pumped APi" is. Also "m/z ratio" should be replaced by mass-to-charge ratio.

p25796, ln3: in this paragraph you should use consistent term for the UCPC (that, or UFCPC).

p25797, ln2: please explain why the experiments were run at different RH (dry and 15% for the CIMS and dry for MARGA).

p25800: for all figures with multiple panels, using letter designators for each panel makes it much easier to understand (e.g., (a) – (d)).

p25801, ln12: If the CPC is saturated in number concentration, then how do you know that coagulation is not an effect?

Reference cited

1. J. H. Zollner et al., Atmos. Chem. Phys. 12, 4399 (2012).

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 25787, 2014.