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

Anonymous Referee #2

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This paper seems to be part introducing a bulk source for H2SO4, part reporting that this makes no difference to nucleation rates measured in their flow reactor, and part questioning the measurement of H2SO4 by CIMS techniques. The first two parts are of little scientific significance (but see the last comment below.) The third is the focus of the rest of this review.

Unfortunately, the authors have not made a case that the work described represents a significant scientific advance. Their main finding is that sulfuric acid measured by them using CIMS is low by up to two orders of magnitude. If the method in general is flawed, this can be an important factor in many atmospheric considerations. This finding if true would be of interest to anybody interested in atmospheric sulfuric acid, particularly those measuring it by CIMS. However, if they do not back up this claim, then the paper is of no interest. If they do choose to clarify that they are making this claim, and therefore call into question previous work in this area, then they would need to explain why others have gotten it so wrong. This reviewer thinks there is plenty to explain about their experiments before they can make this claim.

They should explain in great detail how they are using CIMS, what is special about their sampling method, and how it differs from other deployments of CIMS technique to measure H2SO4. Some points to consider:

Was there actually a calibration of the CIMS systems done in this work? These systems need to be calibrated and preferably in the EXACT same sampling arrangement that they will be used in.

Sampling arrangements are very important. Tanner et al. 1997 put a nozzle on the inlet and saw a 50 % decrease in the SICIMS sensitivity. Brus et al. 2011 determined sulfuric acid with CIMS in the same apparatus as used in this study but with a 1 cm ID sampling tube into the 1.9 cm inlet: they at times measured sulfuric acid that was within a factor of three of the bubbler method. The present method with a 0.4 cm sampling tube into the 1.9 cm inlet will likely have far worse losses.

Bottom line for these two points: if you do not calibrate and have a non-standard sampling arrangement, you cannot use a 5x10ˆ9 calibration factor.

More details: In the discussion of SICIMS (Tanner and Eisele, 1995 and Tanner et al. 1997), it is clear that a ‘jet’ of sample gas can cause severe disruption of the laminar flow and that CIMS sheath gas can mix in with sample gas. Even the small conical inlet introduced in their latter work disrupted the flows enough to contribute about half of the factor of two drop in sensitivity. At a worst case, this mixing down of sample gas by sheath gas can cause an 80 % loss of OH/H2SO4. There is also additional wall loss because of departure from laminar flow: the swirling eddies induced by the ‘jet’ of sampled gas (10 Lpm collimated along a 0.4 cm ID tube) can cause significant loss to the walls. This was the other contribution to the sensitivity decrease mentioned by Tanner et al. 1997. Experimental evidence for sampling issues exists in work out of the group of present authors: (i) the data in figure 3 shows that 6 lpm sampling is better than 10 lpm indicating a sampling flow dependence and (ii) the aforementioned Brus et al 2011 measurement with a 1.0 cm tube was closer to the expected. (A technical note: The amount of loss along an additional 1 m length of sample line is probably small compared to a factor of 100.)

Detailed and accurate drawings of the sampling tubes need to be presented. MARGA also samples aerosol (the 'AR'): how much of the difference between the two can be attributed to aerosol? What are the SJAC results? MARGA is designed precisely to scavenge everything that hits its walls: SICIMS is designed with exactly the opposite considerations in mind.

One also needs to consider how the sampling tube entrains gas from the flow reactor or the saturator mixer.

I would suggest that the CIMS and its sampling arrangement WAS INDEED calibrated using the saturator but it is not clear that aerosol was not also present.

Saturator and nucleation comments: The use of an H2SO4 saturator is not new. The use of HEPA filters can introduce all kinds of contaminants. Were these filters also used in the previous Brus et al. papers? Perhaps they are the reason for the agreement between the current work and the previous results (these are both very much higher than binary nucleation)?

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 2313, 2013.