

## ***Interactive comment on “Total sulphate vs. sulphuric acid monomer in nucleation studies: which represents the “true” concentration?” by K. Neitola et al.***

**Anonymous Referee #3**

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The authors describe findings from a flow experiment investigating H<sub>2</sub>SO<sub>4</sub> measurements using different detection techniques, i.e. a denuder technique measuring total sulphate (MARGA) and nitrate CIMS and CI-API-TOF measuring the H<sub>2</sub>SO<sub>4</sub> monomer. Gas-phase H<sub>2</sub>SO<sub>4</sub> is provided by flushing a part of the carrier gas through a saturator with concentrated sulphuric acid. The main message of this paper is that there exists a large discrepancy of about two orders of magnitude for the total sulphate concentration by MARGA vs. H<sub>2</sub>SO<sub>4</sub> monomer concentration measured by the mass specs analysing the same sample. Furthermore, the MARGA results confirm roughly the ex-

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pected H<sub>2</sub>SO<sub>4</sub> concentration derived from the vapour pressure. The authors are not able to explain the large discrepancy although a state-of-the-art measurement technique was available in the experiments (CI-API-TOF). At the moment, the whole story sounds a bit mysterious for me. Here my comments:

- Nothing is said regarding the CI-API-TOF results other than H<sub>2</sub>SO<sub>4</sub> monomer concentrations! Are there any other clusters visible? What's the matter with H<sub>2</sub>SO<sub>4</sub>-base or H<sub>2</sub>SO<sub>4</sub>-organic compounds? How the authors checked the carrier gas impurities? How can carrier gas impurities influence or explain the observed disagreement of total sulphate and H<sub>2</sub>SO<sub>4</sub> monomer concentration?
- In a single paragraph the MARGA technique should be compared with CIMS and CI-API-TOF stating the detection limits, upper detectible concentrations, calibration results and the expected measurement errors.
- The authors should explain more in detail equation (1) regarding the “simple” equation of H<sub>2</sub>SO<sub>4</sub> vapour pressure as derived from experimental data by Ayers et al.! I guess it is not enough to reference only to the work by Kulmala and Laaksonen.
- The authors observed nucleation for H<sub>2</sub>SO<sub>4</sub> concentrations of about 10<sup>(7)</sup> cm<sup>(-3)</sup> in line with former results from the same experiment but using another H<sub>2</sub>SO<sub>4</sub> source. Do they believe that there was no third body involved in the nucleation process? They should explain their findings in light of the current knowledge of atmospheric nucleation.
- The work by Ball et al.(1999) and Zollner et al.(2012) has been mentioned in the manuscript. Both studies used also a liquid H<sub>2</sub>SO<sub>4</sub> source and H<sub>2</sub>SO<sub>4</sub> monomer measurements by CIMS. A discussion of the findings of this manuscript regarding the former papers would be fine.

Finally, I guess, the authors should try to find out the reason for the missing H<sub>2</sub>SO<sub>4</sub>. They have the best technique at the moment doing that.