**Atmospheric
Chemistry
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Discussions

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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.

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We thank the referee for their helpful comments and observations.

R2C: 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.

Au A: Referee states that in this study we find CIMS measuring two orders of magnitude low values and the CIMS method is discredited in this study. Authors have full confidence that CIMS is measuring exactly what it is expected and proven to measure. This is concentration of sulphuric acid molecules (and in some extent dimer sulphuric acid) in gas phase which are not bound to other molecules (for example organics) that inhibit the charging in the CI-inlet. As stated in the manuscript, most of the base molecules do not inhibit the charging as the nitrate ion will substitute weaker base molecules out (page 2332, lines 26-27)). In the strongly clustering systems like sulphuric acid, the presence of higher clusters (containing not only sulphuric acid alone) is expected, and we also expect that these clusters cannot be registered with CIMS as pure sulphuric monomer or dimer. Also charging efficiency for these clusters is not known yet. We state this in the manuscript (from page 2332, lines 28-29 to page 2333, lines 1-2).

R2C: 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.

Au A: CIMS was calibrated before the actual experiment with sulphuric acid produced from SO2 with UV light in the same way as described in Mauldin et al., (1998). The CIMS calibration cannot be done with our system, since the neat sulfuric acid is used as a sulfuric acid vapor source. And as stated above, in strongly clustering systems and more over in the system with decent levels of impurities it is impossible to determine

the selective rate constants for each particular cluster involved in the system. Identification of these clusters from CI-APi-TOF is not possible at the moment as the sulphuric acid molecules are distributed in great number of clusters with different impurities and combination of these impurities. That is why the exactly same way of calibration and device parameters were used as in atmospheric measurements.

R2C: 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 5x10Ë9 calibration factor.

Au A: As the referee states, sampling arrangement is very important. We apologize for not putting a complete description with good detail of the saturator test inlet / mixer /outlet configuration. This mistake by us has caused a misunderstanding by the referee. I.D. 4mm tube is only used in the outlet of saturator (length 6 cm) and the flow through this tube was always below 1.5 lpm and usually 0.5 lpm or below. This mistake will be corrected by adding a detailed explanation in to the manuscript (page 2319, line 7): "The sampling line between saturator and instruments consist of three parts: outlet of saturator (I.D. 4 mm, length 6 cm), mixer (I.D. 10mm, 10 cm) and CIMS / CI-APi-TOF inlet (I.D. $\frac{3}{4}$ inches). See figure S2 in supplementary material." as well as the detailed drawing of the mixing system to the supplementary material, which can be found in this answer too (Figure S2).

We were worried that the losses would arise from the wall losses in the saturator outlet (I.D. 4 mm, length 6 cm), so to test this we inserted an extra 1 meter tube (I.D. 4 mm) after the saturator, but before mixing unit which is connected to the CIMS / CI-APi-TOF. As shown in figure 3 in the manuscript (blue and red open circles) this 1 m tube does

not affect the measured sulphuric acid monomer concentration. The flow rate through saturator was changed in tests from 0.5 to 1.5 lpm (see the flow rate test in Figure S3). In figure S2 is shown that the excess flow went straight and instruments were behind 90 degree angle. We tested different configurations (i.e. putting one instrument with flow going straight and other behind 90 degree angle) and it did not affect the results more than 10%, which is well within the experimental uncertainty of CIMS / CI-APi-TOF methods, factor of 2.

In Brus et al. (2011) no bubbler method is used, the prepared sample of weak sulphuric acid solution is analyzed with Ion Chromatography method, the IC dataset is then compared against initial concentration of sulphuric acid measured with CIMS. On average the methods show one order of magnitude difference.

R2Q: 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 ïňĆow and that CIMS sheath gas can mix in with sample gas. Even the small conical inlet introduced in their latter work disrupted the ïňĆows 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 ïňĆow: the swirling eddies induced by the 'jet' of sampled gas (10 Lpm collimated along a 0.4 cm ID tube) can cause signiïňĄcant 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 ïňĄgure 3 shows that 6 lpm sampling is better than 10 lpm indicating a sampling ïňĆow 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.)

Au A: As stated above, we sincerely apologize the lack of mixing unit dimensions and description, and these will be added. Referee has noticed the difference between the

CIMS measured sulphuric acid concentration between the nominal flow rate (10 lpm) and the reduced flow rate (6 lpm) shown on figure 3 in the manuscript. Thanks to referee's attention, an error was found in Fig 3 dataset, which can explain the difference. The mixing flows as stated in the figure caption are 40 lpm (dry CIMS / CI-APi-TOF and RH 15%) and 20 lpm (MARGA and RH 29%) also for the prediction by Kulmala and Laaksonen, (1990). So the dilution for 6 lpm inlet flow rate for CIMS/CI-APi-TOF with RH 29% has only half of the dilution as compared to 10 lpm inlet flow rate, which doubles the difference between these measurements. While double checking the data, we found another error in the data set, as the measured background from MARGA data was not subtracted. This is done to ensure that all of the sulphate originates from the saturator. Both errors will be corrected in manuscript figure 3, and the corrected figure can be found also at the bottom of this answer. This error does not change the overall picture but only the results measured with different inlet flow rate (6 lpm) with RH fits within the experimental uncertainty.

R2C: 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.

Au A: Unfortunately MARGA is not providing any size resolved data. MARGA is designed to separate aerosols from the gas phase based on diffusion velocities. At the moment there are no laboratory measurements with MARGA to distinguish the size of particles which are counted as aerosol phase and which are counted as gas phase. Small particles have quite large diffusion velocities and can be counted also as gas. Also, due to the high flow rates of the MARGA instrument, it is not convincing to say that all of the gas is absorbed by the WRD and some of the gas can be measured as particles. We made test with filtering the particles out and MARGA still showed relatively high values for aerosol part. This is why we decided to use total sulphate

(aerosol + gas phase). MARGA SJAC results show that 30% at 276 K and 90% at 303 K of the total sulphate can be in the aerosol phase. Most of these particles registered as aerosol phase in MARGA, if formed in saturator, would be lost during the turbulent mixing with the mixing flow in the mixer .When background concentration were measured, bypassing the saturator, the ratio of concentrations of sulphate in gas and aerosol phase was roughly 1:1, even though no particles were present at all. This should have been mentioned in the manuscript also, and it will be added to page 2323, line 5.

R2C: One also needs to consider how the sampling tube entrains gas from the ïňĆow reactor or the saturator mixer.

Au A: Paragraph describing the inlet of MARGA will be added to the manuscript (page2321, line 12). The same inlet (1 m teflon tube, I.D. 10 mm) was used in both, saturator test and flow tube measurements.

R2C: 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.

Au A: As stated above already, direct calibration with saturator is not possible due to strongly clustering neat sulphuric acid. The obtained rate constant from the calibration would represent an 'effective' rate constant, a combination from all the clusters which would contain sulphuric acid. The only known rate constant from literature is for monomer (Viggiano et al., 1997), $k \approx 2 \cdot 10^{-9}$ cm3/s. The k obtained from our calibration done in same way as in Mauldin et al., (1998) was $k = 1 \cdot 10^{-9}$ cm3/s. Since the drift tube time is given by device geometry and is t=200 ms, calibration constant for integer mass 97 Da is $K = 5 \cdot 10^{-9}$ cm-3.

R2C: Saturator and nucleation comments: The use of an H2SO4 saturator is not new. The use of HEPA ïňĄlters can introduce all kinds of contaminants. Were these ïňĄlters 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)?

Au A: Referee points out that saturator method is not a new way to produce sulphuric acid vapour. This is true and will be corrected in the manuscript.

HEPA filters were used to remove possible particles coming from the air lines including mass flow controllers (that are known to produce particles). New HEPA filters were used and particle zero count was checked with PSM counter when nucleation measurements were done. Also when saturator was by-passed and also when very low flow (0.1 lpm) through the saturator was applied zero count was observed at the end of flow tube. It is true that HEPAs can be source of contaminants, but it is not stated within the whole manuscript that we are measuring binary nucleation, but sulfuric acid and water system. The contaminants are not named as it is not known which substances and how many of them might be involved in the nucleation process. It is also known that source of the contaminants is mostly humidification with water. We are aware of presence of contaminants but in our system the levels of contaminats are mostly under the detection limits of MARGA. Only ammonia concentrationwas measured inlevels of 60-126 pptv , the same order of magnitude as ones found in CLOUD experiments, which is considered to be one of the most clean environments up to date (Kirkby et al., 2011).

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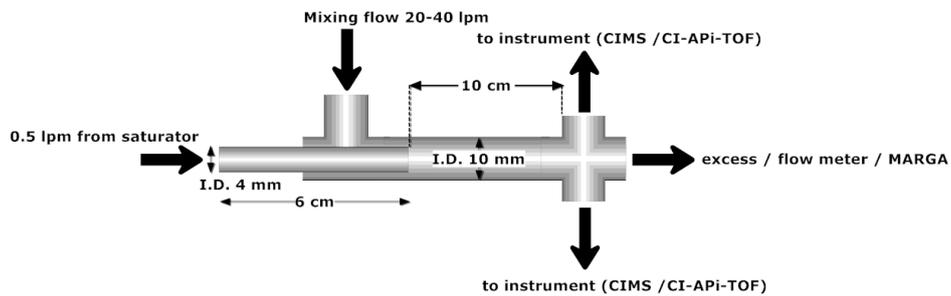
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Fig. 1. Figure S2. Inlet design during saturator tests. 0.5 lpm flow from the saturator is brought through a SS-tube (I.D. 4 mm, length 6 cm). Mixing flow (20-40 lpm) comes through an SS-tube (I.D. 10 mm). Th
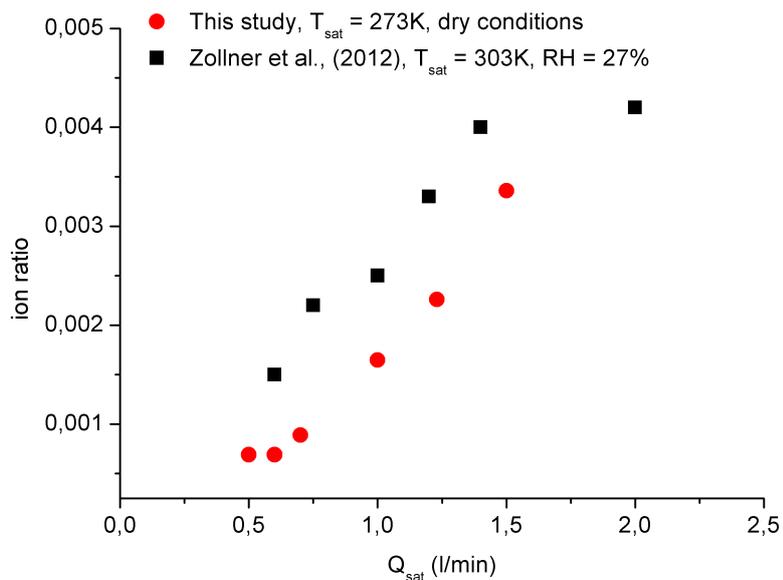
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Fig. 2. Figure S3. ratio of core ion and reagent core ion measured by CIMS as a function of saturator flow rate from this study and from Zollner et al., (2102) supplementary material.
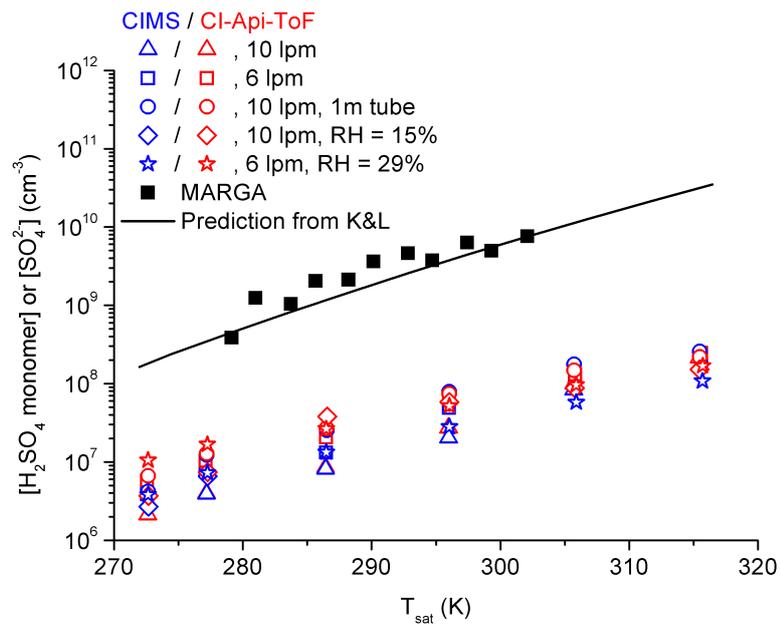
Fig. 3. Updated figure 3 for manuscript. In the original figure, from MARGA measured points the background was not subtracted. In this one subtraction has been done. Also, there were to different amounts of d

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