Author’s response

Response has first answers to referee #1 and # 2. After these is the complete manuscript with all tracked changes.

Answer to referee #1.

We thank the referee for very important comments and suggestions. The author would like to apologize for inconvenience in reading the manuscript, due to numerous grammatical mistakes. The manuscript has been proof-read by a native speaker.

The focus of the manuscript changed during the writing process, causing the message of the manuscript not to be very clear. Now the manuscript focuses mainly to the observed discrepancy between measured sulphuric acid and total sulphate, comparison to our previous study and thus excluding the possibility that the discrepancy is connected to production method of SA vapour. The most important changes (additions) are written in answers to referee below. The whole manuscript is also included with the chances tracked, (red = removed, blue =added) to help the referee to spot the changes.

Referee’s main comment #1:

The observed discrepancy in measured concentrations between the instruments could be of importance for the scientific community. However, the way it is communicated in this manuscript I cannot recommend it for publication. There is not any explanation for the observed discrepancy until the conclusions section (which looks more like a discussion section in the current state). In that section, the authors mention the possibility of sulphuric acid forming clusters with contaminants like e.g. ammonia. That is a possible explanation but to prove that it would have to be measured and quantified. And even then, the authors would have to motivate why they think that would be an important observation (like e.g. a higher fraction of sulphuric acid-base clusters than expected). In the abstract, there is nothing written about possible explanations for the discrepancy.

Answer #1: An explanation is now added to the abstract, together with a motivation why it is important:

“Possible reasons for the discrepancy are discussed and some suggestions include that the missing sulphuric acid is in clusters, formed with contaminants found in most laboratory experiments. One-to-two orders-of-magnitude higher sulphuric-acid concentrations (measured as total sulphate in this study) would contribute to a higher fraction of particle growth rate than assumed from the measurements by mass spectrometers (i.e. sulphuric-acid monomer). However, the observed growth rates by sulphate-containing vapour in this study does not directly imply similar situation on field, where the sources of sulphate are much more diverse."

To prove that the missing sulphuric acid is in the clusters, one should be able to identify the peaks containing sulphuric acid from the CI-Api-TOF mass spectra, determine their charging probability (calibration factor) in the CI-inlet, then sum the concentrations of those peaks and compare it to the theoretical predictions of the concentration. However, even the identification is a huge task and will take a long time to do, not to mention determination of the charging probability. This task was out of the scope of this paper. These reasons were stated in the supplementary material and in the conclusions section, but probably not well enough. A paragraph was added to the section 3.1, where a summary of the supplementary material is presented, including above mentioned reasoning:

"Extra saturator tests with mass spectrometers were done using three different carrier gas purities (N_2 6.0, N_2 5.0 and pressurized air) to check if the carrier gas used in our experiments (pressurized air) was more dirty than the most pure commercial ones. Two different purity sulphuric acids (~97 % and 100 %) were tested also to check if the purity of the acid itself has an influence. Changing the carrier gas or the sulphuric acid purity did not affect the observed sulphuric-acid concentration (see supplementary material, Fig. S3 and S4). The measured sulphuric-acid monomer concentration was one-to-two orders-of-magnitude lower than the prediction by Eq. 1. Tests with different saturator flowrates (0.05-2 lpm) showed that with flowrates below 0.1 lpm, diffusion losses dominated: causing the measured concentration to decrease as a function of the saturator flowrate. Above 0.15 lpm, the observed results behaved as expected. The measured cluster distributions (monomer, dimer and trimer) with different carrier gas purity were constant through the measured saturator flowrate range (Fig. S5). The ratios between monomer-to-dimer and dimer-to-trimer were between 1:10 and 1:100 with all carrier gases. From these results it is evident that the carrier gas used in our studies does not contain more contaminants than the most pure ones commercially available. CI-Api-TOF mass spectra observed with different carrier gases were investigated further to find the missing sulphuric acid. A large number of peaks were found to correlate with mass 97

(HSO_4^-), which is the ionized sulphuric-acid monomer, with all carrier gases. The number of these peaks increased as a function of the saturator temperature, suggestive that the sulphuric acid forms clusters with contaminant substances (Supplementary, section 6, Fig. S6-S8). The correlating peaks in Fig. S6-S8 are stick masses (i.e. rounded to nearest integer), which means that many of those peaks have actually several peaks within them. This is shown in Fig. S9-S11 where the mass spectrum from CI-Api-TOF is zoomed in. Unfortunately, summing up all of these correlating peaks to calculate the total sulphuric acid concentration is not feasible, since these clusters are not identified (i.e. it is not known what molecules those clusters are composed of) and the sheer number of these peaks is overwhelming. For more details and discussion of the extra saturator tests, see supplementary material."

The conclusion section has been improved and it is named discussion and conclusions.

Referee's main comment #2:

The authors seem to have done a good job in performing their measurements and in evaluating the importance of potentially important factors like e.g. relative humidity, wall losses, and flow rates on measured concentrations. However, since the reason for the discrepancy in the measured concentrations is not known there is no clear message in this manuscript. The manuscript is generally unfocused, and it is unclear what the actual goal is of the study. When introducing the study in the introduction the authors write: "Here we present a way to produce sulphuric-acid vapour from thermally controlled saturator in a wide range of sulphuric-acid concentrations". Reviewer 2 from the review of this manuscript in ACPD in 2013 pointed out that the use of an H2SO4 saturator is not new" and the authors seemed to agree on this in their response. Still one gets the feeling when reading both the introduction and conclusions sections that this method of producing H2SO4 is one of the main points of the paper. In addition, the language would have to be checked by a native English speaker.

Answer #2: The manuscript was not clearly focused, with the weight on the saturator as it should have been on the discrepancy between the measured sulphuric-acid and total-sulphate concentrations. The explanation why the nucleation measurements were done and motivation for the measurement conducted with different production method (mentioned in the answer #1) were added in to the Abstract section:

“The saturator provided an independent vapour-production method, compared to our previous method of the furnace (Brus et al., 2010 and 2011), to find out if the discrepancy is caused by the production method itself. The saturator was used in a sulphuric acid-water nucleation experiment, using a laminar flow tube to check reproducibility of the nucleation results with the saturator method, compared to the furnace.”

The importance of the discrepancy is motivated also at the end of the introduction and conclusions section and the motivation of the whole manuscript is shifted towards the saturator-test results, instead of the saturator usage.

The reason for the discrepancy is not known and proven in the manuscript, as the referee mentioned. However, there are quite reasonable suggestions towards the sulphuric acid to be “hidden” in the clusters. Even though it is not quantified, the results presented in Fig. S7-S11 in the supplementary material are pointing quite clearly towards the clusters. In the Fig. S7-S11 it is shown that there are numerous clusters containing sulphuric acid, which are not taken into account when determining the sulphuric-acid concentration from CIMS or CI-Api-TOF measurements. These results are more exposed with the added paragraph (mentioned in answer #1) in the section 3.1.

Detailed comment #1:

The motivation of sections 3.3-3.4 is vague. The authors should spend more effort in motivating why they compare their formation rates with Brus et al. rather than presenting a lot of figures and describing what they show. There seems to be no important lesson to be learnt here, or at least it is not communicated well enough.

Answer to detailed comment #1: The motivation for the flow tube nucleation measurements and comparison to our previous results is: a) to remove the sulphuric-acid vapour-production as possible reason for the discrepancy and b) to be able to compare the measured sulphuric-acid monomer and total-sulphate concentrations with similar particle formation rates. With the flow tube we can ensure that conditions are similar (temperature, relative humidity and particle formation rates), in which the sulphuric-acid concentrations are measured. The motivation for sections 3.3-3.4 has been improved for the whole manuscript. Here are listed the larger changes including the additions to the Abstract:

“The saturator provided an independent vapour-production method, compared to our previous method of the furnace (Brus et al., 2010 and 2011), to find out if the discrepancy is caused by the production method itself. The saturator was used in a sulphuric acid-water nucleation experiment, using a laminar flow tube to check reproducibility of the nucleation results with the saturator method, compared to the furnace.”

Introduction:

“Brus et al. (2011) found a discrepancy in sulphuric-acid mass-balance between a known concentration of weak sulphuric-acid solution introduced to the experimental setup and a measured sulphuric-acid concentration, even though correction for wall losses and losses to particle-phase was applied, one-and-half orders-of-magnitude difference in sulphuric acid concentration was found (see Fig. 5 in Brus et al., 2011). A large discrepancy between measured sulphuric-acid monomer and total-sulphate concentration was observed in the present study. To investigate the reason for this discrepancy, we applied a thermally controlled saturator (e.g. Wyslouzil et al., 1991; Ball et al., 1999) to produce sulphuric-acid vapour. The output of the saturator was tested with two independent detection methods (mass spectrometry and ion chromatography) before using the saturator in a sulphuric acid-water nucleation study in a laminar flow tube.

Applying the saturator as the source of the sulphuric-acid vapour made it possible to compare the saturator to the furnace, which was used as the source of the sulphuric acid previously (Brus et al., 2010 and 2011) and eliminate the production method as a reason for the discrepancy. The flow-tube measurements with the saturator and the two sulphuric-acid or total-sulphate detection methods were conducted to check reproducibility of particle formation rates between the saturator and the furnace, with similar observed sulphuric-acid or total-sulphate concentrations.”

as well as in the section 3.3:

“The purpose of these nucleation measurements is to be able to compare the formation rates and the sulphuric-acid or total-sulphate concentrations, between the two sulphuric-acid vapour-production methods.”

and 3.4:

“Figures 8 and 9 show that apparent formation rates are reproducible with both sulphuric-acid production methods, with similar observed sulphuric-acid or total-sulphate concentrations.

This eliminates the sulphuric-acid production method as a reason for the discrepancy between the measured monomer and total sulphate concentrations."

Detailed comment #2:

Figure 5 shows how the particle number concentration and diameter change as the sulphuric-acid monomer concentration increases. The sulphuric-acid concentration is within the range of typical atmospheric concentrations, so what is the reason for the rapid growth when the vapour concentration increases? In the atmosphere, growth rates are normally a few nm per hour and organics do most of the job. Here the residence time is only 30 s.

Answer to detailed comment #2: The referee has pointed out one of the possible consequences arising from the discrepancy. If sulphuric-acid concentration in the flow tube is between 10^6 and 10^7 cm^{-3}, the growth rate should not be as high as observed in the flow-tube experiment. However, if the concentration is one-to-two orders-of-magnitude higher, measured growth rates are consistent with the amount of sulphate containing vapour available. We used the model described in Škrabalová et al. (2014) to calculate the particle diameter (D_p) and growth rate (GR) of the particles accounting for the initial sulphuric-acid monomer and total-sulphate concentrations as an input. Measured sulphuric-acid monomer and total-sulphate concentrations (presented in Fig. 6 and 7, panel d)) were converted to initial concentration (i.e. at the beginning of the flow tube) with the determined *TLF*s (factor of 10 sulphate and 14.2 for SA monomer concentrations). Diameter of 1.5 nm was used as an initial cluster size (Kulmala et al., 2007). Three different scenarios of particle neutralisation by ammonia were used in the model: (0) no neutralisation, sulphuric acid-water particles, (1) neutralisation to ammonium bisulphate-water particles and (2) neutralisation to ammonium sulphate-water particles. Using the sulphuric-acid monomer concentration as an input resulted in growth rates ranging from 1 to 15 nm h^{-1}, as the referee is stating. With these growth rates the particles grew up to 2 nm only, which is well below the observed diameters (Fig. 6, panel b)). Using total-sulphate as an input, the growth rates ranged from 1250 to 2300 nm h^{-1} resulting in diameters fitting well with the observed diameters. The results of the model are presented in supplementary material section 7 and Fig. S12. A paragraph was added in the end of section 3.3:

"The measured sulphuric-acid monomer concentration is at typical atmospheric levels, but the growth rates are much higher: indicating much larger concentration of condensing vapour than the detected sulphuric-acid-monomer concentration by CIMS. The growth is rather driven by the total sulphate, originating exclusively from the sulphuric acid inside the saturator, than the sulphuric-acid-monomer concentration.

To show the contribution of the sulphate to the growth rate, the model from Škrabalová et al. (2014) was used to calculate the diameter (D_p) and growth rate (GR) of the particles. Measured sulphuric-acid monomer and total-sulphate concentrations (Fig. 6 and 7, panel d), RH 30 %) were multiplied by the TLFs to obtain the initial concentrations at the beginning of the flow tube. Diameter of 1.5 nm was chosen as the initial cluster size according to Kulmala et al. (2007). The model was used with three scenarios of particle neutralization by ammonia: (0) no neutralization, particles composed of sulphuric acid and water, (1) neutralization to ammonium bisulphate-water particles and (2) neutralization to ammonium sulphate-water particles. When accounting for the initial sulphuric-acid monomer concentration as an input, the resulting diameter (D_p) was always below 2 nm with growth rates (GR) ranging approximately from 1 to 15 nm h-1 as a function of the sulphuric-acid concentration (i.e. saturator temperature T_{sat}) with all scenarios. When total-sulphate concentration was used as an input, the resulting particle diameters and growth rates fit well with the measured particle diameters presented in Fig. 7 for all scenarios (see suppl. Material, section 7 and Fig. S12).”

Detailed comment #3:

Is there a reason for the total sulphate concentration measured by the MARGA (saturator only) being higher in Fig. 4 (2*109 at 280K) than in Fig. 3 (1*109 at 280K)?

Answer to detailed comment #3: The values presented in Fig. 3 are the actual measured values. In Fig. 4 the different mixing ratios of saturator flow and the mixing flow between saturator tests and nucleation measurements has been taken into account to be able to determine the Total Loss Factors (*TLF*) in the section 3.2. In the nucleation measurements, the mixing flow was kept at appr. 11 lpm to have similar conditions as in our previous experiments where the furnace was used, but the saturator flow rate was varying. To account for the different mixing ratios, total-sulphate concentration (saturator only) was divided by a factor of 1.9. The usage of the mixing ratios is mentioned in the section 3.2 (page 25798, line 17):

“By accounting for the different mixing ratios of saturator flowrate and mixing flowrate, these measurements become comparable and the total losses in the flow tube can be determined.

The Total Loss Factor (*TLF*) includes wall losses and losses to the particle phase (nucleation and condensational losses).”

Detailed comment #4:

Some of the typing errors.

Answer to detailed comment #4: All mentioned and lot more typing errors have been corrected by help from a native English speaker. Thank you for listing some of these out.

References:

Kulmala, M., Riipinen, I., Sipilä, M., Manninen, H. E., Petäjä, T., Junninen, H., Dal Maso, M., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R. M., Hanson, I., Leung, C., Lehtinen, K. E. J., Kerminen, V.-M.: Towards direct measurement of atmospheric nucleation, Science, 318, 89, DOI: 10.1126/science.1144124, 2007.

Škrabalová L., Brus, D., Anttila, T., Ždímal, V. and Lihavainen H.: Growth of sulphuric acid nanoparticles under wet and dry conditions, Atmos. Chem. Phys. 14, 6461-6475, doi:10.5194/acp-14-6461-2014, 2014.

Answer to referee #2.

We thank the referee for very important comments and suggestions. The author would like to apologize for inconvenience in reading the manuscript, due to numerous grammatical mistakes. The manuscript has been proof-read by a native speaker.

The focus of the manuscript changed during the writing process, causing the message of the manuscript not to be very clear. Now the manuscript focuses mainly to the observed discrepancy between measured sulphuric acid and total sulphate, comparison to our previous study and thus excluding the possibility that the discrepancy is connected to production method of SA vapour. The most important changes (additions) are written in answers to referee below. The whole manuscript is also included with the chances tracked, (red = removed, blue =added) to help the referee to spot the changes.

Referee’s comment #1:

In my view, the most interesting results are those from the saturator itself (Figure3). 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).

Answer #1: The motivation for the flow tube nucleation measurements and comparison to our previous results was added to manuscript: Abstract:

“The saturator provided an independent vapour-production method, compared to our previous method of the furnace (Brus et al., 2010 and 2011), to find out if the discrepancy is caused by the production method itself. The saturator was used in a sulphuric acid-water nucleation experiment, using a laminar flow tube to check reproducibility of the nucleation results with the saturator method, compared to the furnace.”

, Introduction:

“Brus et al. (2011) reported a discrepancy in sulphuric-acid mass-balance between a known concentration of weak sulphuric-acid solution introduced to the experimental setup and a measured sulphuric-acid concentration, even though correction for wall losses and losses to particle-phase was applied, one-and-half orders-of-magnitude difference in sulphuric acid concentration was found (see Fig. 5 in Brus et al., 2011). A large discrepancy between measured sulphuric-acid monomer and total-sulphate concentration was observed in the present study too. To investigate the reason for this discrepancy, we applied a thermally controlled saturator (e.g. Wyslouzil et al., 1991; Ball et al., 1999) to produce sulphuric-acid vapour. The output of the saturator was tested with two independent detection methods (mass spectrometry and ion chromatography) before using the saturator in a sulphuric acid-water nucleation study in a laminar flow tube.

Applying the saturator as the source of the sulphuric-acid vapour made it possible to compare the saturator to the furnace, which was used as the source of the sulphuric acid previously (Brus et al., 2010 and 2011) and eliminate the production method as a reason for the discrepancy. The flow-tube measurements with the saturator and the two sulphuric-acid or total-sulphate detection methods were conducted to check reproducibility of particle formation rates between the saturator and the furnace, with similar observed sulphuric-acid or total-sulphate concentrations."

as well as in the section 3.3:

"The purpose of these nucleation measurements is to be able to compare the formation rates and the sulphuric-acid or total-sulphate concentrations, between the two sulphuric-acid vapour-production methods."

and 3.4:

"Figures 8 and 9 show that apparent formation rates are reproducible with both sulphuric-acid production methods, with similar observed sulphuric-acid or total-sulphate concentrations. This eliminates the sulphuric-acid production method as a reason for the discrepancy between the measured monomer and total sulphate concentrations."

Referee's comment #2:

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.

Answer #2: Referee is right on the fact, that actual nucleation rates are not directly measured in our study. Relatively long residence time will affect the observed formation rates. The point was here to compare to our previous results measured with the same experimental setup, except for the different sulphuric-acid-vapour production method. As the conditions and the setup are the same in our previous measurements (Brus et al. 2010 and 2011) and in this study, comparison of the apparent formation rates are justified. As mentioned above, this was done to rule out the vapour production method as a reason for the discrepancy. The reported slopes in Fig. 8 are presented to show the similarity of the apparent formation rates, not to argue anything about the overall power dependency of nucleation rates on the sulphuric-acid concentration. The text within the manuscript is corrected to emphasize that the observed formation rates are rather apparent formation rates and not actual nucleation rates.

Referee's comment #3:

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.

Answer #3: It is true that comparison to other studies might help to put the nucleation experiment results more into context. The comparison to other results found in literature was left out from this study as it is not in the main scope of this manuscript. A paragraph was added to the end of section 3.4:

"The comparison to literature data was omitted in this manuscript as the formation rates in the present study are very similar to our previous results (Brus et al., 2010 and 2011). However, for comparison and review of experimental data on sulphuric-acid nucleation, we refer to Zollner et al., (2012) and Zhang et al., (2012)."

Referee's comment #4:

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.

Answer #4: The purpose of Fig. 6 and 7 is to show reproducibility of the results between the experiments with mass spectrometers and with MARGA, as well as to show the response of different variables to the increasing saturator temperature to justify the use of the saturator in the experiments. The most interesting of these variables is the mean diameter of the particles, as it points out fast growth rate in the flow tube. To emphasize the effect of the sulphate to the growth, we used the model described in Škrabalová et al. (2014) to calculate the resulting particle diameter (D_p) and growth rate (GR) of the particles using the initial sulphuric-acid monomer and total-sulphate concentrations as an input. A paragraph was added in the end of section 3.3:

“The measured sulphuric-acid monomer concentration is at typical atmospheric levels, but the growth rates are much higher: indicating much larger concentration of condensing vapour than the detected sulphuric-acid-monomer concentration by CIMS. The growth is rather driven by the total sulphate, originating exclusively from the sulphuric acid inside the saturator, than the sulphuric-acid-monomer concentration.

To show the contribution of the sulphate to the growth rate, the model from Škrabalová et al. (2014) was used to calculate the diameter (D_p) and growth rate (GR) of the particles. Measured sulphuric-acid monomer and total-sulphate concentrations (Fig. 6 and 7, panel d), RH 30 %) were multiplied by the TLFs to obtain the initial concentrations at the beginning of the flow tube. Diameter of 1.5 nm was chosen as the initial cluster size according to Kulmala et al. (2007). The model was used with three scenarios of particle neutralization by ammonia: (0) no neutralization, particles composed of sulphuric acid and water, (1) neutralization to ammonium bisulphate-water particles and (2) neutralization to ammonium sulphate-water particles. When accounting for the initial sulphuric-acid monomer concentration as an input, the resulting diameter (D_p) was always below 2 nm with growth rates (GR) ranging approximately from 1 to 15 nm h-1 as a function of the sulphuric-acid concentration (i.e. saturator temperature T_{sat}) with all scenarios. When total-sulphate concentration was used as an input, the resulting particle diameters and growth rates fit well with the measured particle diameters presented in Fig. 7 for all scenarios (see suppl. Material, section 7 and Fig. S12).”

Referee’s comment #5:

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?

Answer #5: The carbon capsule is commercially available from Pall, Corp., USA, it is a plastic capsule filled with activated carbon, which removes all organic vapour via diffusion to the surfaces from the carrier gas flow. A sentence was added to first paragraph of section 2.1:

"Carrier gas flows were purified in all experiments first with activated carbon capsules (Pall Corp., USA) to remove all organic vapours via diffusion to the surfaces and after with a HEPA (Pall Corp. USA) filters to remove any particles left in the flow."

From the comparison measurements among commercially available N_2 of different purity, it is clear that contaminants of similar level were still present in the carrier gas (pressurized air) used in our experiment. No extra denuders were used in this study.

Referee's comment #6:

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.

Answer #6: This summary of the obtained results was added to section 3.1:

"Extra saturator tests with mass spectrometers were done using three different carrier gas purities (N2 6.0, N2 5.0 and pressurized air) to check if the carrier gas used in our experiments (pressurized air) was more dirty than the most pure commercial ones. Two different purity sulphuric acids (~97 % and 100 %) were tested also to check if the purity of the acid itself has an influence. Changing the carrier gas or the sulphuric acid purity did not affect the observed sulphuric-acid concentration (see supplementary material, Fig. S3 and S4). The measured sulphuric-acid monomer concentration was one-to-two orders-of-magnitude lower than the prediction by Eq. 1. Tests with different saturator flowrates (0.05-2 lpm) showed that with flowrates below 0.1 lpm, diffusion losses dominated: causing the measured concentration to decrease as a function of the saturator flowrate. Above 0.15 lpm, the observed results behaved as expected. The measured cluster distributions (monomer, dimer and trimer) with different carrier gas purity were constant through the measured saturator flowrate range (Fig. S5). The ratios between monomer-to-dimer and dimer-to-trimer were between 1:10 and 1:100 with all carrier gases. From these results it is evident that the carrier gas used in our studies does not contain more contaminants than the most pure ones commercially available. CI-Api-TOF mass spectra observed with different carrier gases were investigated further to find the missing sulphuric acid. A large number of peaks were found to correlate with mass 97 (HSO4-), which is the ionized sulphuric-acid monomer, with all carrier gases. The number of these peaks increased as a function of the saturator temperature, suggestive that the sulphuric acid forms clusters with contaminant substances (Supplementary, section 6, Fig. S6-S8). The correlating peaks in Fig. S6-S8 are stick masses (i.e. rounded to nearest integer), which means that many of those peaks have actually several peaks within them. This is shown in Fig. S9-S11 where the mass spectrum from CI-Api-TOF is zoomed in. Unfortunately, summing up all of these correlating peaks to calculate the total sulphuric acid concentration is not feasible, since these clusters are not identified (i.e. it is not known what molecules those clusters are composed of) and the sheer number of these peaks is overwhelming. For more details and discussion of the extra saturator tests, see supplementary material."

Referee is completely right that 100 ppt of contaminants is in the same order as the measured sulphuric-acid monomer. The ammonia-to-total-sulphate ratio ranges from 1:1 to 1:10 as a function of increasing saturator temperature. The model and discussion of neutralization by ammonia to three different levels was added to manuscript (end of section 3.3 and suppl. Material, section 7 and Fig. S12), see answer #5.

Referee's list of technical corrections.

The manuscript was proof-read by a native speaker.

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

Answer: This is corrected throughout the manuscript.

p25789, ln22: Zollner et al., (2102) is in the list.

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.

Answer: The Fig. 2 is updated.

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.

Answer: Yes, the actual mass specs are different, CIMS has a quadrupole type of MS, and CI-Api-TOF has a Time-of-Flight type of MS. This is added to the manuscript. The Atmospheric pressure interface (Api) has several stages of pumping, lowering the pressure from the atmospheric pressure towards the TOF pressure. m/z ratio is now changed to mass-to-charge.

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

Answer: all is now corrected to UFCPC.

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

Answer: Paragraph was added: "Tests with MARGA were performed with dry conditions, since it was noticed that the RH did not have any influence on the results from the tests with mass spectrometers. MARGA uses supersaturated conditions to grow the particles and collect them in the SJAC, hence initial RH is not expected to have any influence."

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

Answer: Figures have been updated accordingly.

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

Answer: CPC 3772 has lower limit of 10^4 cm^{-3} which is very low compared to other particle counters used in the experiment (10^5 cm^{-3}). As there are no larger particles present, coagulation can be considered to be marginal.

Škrabalová L., Brus, D., Anttila, T., Ždímal, V. and Lihavainen H.: Growth of sulphuric acid nanoparticles under wet and dry conditions, Atmos. Chem. Phys. 14, 6461-6475, doi: 10.5194/acp-14-6461-2014, 2014.

Zhang, R., A.F. Khalizov, L. Wang, M. Hu, W. Xu, Nucleation and growth of nanoparticles in the atmosphere, Chem. Rev. 112, 1957-2011, DOI: 10.1021/cr2001756 (2012).

Total sulphate vs. sulphuric acid monomer in nucleation studies

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Abstract

Sulphuric acid is known to be a key component for atmospheric nucleation. Precise determination of sulphuric acid concentration is a crucial factor for prediction of nucleation rates and subsequent growth. In our study, we have noticed a substantial discrepancy between sulphuric~~-~~-acid monomer and total~~-~~-sulphate concentrations measured from the same source of sulphuric~~-~~-acid vapour. The discrepancy of about one~~-~~-to~~-~~-two orders~~-~~-of~~-~~-magnitude was found with similar particle-formation rates. To investigate this discrepancy, and its effect on nucleation, a method of thermally controlled saturator filled with pure sulphuric acid (97 % wt.) for production of sulphuric~~-~~-acid vapour is ~~introduced~~applied and rigorously tested. ~~Sulphuric~~The saturator provided an independent vapour-production method, compared to our previous method of the furnace (Brus et al., 2010 and 2011), to find out if the discrepancy is caused by the production method itself. The saturator was used in a sulphuric acid-water nucleation experiment~~ was done~~, using a laminar flow tube to check reproducibility of the

nucleation results with the saturator method, compared to the furnace. Two independent methods of mass spectrometry and online ion chromatography were used for detecting sulphuric acid or sulphate concentrations. ~~The results are compared to our previous results, where a method of furnace was used to produce sulphuric acid vapour (Brus et al., 2010 and 2011).~~ Measured sulphuric-acid or total sulphate concentrations are compared to theoretical predictions calculated using vapour pressure and a mixing law. The calculated prediction of sulphuric-acid concentrations agrees very well with the measured values when total sulphate is considered. Sulphuric-acid monomer concentration was found to be about two orders-of-magnitude lower than ~~the prediction~~theoretical predictions, but with a similar temperature dependency as the predictions and the results obtained with the ion-chromatograph method. Formation rates ~~agree well~~are reproducible when compared to our previous results with both sulphuric-acid or total-sulphate detection and sulphuric-acid production methods separately, removing any doubts that the vapour-production method would cause the discrepancy. Possible reasons for the discrepancy are discussed and some suggestions include that the missing sulphuric acid is in clusters, formed with contaminants found in most laboratory experiments. One-to-two orders-of-magnitude higher sulphuric-acid concentrations (measured as total sulphate in this study) would contribute to a higher fraction of particle growth rate than assumed from the measurements by mass spectrometers (i.e. sulphuric-acid monomer). However, the observed growth rates by sulphate-containing vapour in this study does not directly imply similar situation on field, where the sources of sulphate are much more diverse.

1 Introduction

Secondary particle formation by gas-to-liquid conversion is widely recognized as an important source of aerosol particles in the atmosphere worldwide (Weber et al., 1996; Kulmala et al., 2004; Spracklen et al., 2006). These particles may grow to larger sizes and affect the radiative balance of the earth by scattering and absorbing ~~the~~ incoming radiation (Feingold and Siebert, 2009). ~~Aerosols can seriously reduce visibility and have also potential health effects (Davidson et al., 2005).~~ Model calculations and observations suggest that new particle formation events with subsequent growth can contribute a ~~significant~~substantial amount to Cloud Condensation Nuclei (CCN) concentrations, which can alter the lifetime and albedo of clouds (Lihavainen et al., 2003 and 2009; Merikanto et al., 2009). Furthermore, aerosols can reduce visibility and have potential health effects (Davidson et al., 2005).

Significant effort has been mad~~on~~e by field measurements and laboratory studies, together with computer simulations, to understand the particle~~-~~-formation mechanism itself and the atmospheric conditions involved in the gas~~-~~-to~~-~~-liquid conversion. Despite ~~the~~such effort and numerous results, the underlying mechanism is not yet ~~solved~~found.

It is widely accepted that sulphuric acid plays a key role in atmospheric nucleation (Kulmala et al., 2006; Sipilä et al., 2010; Brus et al., 2011; Kirkby et al., 2011). Binary nucleation of sulphuric acid and water (Vehkamäki et al., 2002; Yu, 2006; Kirkby et al., 2011), ternary nucleation involving also ammonia and/or amines (Ball et al., 1999; Korhonen et al., 1999; Napari et al., 2002; Benson et al., 2009; Berndt et al., 2010; Kirkby et al., 2011; Zollner at al., 2012) and ion-induced nucleation (Lee et al., 2003; Lovejoy et al., 2004; Yu et al., 2008, 2010; Nieminen et al., 2011) have been suggested as possible mechanisms for ~~the ~~nucleation to occur in the atmosphere. Ions have been shown to lower the thermodynamic potential of nucleation (Arnold 1980; Winkler et al., 2008; Kirkby et al, 2011~~) ~~), but the role of ions in nucleation occurring in atmospheric boundary layer ~~nucleation have~~has been shown to be minor (Manninen et al., 2010; Paasonen, et al., 2010, Kerminen et al., 2010; Hirsikko et al., 2011).

Recently several laboratory studies have been conducted concerning the role of sulphuric acid in atmospheric nucleation (e.g. Benson et al., 2008, 2011; Young et al., 2008; Berndt et al., 2008, 2010; Brus et al., 2010, 2011; Sipilä et al., 2010; Kirkby et al., 2011; Zollner et al., 2012) with different methods of producing the gas phase sulphuric acid; with their own advantages and ~~drawbacks.~~disadvantages. For example, the evaporation method of weak sulphuric~~-~~-acid solution used by Viisanen et al~~.,~~. (1997) and Brus et al. (2010 and 2011) introduces a thermal gradient~~ into the beginning of the flow tube.~~. Production of ~~the ~~sulphuric acid with a SO_2 + OH reaction is used in most of the experiments, since it is similar to that observed in atmosphere (e.g. Benson et al., 2008; Berndt et al., 2008, 2010; Sipilä et al., 2010; Kirkby et al., 2011). The SO_2 oxidation method involves ~~usage~~the use of UV light to produce OH radicals. The excess OH must be removed so that it ~~would~~does not disturb the nucleation process itself (Berndt et al., 2010). ~~O~~Another way is to have excess ~~of ~~SO_2, so that all the OH reacts rapidly with SO_2; but for the calculation of the produced H_2SO_4 concentration, the exact concentration of OH produced must be known (Benson et al., 2008). Ball et al., (1999) and Zollner et al., (2012) produced sulphuric acid vapour by saturating N_2 flow in a glass saturator~~-~~-containing pure (~96 % and ~98 %, respectively) sulphuric acid. Ball et al., (1999) varied the temperature of the saturator ~~as~~, whilst Zollner et al., (2012) kept the saturator at constant temperature (303 K) and varied the carrier~~-~~-gas ~~flow rate~~flowrate to change the sulphuric acid concentration.

As stated by others in literature (e.g. Benson et al., 2011; Brus et al., 2011; Kirkby et al., 2011~~)~~), contaminants are ~~most probably~~ present in ~~all~~most of the laboratory nucleation studies. These contaminants arise from different sources ~~like~~, such as from the water used for humidifying the carrier gas or from the carrier gas itself which contains ~~some~~ trace levels of contaminants. It is almost impossible to ~~get rid of~~remove these contaminants, which most probably affect the nucleation process itself.

~~Here we~~ Brus et al. (2011) reported a discrepancy in sulphuric-acid mass-balance between a known concentration of weak sulphuric-acid solution introduced to the experimental setup and a measured sulphuric-acid concentration, even though correction for wall losses and losses to particle-phase was applied, one-and-half orders-of-magnitude difference in sulphuric acid concentration was found (see Fig. 5 in Brus et al., 2011). A large discrepancy between measured sulphuric-acid monomer and total-sulphate concentration was observed in the present ~~a way to produce sulphuric acid vapour from~~study too. To investigate the reason for this discrepancy, we applied a thermally controlled saturator ~~in a wide range of~~(e.g. Wyslouzil et al., 1991; Ball et al., 1999) to produce sulphuric~~-~~-acid ~~concentration~~vapour. The output of the saturator was tested with two independent detection methods (mass spectrometry and ion chromatography) before using the saturator in a sulphuric acid-water nucleation study in a laminar flow tube.

Applying the saturator as the source of the sulphuric-acid vapour made it possible to compare the saturator to the furnace, which was used as the source of the sulphuric acid previously (Brus et al., 2010 and 2011) and eliminate the production method ~~is described,~~as a reason for the discrepancy. The flow-tube measurements with the saturator and the two sulphuric-acid or total-sulphate detection methods were conducted to check reproducibility of particle formation rates~~, size of~~ between the ~~particles~~saturator and ~~produced~~the furnace, with similar observed sulphuric~~-~~-acid ~~vapour~~or total-sulphate concentrations ~~of H_2SO_4-H_2O nucleation experiment are presented and~~. The measured sulphuric-acid or total-sulphate concentrations were compared ~~to the results measured with previous setup where furnace was used to produce sulphuric acid vapour (Brus et al., 2010 and 2011). The experimental setup, where saturator is used, was tested with two independent analytical methods to measure sulphuric~~

~~acid concentration based on different principles. Total losses of sulphuric acid within the flow tube~~and the total losses of sulphuric acid or sulphate were determined ~~and~~for both ~~analytical methods of detecting sulphuric acid compared.~~mass spectrometers and the ion chromatograph. The level of ammonia contaminant in the ~~setup~~system was~~ also~~ determined~~.~~ with the ion-chromatograph method.

~~Introducing saturator as the source of sulphuric acid vapour reduces disadvantages associated with other methods, like a temperature gradient arising from usage of furnace, or calculations of OH concentration produced with UV light and removal of excess OH associated with the oxidation of~~ ~~SO_2~~~~. The major disadvantage using this method is the handling of pure sulphuric acid when filling the saturator. Luckily, the saturation vapour pressure of sulphuric acid is very low and therefore, the sulphuric acid is consumed very slowly. Due to the high hygroscopicity of sulphuric acid, the saturator should not be exposed to humid flow as the pure liquid sulphuric acid would draw water vapour from the flow contaminating the sulphuric acid. This would lead to a significant error in the predicted concentration due to a much higher vapour pressure of water compared to sulphuric acid.~~

2 Experimental

The measurement setup presented here is partially introduced in Brus et al~~.,~~. (2010~~)~~), and only the main principle of the method and the most ~~significant~~substantial changes are described here. The setup for testing the output of the saturator with two independent sulphuric~~-~~-acid or total-sulphate detection methods is described. The instrumentation for sulphuric~~-~~-acid or total-sulphate and freshly~~-~~-formed~~-~~-particle~~s~~ detection is shortly presented.

2.1 Saturator

The saturator was a horizontally placed cylinder made of iron with Teflon insert inside the cylinder (inner diameter, I.D~~.~~., of 5 cm). It was thermally controlled with a liquid~~-~~-circulating bath (LAUDA RC 6) and the temperature was measured just above the liquid surface with a calibrated PT100 probe ~~(±~~(accuracy ± 0.05 K) inserted from the outlet side of the saturator (Fig. 1). The saturator was filled with 150~~—~~-200 ml of pure sulphuric acid (~97 % wt., Baker analyzed). H_2SO_4 vapour was produced by flowing purified, dry, particle~~-~~-free carrier gas through the saturator in the range of 0.05~~ to ~~-1 litres per minute (lpm) saturating the flow with vapour according to the temperature of the saturator. Carrier gas flows were purified in all experiments first with activated carbon capsules (Pall Corp., USA) to remove all organic vapours via diffusion to the surfaces and after with a HEPA filters (Pall Corp. USA) to remove any particles left in the flow. The saturator flow was thermally controlled to the same temperature as the saturator before entering it, to ensure temperature stability inside the saturator.

The theoretical prediction of sulphuric~~-~~-acid vapour concentration was calculated using the equation for vapour pressure from Kulmala and Laaksonen~~,~~ (1990) which uses the measurements by Ayers et al~~.,~~. (1980) and theoretically extrapolates the vapour pressure to lower range of temperatures used in this study:

~~$\ln p = \ln p_0 + \frac{\Delta H_v(T_0)}{R} \times \left[\frac{1}{T} + \frac{1}{T_0} + \frac{0.38}{T_c - T_0} \times \left(1 + \ln \frac{T_0}{T} \frac{T_0}{T} \right) \right]$~~

$$\ln p = \ln p_0 + \frac{\Delta H_v(T_0)}{R} \times \left[-\frac{1}{T} + \frac{1}{T_0} + \frac{0.38}{T_c - T_0} \times \left(1 + \ln \frac{T_0}{T} - \frac{T_0}{T} \right) \right], \qquad (1)$$

~~W~~where p is the vapour pressure (atm), $p_0 = -(10156 / T_0) + 16.259$ atm (Ayers et al., 1980), T is the temperature, T_c is critical temperature, 905 K, and T_0 is chosen to be 360 K so $\Delta H_v(T_0) / R = 10156$. See Kulmala and Laaksonen~~,~~ (1990) for more details. Here the predicted sulphuric~~-~~-acid concentration depends only on saturator temperature~~ and flow rate~~, flowrate through the saturator and mixing flow. Measured sulphuric~~—~~-acid or total-sulphate concentration ~~was~~is compared also to empirical fit by Richardson et al~~.,~~. (1986):

~~$\ln p = 20.70 - \frac{9360}{T}$~~ $\ln p = 20.70 - \frac{9360}{T}$.

(2)

The fit is made to their measurement data in the temperature range of 263.15~~ K —~~-303.15 K, which ~~fit well in to~~suits the temperature range of ~~this~~the present study.

2.2 Setup for testing saturator with mass spectrometers and online ion chromatograph

The saturator was tested in two different tests. First with mass spectrometers: Chemical Ionization Mass Spectrometer (CIMS) (Eisele and Tanner, 1993; Mauldin et al., 1998; Petäjä et al., 2009) and Atmospheric Pressure interface Time Of Flight mass spectrometer, (CI-A~~P~~pi-TOF, Tofwerk AG, Thun, Switzerland and Aerodyne Research Inc., USA; Junninen et al., 2010) with a similar Chemical Ionization inlet as the CIMS (Jokinen et al., 2012). ~~Second~~A second test was done with the instrument for Measuring AeRosols and GAses (MARGA, Metrohm Applikon Analytical BV, Netherlands; ten Brink et al., 2007). Both measurements were performed with the same setup~~. The setup is presented in Figure~~ (Fig. 1~~.~~). The flow from the saturator (0.5 lpm) was mixed with ~~dilution~~another flow of ~~carrier~~the same gas (20 or 40 lpm) after the saturator to meet the inlet flows of the instruments. The relative humidity (RH) was set by 2 or 3 Nafion humidifiers (MD-series, Perma pure, USA) and monitored from the excess flow. The design of the inlet system for mixing the different flows and flow schematics to the instruments can be found in the supplementary material (Fig. S2). Different configurations after the mixing were tested and no difference in the observed concentration was found. The temperature of the saturator was increased in 5~~-~~-degree steps from approximately 273 K to 303 K (MARGA) and 313 K (CIMS and CI-A~~P~~pi-TOF) in order to increase the sulphuric~~-~~-acid concentration. The temperature was kept constant from 2 to 8 hours in order to achieve a steady state. The measured sulphuric~~-~~-acid monomer and total~~-~~-sulphate concentrations were compared to theoretical values calculated from the vapour pressure of sulphuric acid using Eq~~s~~. (1) and (2).

2.3 Flow~~-~~-tube setup for nucleation measurements

The flow~~-~~-tube setup consists of four main parts: a saturator, a mixing unit, a flow nucleation chamber~~,~~ and detection of sulphuric acid or total sulphate and ~~particle detection~~particles (Fig. 2). The sulphuric~~-~~-acid vapour is produced in the saturator and turbulently mixed with clean, particle~~-~~-free carrier gas in the mixing unit. Particles formed ~~before~~inside the ~~mixing unit~~saturator are lost in the 1~~-~~-m long, thermally controlled Teflon tube (I.D. 4 mm) before the mixer, by diffusion ~~or~~and by the turbulent mixing in the mixer. After the mixing unit, nucleation and subsequent growth take place in the ~~2 × 100 cm long~~ laminar flow chamber. The flow chamber ~~is a~~ consists of two 100-cm-long stainless steel cylinders (I.D. 6 cm) connected with a Teflon piece (height 3.5 cm, I.D. 6 cm), positioned vertically and ~~it is~~ thermally controlled with a liquid circulating bath (LAUDA RC 6). One of the 100~~-~~-cm~~-~~-long parts of the flow chamber has four holes on the sides every 20 cm from the beginning of the chamber~~ with one hole in~~. The 3.5~~-~~-cm Teflon connector between the two 100~~-~~-cm flow-tube pieces~~.~~ has also a hole (see Fig. 2). These holes are used to continuously measure temperature in the flow tube with PT100 probes to ensure constant desired nucleation temperature. The RH of the mixing flow is controlled by 2 or 3 Nafion humidifiers. RH and temperature are measured also at the end of the tube with Vaisala HMP37E and humidity data processor Vaisala HMI38. Both saturator and mixing flow of the tube are controlled by a mass ~~flow rate~~flowrate controller (MKS type 250) with an accuracy of ± 3 %. ~~Flow rates~~Flowrates through the saturator for nucleation measurements were kept ~~between~~at 0.13~~ lpm and ~~-0.27 lpm. The mixing flow was kept at approximately 11 lpm~~. The line from the saturator to the mixing unit was kept at the same temperature as the saturator to prevent condensation of sulphuric acid~~.

2.4 H_2SO_4 monomer, sulphate and particle detection

Gas phase sulphuric~~-~~-acid monomers were measured with CIMS or CI-A~~P~~pi-TOF. The CI-inlet used in both instruments works as follows: ~~T~~the sulphuric~~-~~-acid molecules are ionized in ambient pressure via proton transfer between nitrate ions (NO_3^-) and sulphuric acid molecules (H_2SO_4). The nitrate ions are produced from nitric acid with radioactive ^{241}Am-source and mixed in a controlled manner in a drift tube~~ utilizing~~, using a concentric sheath and sample flows together with electrostatic lenses.

After the ionization in the inlet, the instruments differ from each other. In the CIMS sample, flow is dried using a nitrogen flow to dehydrate the molecules before entering the vacuum system~~.~~ and detection in the quadrupole mass spectrometer. In the CI-A~~P~~pi-TOF, a ~~flow rate~~flowrate of 0.8 lpm is guided through a critical orifice. The ions are guided through the differentially pumped ~~APi~~Atmospheric pressure interface (Api) and finally to the TOF for detection according to the ions’ ~~*m/z* ~~mass-to-charge ratio.

The monomer concentration is determined by the ratio of the resulting ion signals (HSO_4^- and $HSO_4^- \cdot HNO_3$) and the reagent ion signals (NO_3^-, $HNO_3 \cdot NO_3^-$ and $(HNO_3)_2 \cdot NO_3$~~$^-$).~~$^-$). This ratio is then multiplied ~~with~~by the instrument~~-~~-dependent calibration factor in both instruments. ~~Calibration~~The calibration factor used here was $5 \cdot 10^9$ for both instruments. Neither CIMS nor CI-A~~P~~pi-TOF was ~~not ~~calibrated using the saturator setup, but instead before the experiments using the standard calibration procedure of oxidation of SO_2 with OH (Kürten et al., 2012). For more information about the calibration of CIMS, see Berresheim et al~~.,~~. (2000), Petäjä et al~~.,~~. (2009), Zheng et al~~.,~~. (2010) and Kürten et al~~.,~~. (2012). The nominal sample ~~flow rate~~flowrate of these instruments is ~10 lpm. We considered only the monomer concentration, although detection of dimers and even larger clusters of pure sulphuric acid is possible with CI-A~~P~~pi-TOF. This ~~is due to following reasons:~~was done because the dimer concentration was always in the magnitude of ~1 % of monomer concentration and ~~larger (~~the trimer concentration was in the magnitude of ~1 % of the dimer concentration and ~~tetramer) cluster concentrations were even lower~~so on (e.g. Jokinen et al. 2012). The charging efficiency might not be the same for these clusters as it is for monomer. This would cause the calibration factor to change and the calculated concentration to be erroneous. The uncertainty in the resulting monomer concentration is estimated to be a factor of ~2. The nominal lower detection limit of CIMS and CI-A~~P~~pi-TOF is estimated to be $5\cdot10^4$ cm^{-3}, and the upper limit is approximately 10^9 cm^{-3} for both instruments. At this high concentration, the primary ~~ion concentration~~ions start to deplete causing the calibration ~~constant~~factor to change.

The total sulphate concentration was measured with an online ion chromatograph MARGA 2S ADI 2080. MARGA is able to detect 5 gases ~~from~~in the gas phase (~~-~~HCl, HNO_3, HONO, NH_3, SO_2) and 8 major inorganic species ~~from~~in aerosol phase (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}). The sample flow is ~16.7 lpm. From the sample flow, all (more than 99.7 %) of water~~-~~-soluble gases are absorbed ~~in to~~into a wetted rotating denuder (WRD). Based on different diffusion velocities, aerosols pass the WRD and enter a Steam-~~jet aerosol collector~~Jet-Aerosol-Collector (SJAC) (Slanina et al., 2001). In the SJAC, conditions are supersaturated with water vapour, which condenses onto particles and the particles ~~are collected to~~thus collect at the bottom of the SJAC. Sample solutions are drawn from the WRD and the SJAC into syringes (25 ml) and are analysed one after another once an hour. Samples are injected in cation and anion chromatographs with an internal standard (LiBr). Components are detected by conductivity measurements. The detection limits are 0.1 µg m^{-3} ~~or~~ or better. For more information about the instrument, see Makkonen et al~~.,~~. (2012).

In our previous study (Brus et al., 2010~~)~~), the total sulphate concentration was measured using the method of bubblers~~,~~: where a known ~~flow rate~~flowrate from the flow tube was bubbled through alkaline solution, thus trapping sulphate. This solution was then analysed using offline ion chromatography. See Brus et al., (2010) for details. The method of bubbler is analogous to the MARGA and the main difference is that MARGA is an online ~~as~~method, whilst bubbler is an offline method.

The total~~-~~-particle number concentration was measured with a Particle Size Magnifier (PSM, Airmodus Oy, Finland, Vanhanen et al., 2011, coupled with CPC TSI model 3772) and with Ultra-Fine CPC’s (UFCPC, TSI models 3776, 3025A) with cut-off mobility diameters of ~1.5 nm and ~3 nm, respectively. Differential Mobility Particle Sizer (DMPS) was used to measure particle number size distribution from 3 to ~250 nm in a closed~~-~~-loop arrangement (Jokinen and Mäkelä, 1997) using a blower to measure the wet size of the particles. The DMPS was run with a sheath flow of ~11 lpm and sample flow of 1.5 lpm in the short HAUKE-type Differential Mobility Analyzer (DMA). The DMA was coupled with UFCPC (TSI model 3025A) and with a bipolar radioactive (^{63}Ni) neutralizer. The charging efficiencies were calculated following the parameterization of Wiedensohler and Fissan (1991). The RH of the sheath flow was monitored to ensure that it ~~is~~was same as the RH in the chamber.

3 Results~~ and discussion~~

To quantify the sulphuric acid input for flow~~-~~-tube nucleation measurements, the saturator output was tested in two experiments~~,~~: first with CIMS and CI-A~~P~~pi-TOF and ~~latter~~second with MARGA. After the tests, nucleation measurements of sulphuric acid-water system were conducted. This enabled direct comparison ~~to~~with the sulphuric~~-~~-acid production method used in our previous studies (Brus et al., 2010 and 2011~~).~~), so that the production method can be discounted as a reason for the discrepancy. Presented values from CIMS, CI-A~~P~~pi-TOF and MARGA measurements are residual, i.e. measured values at the end of the flow tube accounting for dilutions, if not otherwise mentioned to be different.

3.1 Test of the saturator

Results of the saturator test are presented in ~~figure~~Fig. 3 as measured sulphuric~~-~~-acid or total-sulphate concentrations and predicted values by Eq~~s~~. (1) and (2) as a function of temperature of the saturator. The mixing flows were 40 (dry and RH 15 %) or 20 lpm (for RH 29 %) for CIMS and A~~P~~pi-TOF and 20 lpm (only dry conditions) for MARGA measurements. Tests with MARGA were performed with dry conditions, since it was noticed that the RH did not have any influence on the results from the tests with mass spectrometers. MARGA uses supersaturated conditions to grow the particles and collect them in the SJAC, hence initial RH is not expected to have any influence. Saturator ~~flow rate~~flowrate was 0.5 lpm. Mass spectrometers were tested ~~at~~in dry and humid conditions. Dry experiments were run with two mass~~-~~-spectrometer inlet ~~flow rates~~flowrates (6 and 10 lpm) and with extra 1 m (I.D. 4 mm) Teflon tubing between the saturator and the mixing unit, to test the effect of wall losses. Humidified experiments were done with two inlet ~~flow rates~~flowrates (6 lpm for RH 29 % and 10 lpm for RH 15 %). MARGA experiments were conducted ~~at~~in dry conditions.

The total sulphate concentration measured with MARGA (black squares) fits the prediction by Eq. (2) (dashed line) very well and the prediction by Eq. (1) (solid line) underestimates the measured total sulphate concentration slightly. MARGA has a relatively ~~high~~fast inlet ~~flow rate~~flowrate (~16.7 lpm) so inlet losses are low~~, but~~; however, with increased temperature of the saturator, diffusional losses are visible.

Sulphuric~~-~~-acid monomer concentration measured with CIMS and CI-A~~P~~pi-TOF fit each other very well, but they show one~~-~~-to~~-~~-two orders~~-~~-of~~-~~-magnitude lower concentrations than predicted by Eq. (1) and (2) and measured total sulphate with MARGA. The slope is similar ~~as~~to the predictions and ~~as~~to the points measured with MARGA. The dimer ~~concentrations were~~concentration was always approximately 1 to 10 % (increasing with increasing saturator temperature) of the monomer concentration and trimer approximately 1 % of the dimer concentration (see supplementary material, Fig. S5).

Relative humidity ~~does~~did not have any ~~significant~~substantial effect on the measured values by CIMS and CI-A~~P~~pi-TOF. RH can affect the wall losses by preventing the sulphuric ~~acid to evaporate~~acid’s evaporation from the inlet walls~~ as~~, since the vapour pressure of water is several orders of magnitude higher than that of the sulphuric acid. The predictions by Eq~~s~~. (1) and (2) do not consider relative humidity~~ as~~, since the flow through the saturator is always dry. The relative humidity of the mixing flow causes the sulphuric acid molecules to get hydrated ~~as~~since sulphuric acid is very hygroscopic; but because the results from humid and dry measurements are very similar, CIMS and CI-A~~P~~pi-TOF can be considered ~~measuring~~to measure well in humid conditions also. The effect of RH is discussed in Eisele and Tanner (1995) and our results agree with the discussion there.

~~Change~~A change of the nominal inlet ~~flow rate~~flowrate of CIMS and CI-A~~P~~pi-TOF ~~do~~did not have large effect~~ either~~. The inlet lines were short (~20 cm) in the saturator tests so the wall losses due to lower inlet ~~flow rate does~~flowrate did not play ~~a big~~any significant role. Using ~~the~~ instruments with a lower ~~flow rate may~~flowrate might alter the measured concentration as the calibration factor ~~as it~~ is acquired with inlet ~~flow rate~~flowrate of 10 lpm.

~~Tests with different saturator flow rates (0.05 – 1 lpm) were conducted to estimate the limits of the saturator flow (not shown in Fig. 3). With 0.05 lpm saturator flow rate diffusional losses to the walls dominated causing the measured sulphuric acid concentrations decrease as a function of the saturator temperature. In the saturator flow rate range from 0.2 up to at least 1 lpm, sulphuric acid concentrations behaved as expected. Results of different flow rate tests,~~

~~as well as results from tests with carrier gases with different purity, can be found in the supplementary material (sections 3 and 4).~~

Extra saturator tests with mass spectrometers were done using three different carrier gas purities (N_2 6.0, N_2 5.0 and pressurized air) to check if the carrier gas used in our experiments (pressurized air) was more dirty than the most pure commercial ones. Two different purity sulphuric acids (~97 % and 100 %) were tested also to check if the purity of the acid itself has an influence. Changing the carrier gas or the sulphuric acid purity did not affect the observed sulphuric-acid concentration (see supplementary material, Fig. S3 and S4). The measured sulphuric-acid monomer concentration was one-to-two orders-of-magnitude lower than the prediction by Eq. 1. Tests with different saturator flowrates (0.05-2 lpm) showed that with flowrates below 0.1 lpm, diffusion losses dominated: causing the measured concentration to decrease as a function of the saturator flowrate. Above 0.15 lpm, the observed results behaved as expected. The measured cluster distributions (monomer, dimer and trimer) with different carrier gas purity were constant through the measured saturator flowrate range (Fig. S5). The ratios between monomer-to-dimer and dimer-to-trimer were between 1:10 and 1:100 with all carrier gases. From these results it is evident that the carrier gas used in our studies does not contain more contaminants than the most pure ones commercially available. CI-Api-TOF mass spectra observed with different carrier gases were investigated further to find the missing sulphuric acid. A large number of peaks were found to correlate with mass 97 (HSO_4^-), which is the ionized sulphuric-acid monomer, with all carrier gases. The number of these peaks increased as a function of the saturator temperature, suggestive that the sulphuric acid forms clusters with contaminant substances (Supplementary, section 6, Fig. S6-S8). The correlating peaks in Fig. S6-S8 are stick masses (i.e. rounded to nearest integer), which means that many of those peaks have actually several peaks within them. This is shown in Fig. S9-S11 where the mass spectrum from CI-Api-TOF is zoomed in. Unfortunately, summing up all of these correlating peaks to calculate the total sulphuric acid concentration is not feasible, since these clusters are not identified (i.e. it is not known what molecules those clusters are composed of) and the sheer number of these peaks is overwhelming. For more details and discussion of the extra saturator tests, see supplementary material.

3.2 Losses of sulphuric acid and sulphate ~~and sulphuric acid~~ in the flow tube

Total losses were not directly measured but they were determined by comparing results from saturator tests ~~to~~with the results from nucleation measurements. The setup of the measurements was similar in both experiments except for the flow tube ~~that was ~~used in nucleation measurements. By accounting for the different mixing ratios of saturator ~~flow rate~~flowrate and mixing ~~flow rate~~flowrate, these measurements become comparable and the total losses in the flow tube can be determined. The Total Loss Factor (*TLF*) includes wall losses and losses to the particle phase (nucleation and condensational losses).

Figure 4 presents the measured sulphuric~~-~~-acid~~-~~-monomer and total~~-~~-sulphate concentration from the saturator tests (squares) and nucleation measurements (stars) as a function of the saturator temperature. Saturator tests ~~a~~were done in dry conditions and nucleation measurements in RH 30 %. ~~Inlet~~An inlet pipe is used to connect ~~a~~the mass spectrometer to the flow tube. Brus et al. (2011) state that the Wall Loss Factor (*WLF*) in the inlet pipe of length 100 + 22 cm is WLF_{inlet} = ~4. This factor, together with the mixing ratios, was ~~used to account~~accounted for to make the data ~~so that they would be~~sets directly comparable.

A linear fit was applied to the data and *TLF* values were determined from the ratio of the fits. The *TLF* values were determined for a saturator temperature range of 286~~–~~-300 K for CIMS and 284~~–~~-297 K for MARGA depending on the measurement range of the data. The average *TLF* values are 14.2 ± 4.2 for CIMS and 10.0 ± 1.2 for MARGA. The R^2~~-~~values for the fits are 0.96, 0.87, 0.90 and 0.61 for CIMS saturator test, CIMS nucleation measurement, MARGA saturator test and MARGA nucleation measurement, respectively.

From ~~figure~~Fig. 4, it is evident that wall losses are not the only losses affecting the measured concentrations ~~as~~since the trends in the fits for nucleation measurements are less steep than the ones from saturator tests. The losses to the particle phase also affect the situation. The maximum losses of sulphuric acid to particle phase are calculated using the DMPS data measured at the end of the nucleation chamber only. The total volume of the particles is calculated within the size distribution assuming that the particles are composed only of pure sulphuric acid with density of 1.84 g cm^{-3}. The losses of sulphuric acid to particles range from 0 % (dry conditions, T_{sat} = 273 K) up to maximum of 1.4 % (RH = 30 %, T_{sat} = 292 K) of the total sulphate concentration. Higher saturator temperature increases the number and the diameter of the particles, and relative humidity increases the diameter of the particles. The losses to the particle phase are ~~significant~~substantial at the highest values of saturator temperature but this estimate is the maximum limit ~~as~~since the particles are not composed only of pure sulphuric~~-~~-acid molecules. Contaminants from the flow condense to the particle phase or ~~get ~~bond with sulphuric acid. ~~Also, when~~When using humid conditions, sulphuric~~-~~-

acid particles uptake water ~~as~~since sulphuric acid is very hygroscopic. At the highest temperature of the saturator, the size distribution unfortunately extends out of the DMPS range (3-250 nm~~) and particles larger than 250 nm are not accounted for the losses to the particle phase,~~), thus ~~on the other hand~~conversely underestimating the losses. Losses to the clusters smaller than the cut-off size of the particle counters are ~~probably significant. For more details about the losses to the particle phase see supplementary material (Section~~ substantial. The maximum losses to the particle phase have been calculated for each of the saturator temperature values and plotted with the measured monomer and total sulphate concentrations together with the prediction from Eq. (1) in Fig. S1 in supplementary material. Even summing up the measured monomer concentration and the losses to the particle phase leaves the summed total concentration at least one order of magnitude lower than the measured total sulphate and the prediction by Eq. (1).

3.3 Nucleation measurements

Formation rates J of sulphuric acid-water were measured in the range from 0.1 to ~300 $cm^{-3}s^{-1}$ with sulphuric acid monomer concentration approximately from $5\cdot10^5$ to 10^7 cm^{-3} or in total sulphate concentration approximately from $4\cdot10^8$ to $3\cdot10^9$ cm^{-3}. Formation rates are usually reported as $J_{1.5}$ or J_3 (cut-off sizes of the particle counters are 1.5 nm for PSM and 3 nm for UFCPC TSI models 3776 and 3025) as discussed in Kulmala et al~~.,~~. (2012). However, particles measured at the end of our flow tube were almost always in the range of 8~~–~~-20 nm, so we report formation rates as they were determined with our particle counters. The purpose of these nucleation measurements is to be able to compare the formation rates and the sulphuric-acid or total-sulphate concentrations, between the two sulphuric-acid vapour-production methods. The results are discussed below.

Figure 5 presents DMPS and CIMS data for one cycle of saturator temperatures. ~~The upper most panel~~Panel a) presents the number size distribution as a function of time, ~~2nd-~~panel ~~from top~~b) the total particle number concentration, ~~3rd-~~panel ~~from top~~c) shows the hourly averaged sulphuric~~-~~-acid monomer concentration with standard deviation as the error bars and ~~the lower most~~ panel d) shows hourly averaged saturator temperature. One can see from ~~figure~~Fig. 5, ~~1st and 2nd-~~panels ~~from the top~~a) and b), that when the temperature of the saturator changes, the number concentration and the number size distribution are not stable immediately. The sulphuric~~-~~-acid concentration overshoots ~~a bit~~slightly at the beginning ~~as~~whilst the system ~~is stabilizing~~stabilizes to steady state. ~~First~~The first hour ~~from~~of averages from each of the saturator temperatures ~~were~~was excluded to ensure only ~~stable~~ steady-state data (std(T) = ± 0.05 K) were included in the averages. When a new cycle started, the T_{sat} dropped from the maximum value (~315 K) to the minimum (273 K) causing a long period of unstable data, and the first two hours were excluded from the beginning of the cycle. In ~~the upper most~~ panel a) in ~~figure~~Fig. 5, nucleation is the main process below temperature of ~290 K and growth takes over at higher temperatures. This can be seen as the bimodal distribution at highest saturator temperatures.

Figures 6 and 7 present the number concentration N_{exp} (~~upper left~~ panel~~),~~ a)), geometric mean diameter D_p (~~upper right~~ panel~~)~~ b)) and apparent formation rate J (~~lower left~~ panel~~)~~ c)) of freshly nucleated particles with sulphuric~~-~~-acid monomer concentration [H_2SO_4 monomer] or total sulphate [SO_4^{2-}] (~~lower right~~ panel~~)~~ d)) as a function of saturator temperature T_{sat} for nucleation temperature of 298 K with several different relative humidity values (Fig. 6) and saturator ~~flow rates~~flowrates (Fig. 7). The formation rate is reported the observed particle concentration N_{exp} divided by the residence time τ.

From ~~figure~~Fig. 6 ~~one can see~~, it is evident that ~~in the flow tube measurements with CIMS and CI-APi-TOF~~ all ~~the~~measured variables behave as expected ~~to~~as a function of the ~~increasing~~ saturator temperature~~. Increasing saturator temperature increases number concentration and diameter of freshly nucleated particles. The number concentration and formation rate seems to saturate at the highest temperatures but this~~, except for the apparent saturation ~~is due to the limits~~ of the ~~PSM (coupled with CPC, TSI model 3772). The upper limit of~~ observed particle concentration ~~for CPC 3772 is~~ (and hence, the formation rate). PSM was coupled with the TSI model 3772 CPC's, which has an upper limit of 10^4 cm^{-3}~~, so higher concentrations were still measured as 10^4 cm^{-3}.~~ for the particle concentration. This ~~is also supported by DMPS data which shows higher total~~caused the observed particle concentration to saturate in Fig. 6, even though the particle concentration ~~than PSM.~~was confirmed to increase to higher values by DMPS data (not shown in the Fig. 6). Coagulation has a minor effect on the particle number due to a short residence time (τ = 30 s) and relatively low particle concentration. The relative humidity affects mostly the diameter of the particles, but also decreasing RH decreases the formation rate if similar sulphuric acid concentration is considered. ~~Lower~~A lower formation rate with decreased RH might be caused by the diminishing of the particle diameter below the detection limit of ~~UCPC~~the UFCPC (TSI model 3776).

In ~~figure~~Fig. 7, the squares present measurements ~~at~~during dry conditions and stars ~~with~~during RH of 30 %. ~~The lower right panel~~Panel d) shows also the detection limit of MARGA for total sulphate concentration. ~~Detection~~The detection limit was determined from 20 hours of measurements with saturator ~~flow rate~~flowrate set to zero and averaged over the time period. ~~Detection~~The detection limit was $1.35 \cdot 10^9$ cm^{-3}. All the total sulphate concentrations measured below this detection limit were considered as erroneous and rejected from further analysis, even though these values are presented in ~~figure~~Fig. 7. MARGA can be used with concentration columns to measure lower concentrations of species but it was not available in this study.

From ~~figure~~Fig. 7, one can see that all the variables responded in a similar manner as CIMS and CI-A~~P~~pi-TOF experiment (Fig. 6). As the temperature of the saturator approaches ~~to~~ the temperature of the mixing unit (laboratory temperature, ~294 K) the number concentration of particles ~~drops~~decreases and starts to increase again when saturator temperature is ~~higher~~greater than that of the mixing unit. This is an artefact of the setup.

~~Main~~The main difference between ~~figures~~Fig. 6 and 7 ~~can be found in the mean diameter of the particles. In the experiment with CIMS and CI-APi-TOF, the diameter ranges all the way up to ~130 nm (Fig. 6, right upper panel) as in the experiment with MARGA,~~ is the maximum diameter ~~is only approximately ~23 nm (Fig. 7 right upper panel). The main reason is that in the CIMS and CI-APi-TOF experiment the~~reached. Due to the greater maximum saturator temperature ~~was increased 15~~ (315 K ~~higher than in the MARGA experiment. This increases sulphuric acid vapour concentration approximately order of magnitude which condenses on the surface of the particles growing their diameter. At lower saturator temperatures (< 290 K) the mean diameters are closer to each other at similar saturator temperatures and relative humidity.~~) in the experiment with the mass spectrometers, the maximum diameter reached up to ~130 nm compared to the ~23 nm with the experiment with MARGA. The residence times in the flow tube are the same in both experiments (~30 s). The measured sulphuric-acid monomer concentration is at typical atmospheric levels, but the growth rates are much higher: indicating higher concentration of sulphuric-acid-containing condensing vapour than the detected sulphuric-acid-monomer concentration by CIMS. The growth is rather driven by the total sulphate, originating exclusively from the sulphuric acid inside the saturator, than the sulphuric-acid-monomer concentration.

To show the contribution of the sulphate to the growth rate, the model described in Škrabalová et al. (2014) was used to calculate the diameter (D_p) and growth rate (GR) of the particles. Measured sulphuric-acid monomer and total-sulphate concentrations (Fig. 6 and 7, panel d), RH 30 %) were multiplied by the TLFs to obtain the initial concentrations of vapour at the beginning of the flow tube. Diameter of 1.5 nm was chosen as the initial cluster size according to Kulmala et al. (2007). The model was used with three scenarios of particle neutralization by ammonia: (0) no neutralization, particles composed of sulphuric acid and water, (1) neutralization to ammonium bisulphate-water particles and (2) neutralization to ammonium sulphate-water particles. When accounting for the initial sulphuric-acid monomer concentration as an input, the resulting diameter (D_p) was always below 2 nm with growth rates (GR) ranging approximately from 1 to 15 nm h^{-1} as a function of the sulphuric-acid concentration (i.e. saturator temperature T_{sat}) with all scenarios. When total-sulphate concentration was used as an input, the resulting particle diameters and growth rates fit well with the measured particle diameters presented in Fig. 7 for all scenarios (see suppl. Material, section 7 and Fig. S12).

3.4 Formation rates and comparison to our previous results

The comparison to literature data was omitted in this manuscript as the formation rates in the present study are very similar to our previous results (Brus et al., 2010 and 2011). However, for comparison and review of experimental data on sulphuric-acid nucleation, we refer to Zollner et al., (2012) and Zhang et al., (2012). Figure 8 presents formation rates J of the H_2SO_4-H_2O system as a function of sulphuric~~-~~-acid monomer concentration measured with CIMS at nucleation temperature of T = 298 K and ~~relative humidity~~ RH of ~~RH~~ ~30 %. Sulphuric acid was produced with the method of furnace (red squares, Brus et al., 2011) and with saturator (the black squares, ~~this~~present study). ~~Sulphuric~~ The sulphuric-acid concentration for data from Brus et al~~.,~~. (2011) is presented here as residual concentration (i.e. at the end of the flow tube) so that these two measurements would be comparable. Brus et al~~.,~~. (2011) present their data as the initial concentration. Both ~~data sets~~datasets have almost identical slopes (1.3 and 1.2) and the ~~data sets~~formation rates J have a difference of a factor of 2. For the ~~data set~~dataset measured with the production method of the furnace, the residence time (τ = 15 s) is defined as the time that the particles spend in the flow tube after the nucleation zone. ~~Nucleation~~The nucleation zone was experimentally determined (Brus~~,~~ et al., 2010) and confirmed with CFD model (Herrmann et al., 2010) to be ~~at~~in the middle of the flow tube in the measurements with the furnace, where a thermal gradient was present. For the saturator measurements (~~this~~present work), the residence time (τ = 30 s) was defined as the whole time the particles spend in the flow tube. The difference of the residence time is exactly a factor of 2. Formation rate is defined as the number concentration divided by the residence time, so these two sets of data lie on top of each other if the same residence time would have been used for formation~~-~~-rate determination.

Figure 9 presents formation rates J of H_2SO_4-H_2O as a function of residual total sulphate concentration $[SO_4^{2-}]$ at ~~relative humidity~~RH of~~ RH~~ ~30 % and at nucleation temperature of T = 298 K. Stars ~~presents~~are the data from measurements where sulphuric~~-~~-acid vapour was produced with the furnace and total sulphate measured with bubbler method (Brus et al., 2010). The residence time used in there was τ = 15 s. Squares ~~presents~~are total sulphate measured with MARGA in this study with different ~~flow rates~~flowrates through the saturator, and the residence time was τ = 30 s. All the points have the standard deviation as error bars. The detection limit of MARGA is also marked as a dashed vertical line. Formation rates are similar with both production methods. As~~ in~~ previously, the factor of two difference in the residence time increases the scatter~~ing~~ between the two ~~data sets~~datasets.

Figures 8 and 9 show that apparent formation ~~rate data is~~rates are reproducible with both sulphuric~~-~~-acid production methods~~.~~, with similar observed sulphuric-acid or total-sulphate concentrations. This eliminates the sulphuric-acid production method as a reason for the discrepancy between the measured monomer and total sulphate concentrations. The data ~~is~~are more scattered in ~~figure~~Fig. 9 due to the larger integration times used in MARGA and bubbler measurements. During several hours of integration time, a small change in ~~flow rates~~flowrates can cause a ~~significant~~substantial difference in the resulting concentration. MARGA data ~~is~~are close to the detection limit of the instrument, which also causes larger scatter~~ing~~.

Figure 10 shows comparison of the apparent formation rates J as a function of residual sulphuric~~-~~-acid monomer [H_2SO_4 monomer] or total sulphate concentration [SO_4^{2-}] from this study to our previous studies with the standard deviation as error bars. Note the difference of a factor of two~~ difference~~ between the residence times. Squares show values measured using mass spectrometers (PSM, red and black squares; TSI 3776, green squares). Stars ~~presents~~are data measured using ion~~-~~-chromatograph (i.e. total sulphate) methods with two different UFCPC's (TSI 3025A, black stars and TSI 3776, red stars). Figure 10 shows that the production method does not have ~~significant~~substantial effect ~~as~~since the results lie on same line when comparing results obtained with mass spectrometers or MARGA and bubbler method. The conditions for all the measurements were similar (T = 298 K, RH ~30 %).

The slope of the data measured using MARGA or bubblers is steeper than the slope of the results measured with mass spectrometers. There is a discrepancy of one~~-~~-to~~-~~-two orders~~-~~-of~~-~~-magnitude between sulphuric~~-~~-acid monomer and total~~-~~-sulphate concentration for similar formation rates. The UFCPC 3776 (green squares) was probably undercounting at the lowest sulphuric acid concentrations. This can be seen in ~~figure~~Fig. 10 ~~as~~where the ~~green squares~~lowest observed formation rates are not ~~on line~~consistent with the ~~other squares.~~rest of the data. This is probably caused by the small size of the particles at ~~so~~such low sulphuric~~-~~-acid concentration (1-2·10^6 cm^{-3}) (Sipilä et al., 2010).

3.5 Contaminants

In our previous study (Brus et al., 2011~~)~~), an ion chromatograph was used to determine the background levels of ammonia and it was found that the background concentration was below the detection limit of the IC (500 pptv), accounting for the ~~flow rates~~flowrates in the nucleation chamber. The concentration of background ammonia was measured with the MARGA system in this study. An average total concentration (gas and particle phase) of ammonia was 60 pptv for dry conditions and 126 pptv for RH 30 ~~%~~%, supporting our previous results. The concentration did not change as a function of saturator temperature~~ and~~, thus~~,~~ it is assumed to originate from the purified, particle~~-~~-free air used as carrier gas in all measurements and the ultrapure water (Milli-Q, Millipore) used for humidification. The concentration for dry conditions is in the same order of magnitude as the concentration of total sulphate at the lowest (273 K) temperature of the saturator. W~~it~~hen increasing the saturator temperature, ammonia to total sulphate-ratio decreases from ~1:1 to ~1:10 or less for dry conditions and from ~3:1 to ~1:5 for humid conditions. ~~Results of extensive measurements and discussion of the influence of several different carrier gases on measured sulphuric acid concentration by mass spectrometers can be found in the supplementary material (section 3).~~The extra saturator tests, mentioned in section 3.1 and found in supplementary material, showed that the carrier gas used in this experiment was at least as pure as the most pure gas available commercially (AGA, N$_2$, 6.0), which has impurities less than 1 ppm, including hydrocarbons less than 0.1 ppm. According to the results found in supplementary material, the actions taken to purify the carrier gas in these experiments were sufficient. Nevertheless, there were contaminants left in the carrier gas at levels which will affect the nucleation process.

4 Discussion and Conclusions

A ~~method of~~ saturator was used to produce sulphuric~~-~~-acid vapour from neat~~-~~-liquid sulphuric acid for laboratory studies~~ is presented.~~. It was tested and shown to produce similar apparent formation rates at similar conditions to our previous vapour-production method of the furnace. The sulphuric~~—~~-acid or total-sulphate concentration was measured with two independent methods and it was shown to produce exact concentrations as prediction from Richardson et al~~.,~~. (1986) and slightly higher than the prediction from Kulmala and Laaksonen (1990) when measured with MARGA (Fig. 3). Concentrations of sulphuric~~-~~-acid monomer measured with CIMS and CI-A~~P~~pi-TOF was one~~-~~-to~~-~~-two orders~~-~~-of~~-~~-magnitude lower than the total~~-~~-sulphate values measured with MARGA and the prediction by Eq~~s~~. (1) and (2). The only source of sulphuric acid (sulphate measured by MARGA) is the liquid sulphuric acid inside the saturator as seen in Fig. 3. ~~Possible~~A possible reason for the discrepancy is that the sulphuric acid is in particle phase ~~as~~since the saturator is a ~~significant~~substantial source of particles. However, these particles are lost ~~in~~on the way from the saturator to the nucleation chamber due to two main reasons~~; The flow rate~~: (i) the flowrate (0.5 lpm) in the tube (length: 1 m, I.D. 4 mm) from the saturator to the nucleation chamber is relatively low ~~(0.5 lpm)~~ increasing diffusional losses and (ii) the highly turbulent mixing of the saturator flow with the mixing flow (Q_{sat} : Q_{mix} ≈ 1:30 or more) ~~in~~transforms the mixer ~~which is~~into an effective trap for the particles. The loss of the particles is confirmed with DMPS measurements which cannot explain the discrepancy (supplementary material, Fig. S1). Maximum losses to the particle phase ~~range from~~in the flow tube are 0~~ % up to ~~-1.4 % with an average below 1 % of the total ~~sulphuric acid~~sulphate. The discrepancy cannot be explained by the formation of larger clusters containing solely sulphuric acid (dimer, trimer, etc.) either, because the concentration of these clusters ~~are~~is in the order of few percent~~s~~ or lower than the monomer concentration (Supplementary material, Fig. S5).

~~The saturator has been used in combination with a flow tube described earlier (Brus et al., 2010) to measure characteristics of H_2SO_4-H_2O nucleation. It takes about 1 hour to stabilize the sulphuric acid vapour concentration after changing the saturator temperature.~~ The characteristics of the freshly nucleated particles together with the conditions used for the nucleation has been identified and presented (Fig~~s~~. 4~~ to ~~-7). Total losses of sulphuric acid or total sulphate to the whole flow~~-~~-tube setup have been determined for both methods to detect the concentration of sulphuric acid or total sulphate.

The average Total Loss Factors determined are $TLF = 10.0 \pm 1.2$ ($T_{\mathrm{sat}} = 284$~~ K – ~~-297 K) for MARGA and $TLF = 14.2 \pm 4.2$ ($T_{\mathrm{sat}} = 286$~~ K – ~~-300 K) for CIMS both having a slight increasing deviation from the first~~-~~-order losses as a function of saturator temperature (Fig. 4). The second~~–~~-order losses are caused by losses to the particles ~~(minor) ~~and losses to the clusters ~~(major) ~~which are too small to be detected by particle counters.

Formation rates of sulphuric acid-water system were compared to our previous studies (Brus et al., 2010 and 2011), where a method of the furnace was used (Fig~~s~~. 8-10). ~~Results obtained using mass spectrometers lie on the same line~~Obtained apparent formation rates as a function of sulphuric-acid or total-sulphate concentrations were independent of the sulphuric~~-~~-acid vapour~~–~~-production method (furnace vs~~.~~ saturator). ~~At a lower sulphuric acid monomer concentration (1-2·10^{6} cm^{-3})~~Conditions for these studies were similar (T = 298 K, RH ~30 %) but at similar formation rates, the ~~UCPC used (TSI model 3776) was probably undercounting compared to more efficient counter (PSM), which ~~sulphuric-acid monomer concentration is ~~caused by~~one-to-two orders-of-magnitude lower than the ~~small size~~total sulphate. The slope of the ~~particles. The slopes of the fits~~fit to the formation~~-~~-rate data as a function of sulphuric~~-~~-acid monomer concentration ~~are~~(1.3 ± 0.2) is very similar ~~(1.3 and 1.2 for using furnace and saturator, respectively) ~~as obtained in Brus et al~~.,~~. (2011~~).~~) (1.2 ± 0.1). The comparison to our previous measurements was done to check reproducibility of the nucleation-experiment results between the sulphuric-acid vapour-production methods and to eliminate the production method as a possible reason for the discrepancy. The discussion and interpretation of the slopes (section 3.1) and comparison to the atmospheric data (section 3.5) can be found in Brus et al~~., (2011). Nucleation results obtained using bubblers or MARGA agree well when compared to each other. Conditions for these studies were similar (T = 298 K, RH ~30 %) but at similar formation rates, the sulphuric acid monomer concentration is one to two orders of magnitude lower than the total sulphate.~~. (2011).

~~Other possible reasons for this difference between sulphuric acid monomer and total sulphate is that sulphuric acid molecules are most probably bond to some molecule(s) (e.g. amines, ammonia, organics) and not been detected by CIMS or identified from the CI-APi-TOF spectra (Kulmala et al., 2013). As Kurten et al., (2011) state, base molecules can be only in~~

~~minor importance due to the fact that nitrate ion (NO_3^-) will most probably substitute the base out in the CIMS charging process. Nevertheless, there is expected to be a substantial pool of clusters formed of sulphuric acid-base molecules in our system, which are too small to be detected by current state-of-art particle counters such as PSM. These clusters are the main reason for the discrepancy between measured total sulphate and the monomer concentrations. Same or similar clusters are most probably forming in all laboratory nucleation experiments involving sulphuric acid, as there are always contaminants present in the carrier gases (see supplementary material, section 6 and Figs. S6 to S11).~~ Average ammonia concentration of 60 pptv was found in the system for dry conditions and 126 pptv for RH 30 % as a contaminant and it was independent of the saturator temperature. It is assumed to originate from the purified, dry, particle~~-~~-free air used as carrier gas and from the ultrapure water used for humidifying the mixing flow. Ammonia concentration is enough to affect the nucleation process itself ~~significantly~~substantially but the magnitude of this effect was not studied in this work. Ammonia can bind sulphuric acid by forming clusters, which might reduce the monomer concentration measured with CIMS and CI-A~~P~~pi-TOF slightly~~ but as~~. Since the contaminant level was constant and saturator temperature was increased, reducing the contaminant to total sulphate-ratio from ~1:1 to ~1:10 for dry conditions and from ~3:1 to ~1:5 for humid conditions, ~~it~~ does not explain the discrepancy between the two sulphuric~~-~~-acid~~-~~- or total-sulphate-detection methods. Even though the contaminant levels might sound high, those are still below the most-pure commercially available gases (AGA, N_2, 6.0).

Other possible reasons for the difference between sulphuric acid monomer and total sulphate is that sulphuric acid molecules are most probably bonded to some molecule(s) (e.g. amines, ammonia, organics) and not detected by CIMS or identified from the CI-Api-TOF spectra (Kulmala et al., 2013). As Kurten et al. (2011) state, base molecules can be only in minor importance due to the fact that nitrate ion (NO_3^-) will most probably substitute the base out in the CIMS charging process. Nevertheless, there is expected to be a substantial pool of clusters formed of sulphuric acid-base molecules in our system, which are too small to be detected by current state-of-art particle counters such as PSM. These clusters are the main reason for the discrepancy between measured total-sulphate and the monomer concentrations. Same or similar clusters are most probably forming in all laboratory nucleation experiments involving sulphuric acid, as there are always contaminants present in carrier gases. Further analysis of the CI-Api-TOF mass spectra showed a large number of stick-unit masses correlating with sulphuric-acid monomer ion (HSO_4^-) suggesting a large number of clusters containing sulphuric acid which are not used for calculating the sulphuric-acid concentration measured by mass spectrometers (see supplementary material, section 6 and Fig. S6-S11). Sulphuric acid (measured here as sulphate) can contribute to the early growth of ultrafine particles to a much larger extent than currently thought, since most of the sulphuric acid remains undetected. Also the huge number of correlating masses with increasing sulphuric-acid concentration implies that there are numerous substances that can form stable clusters with sulphuric acid that may be the starting point for particle formation.

The total sulphate (originally total sulphuric acid) is responsible for the particle growth as demonstrated in Skrabalova et al~~.,~~. (2014). The contribution of the total sulphate to the nucleation process itself is not yet fully understood. However, recent results suggest that sulphuric acid monomer is the main component in nucleation (Brus et al., 2014) and not the overall sulphuric acid. ~~The ~~To find out which molecules are possibly involved in nucleation, the clusters ~~where the~~with sulphuric acid ~~is bond ~~must be identified from the CI-A~~P~~pi-TOF spectra~~ to understand the possible other molecules involved in the nucleation process.~~.

Acknowledgements

The financial support by the Academy of Finland Centre of Excellence program (project no. 1118615), KONE foundation ~~(grant no. 46-6817) ~~and by the Maj and Tor Nessling Foundation are gratefully acknowledged. The language improvements provided by Curtis Wood are gratefully acknowledged.

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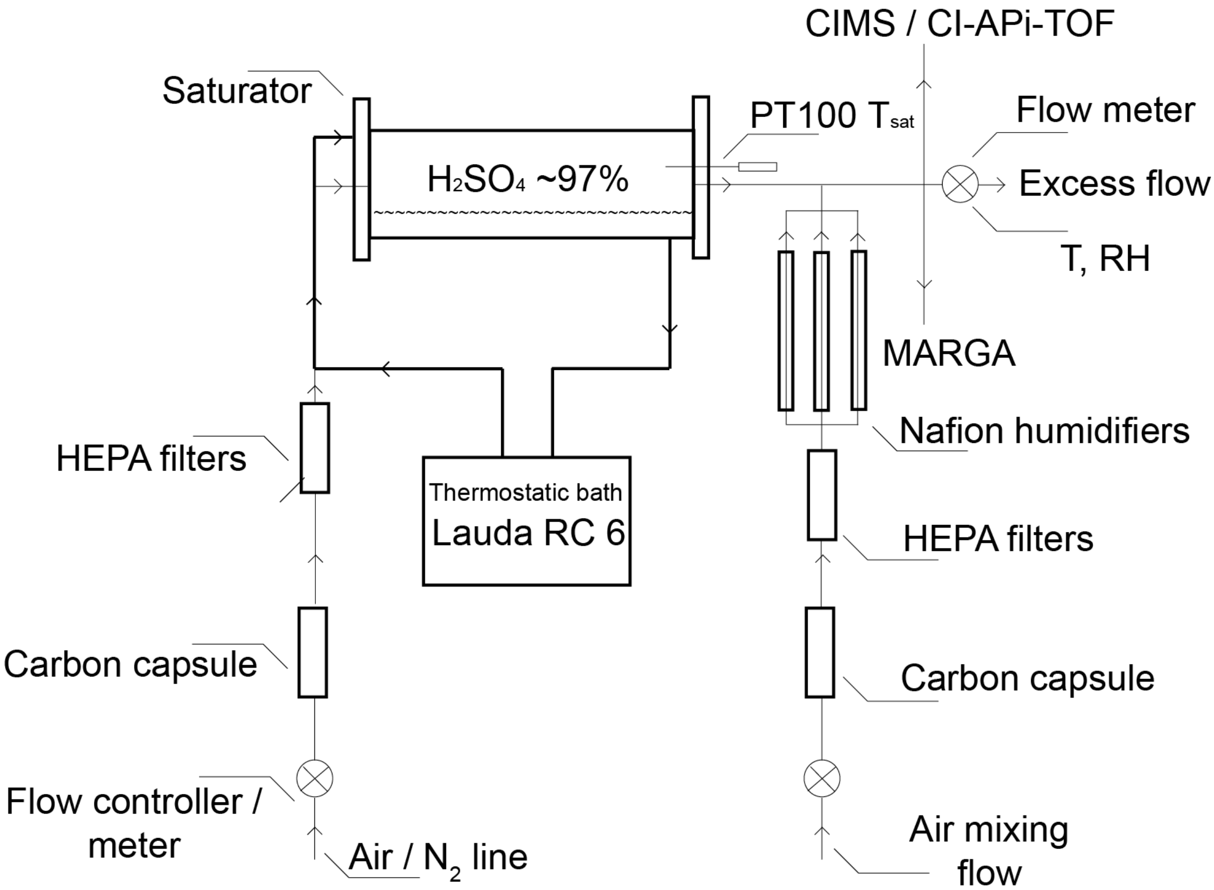

Figure 1. Sechematic figure of the setup for testing the saturator.

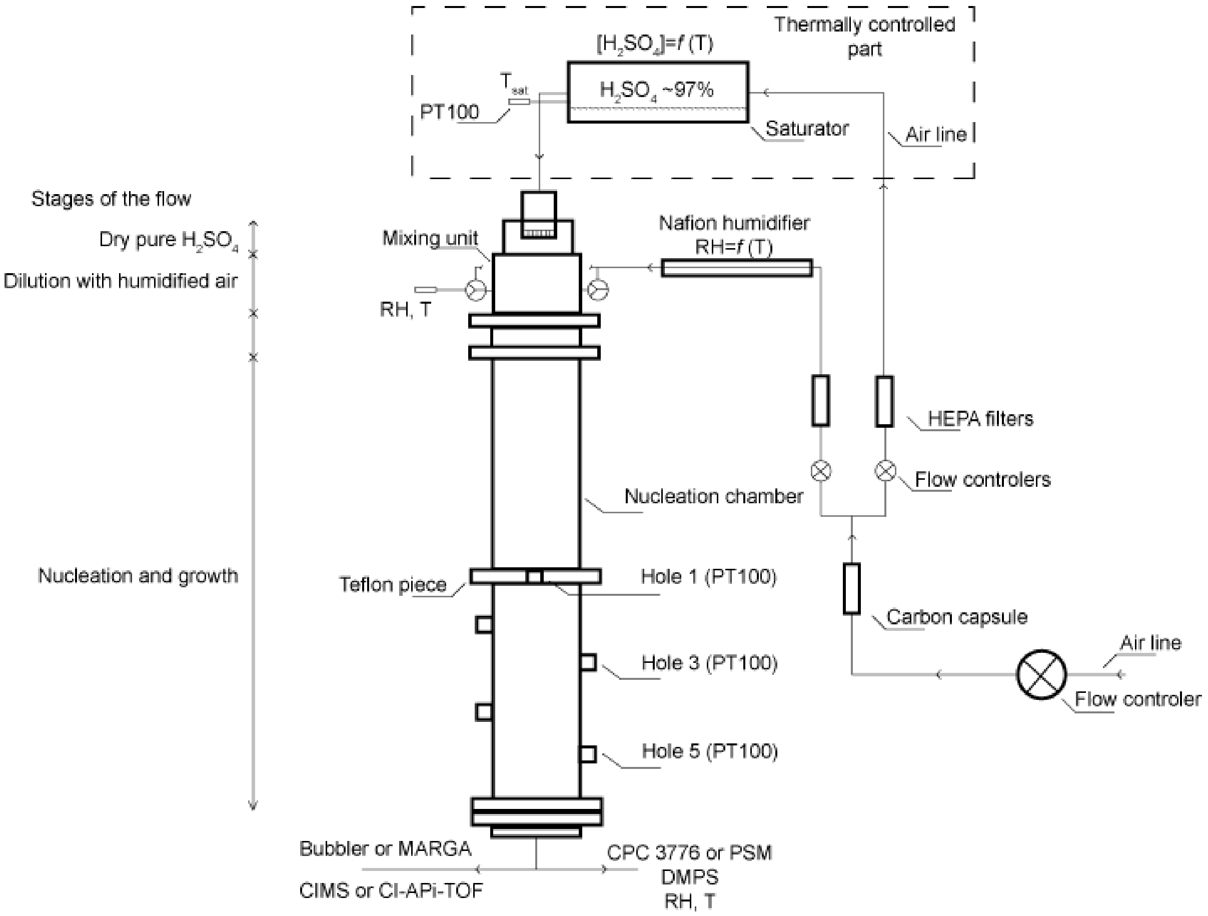

Figure 2. Flow~~-~~-tube setup.

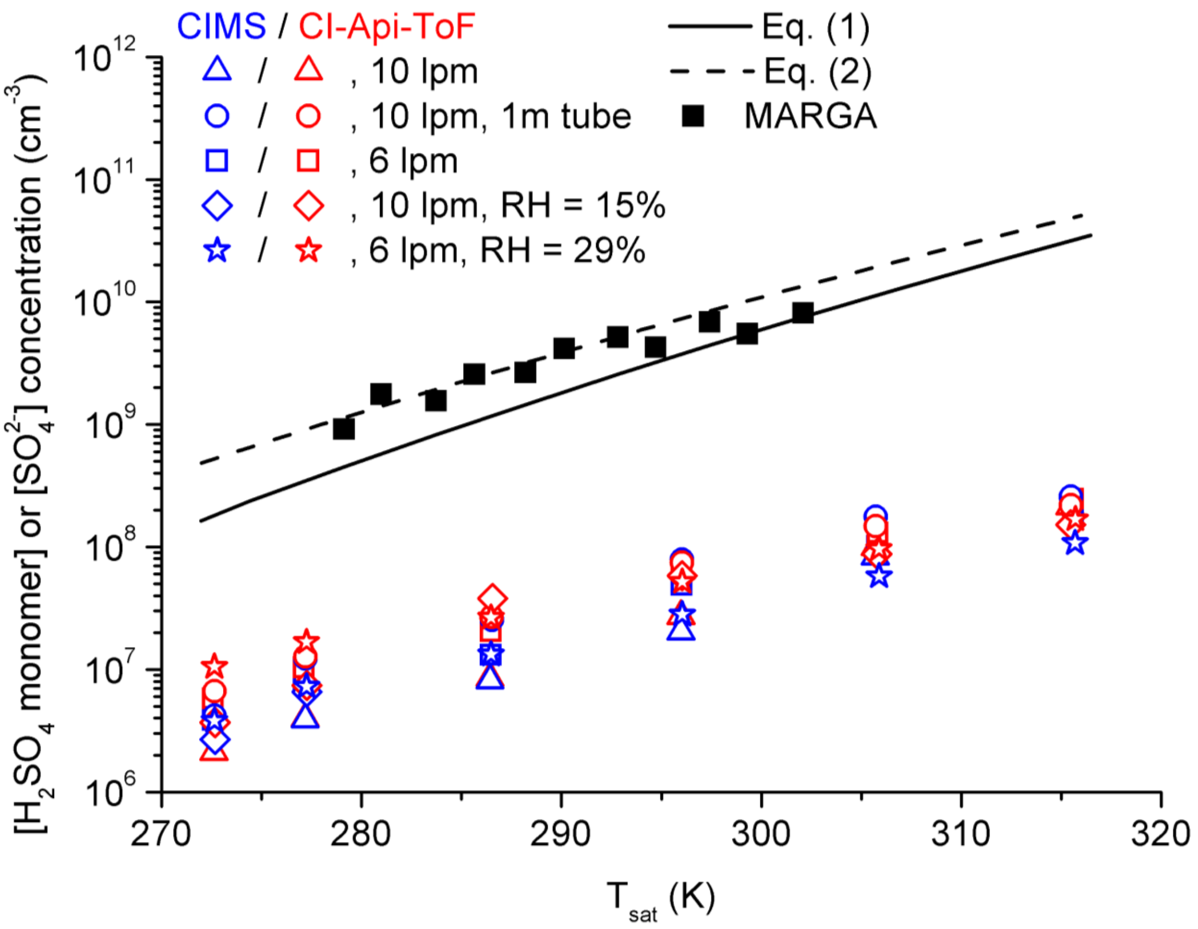

Figure 3. Measured sulphuric~~-~~-acid monomer [H_2SO_4 monomer] and total~~-~~-sulphate [SO_4^{2-}] (black squares) concentrations together with predicted values by Eq~~s~~. (1) and (2) as a function of saturator temperature T_{sat}. Saturator ~~flow rate~~flowrate is Q_{sat} = 0.5 lpm and mixing ~~flow rates~~flowrates were 40 lpm (dry for CIMS and CI-A~~P~~pi-TOF and RH 15 %) and 20 lpm (MARGA and RH 29 %). CIMS (blue markers) and CI-A~~P~~pi-TOF (red markers) have been tested with 6 lpm and 10 lpm (nominal) inlet total ~~flow rates~~flowrates and also with an extra 1 m Teflon tubing after saturator.

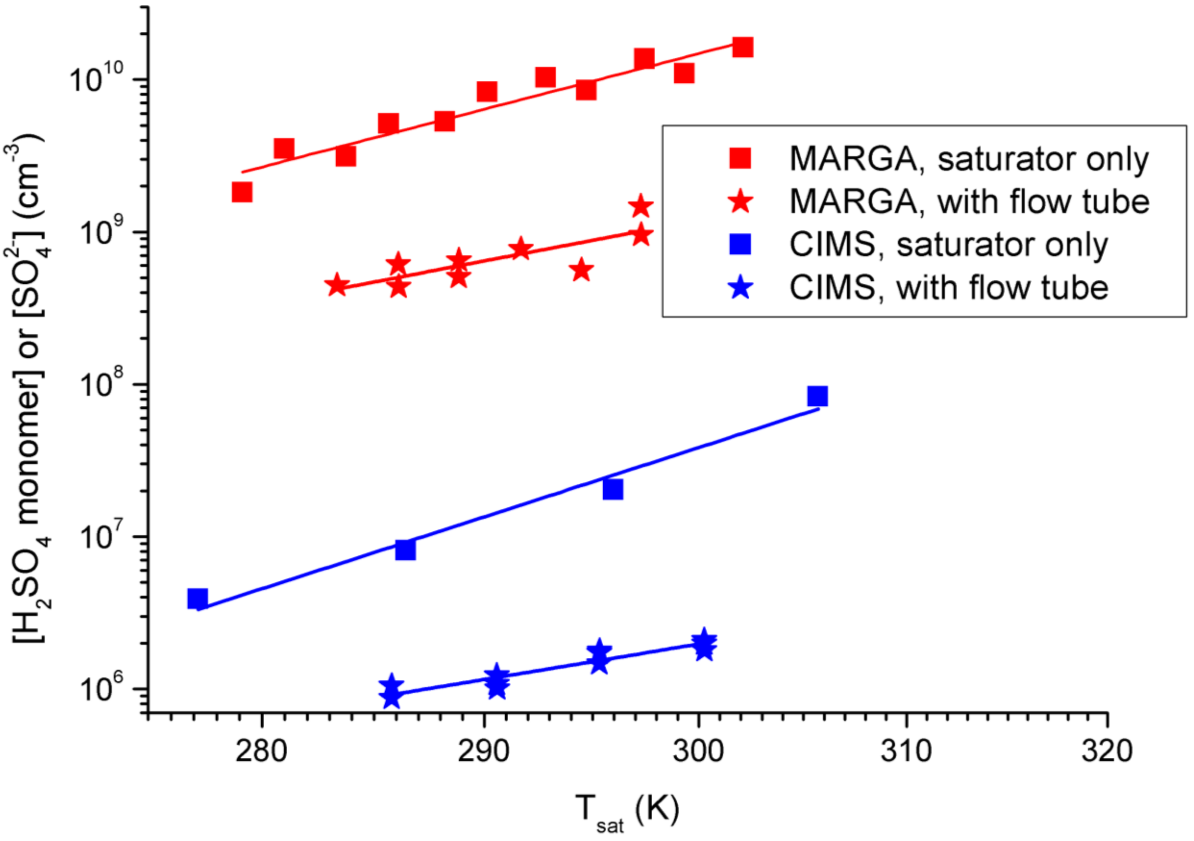

Figure 4. Comparison of MARGA and CIMS data between test with only saturator (dry conditions, squares) and with saturator and flow tube (RH ~30 %, stars). Different ~~flow rates~~flowrates through saturator have been accounted for. Average total loss factors are $TLF_{MARGA} = 10.0 \pm 1.2$ and $TLF_{CIMS} = 14.2 \pm 4.2$. See text for details.

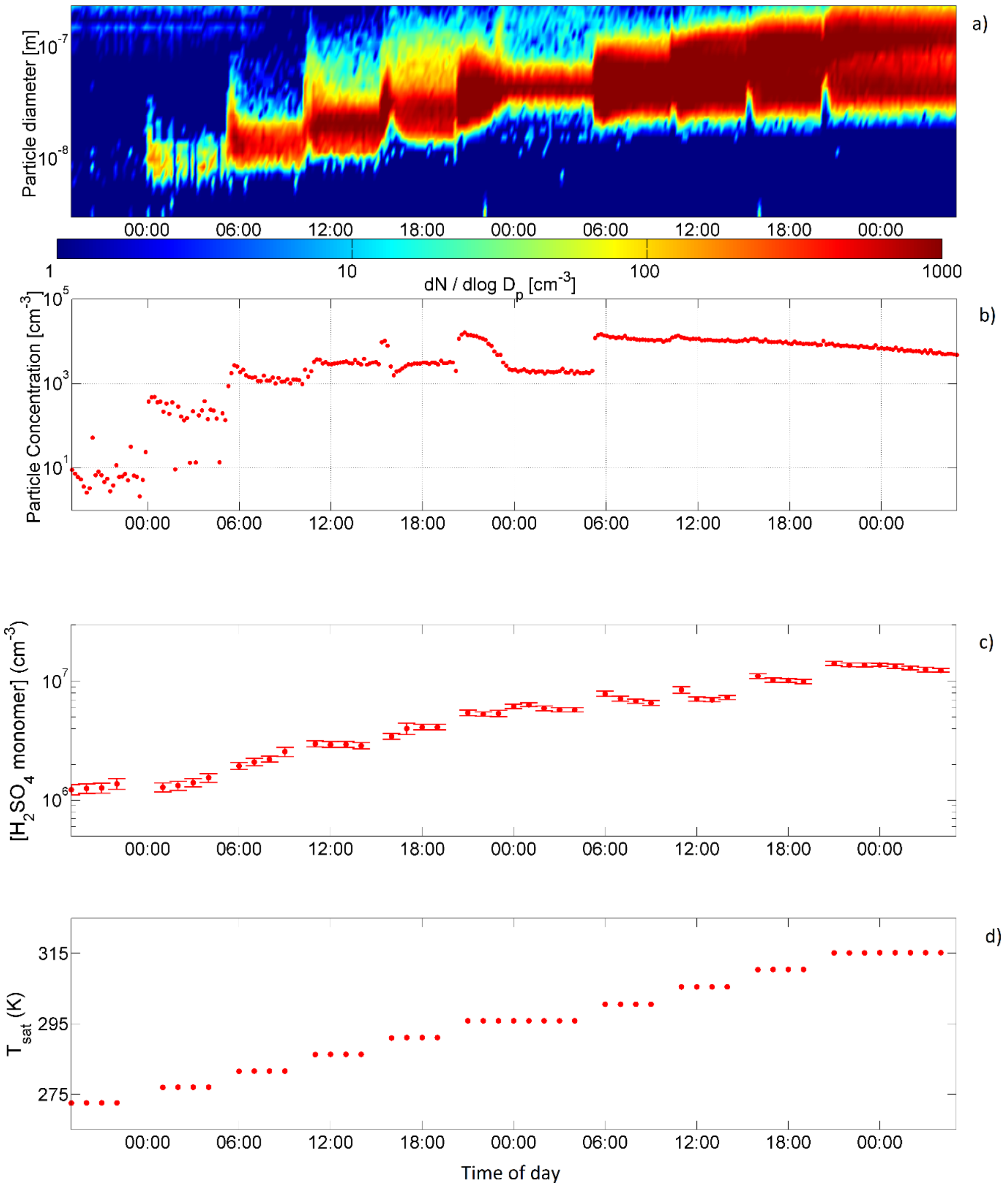

Figure 5. DMPS and CIMS data from one T_{sat} cycle. ~~Upper most panel~~ Panel a) shows the number size distribution, ~~2nd~~ panel ~~from top~~b) shows the total number concentration from DMPS, ~~3rd~~ panel ~~presents~~c) shows the CIMS~~—~~-measured sulphuric~~—~~-acid monomer concentration averaged over one hour with standard deviation as error bars and ~~the last~~ panel d) shows hourly averaged temperature of the saturator.

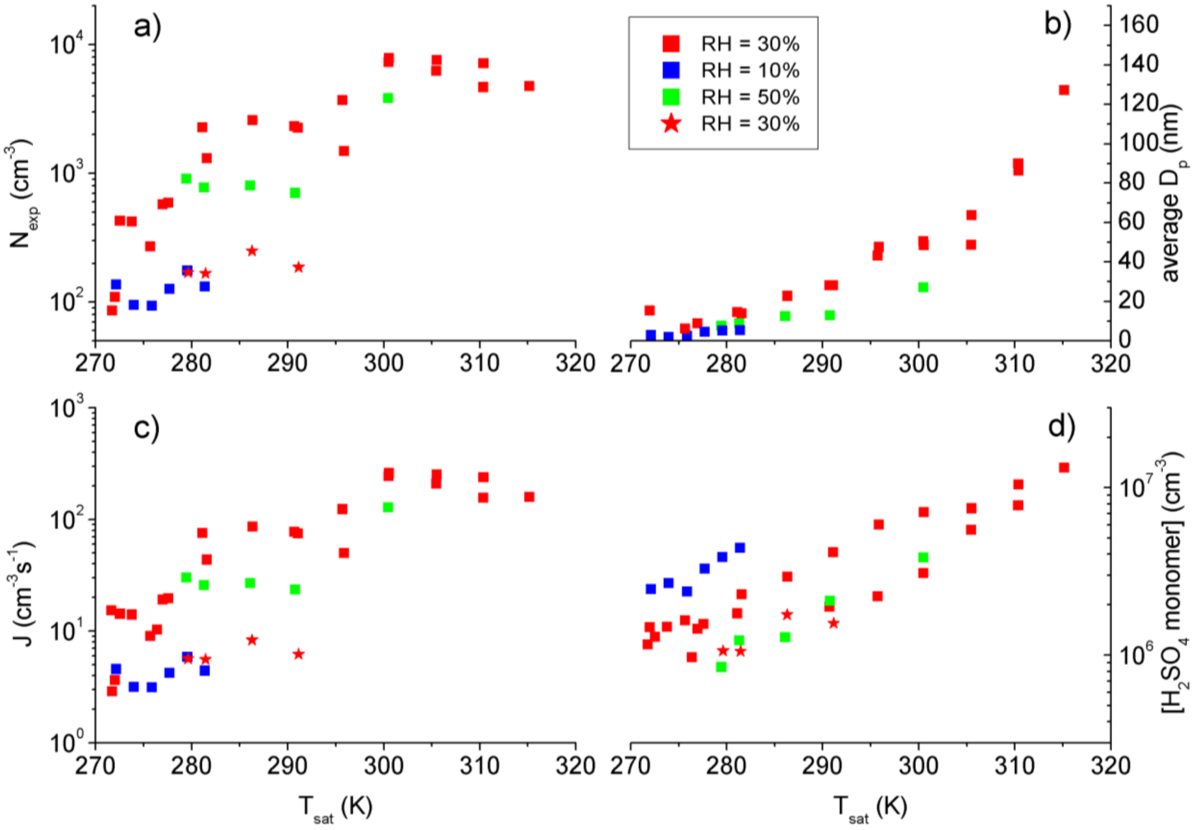

Figure 6. Number concentration N_{exp} (~~left upper~~ panel~~)~~ a)) measured with PSM and TSI 3776, geometric~~-~~-mean diameter D_p (~~right upper~~ panel~~),~~ b)), apparent formation rate J (~~left lower~~ panel~~)~~ c)) of the freshly nucleated particles and sulphuric~~–~~-acid monomer concentration measured (panel d)) with CIMS (squares) or CI-A~~P~~pi-TOF (stars) with several relative humidit~~ies~~y as a function of saturator temperature with saturator flow of 0.1 lpm. All data ~~is~~are averaged over ~~time~~a period of constant saturator temperature ex~~tra~~c~~t~~luding first hour~~.~~ to ensure steady-state. Stars are measured with CI-A~~P~~pi-TOF and squares with CIMS. All data ~~is~~are averaged over ~~time~~a period of constant saturator temperature (± 0.05 K) extracting first hour.

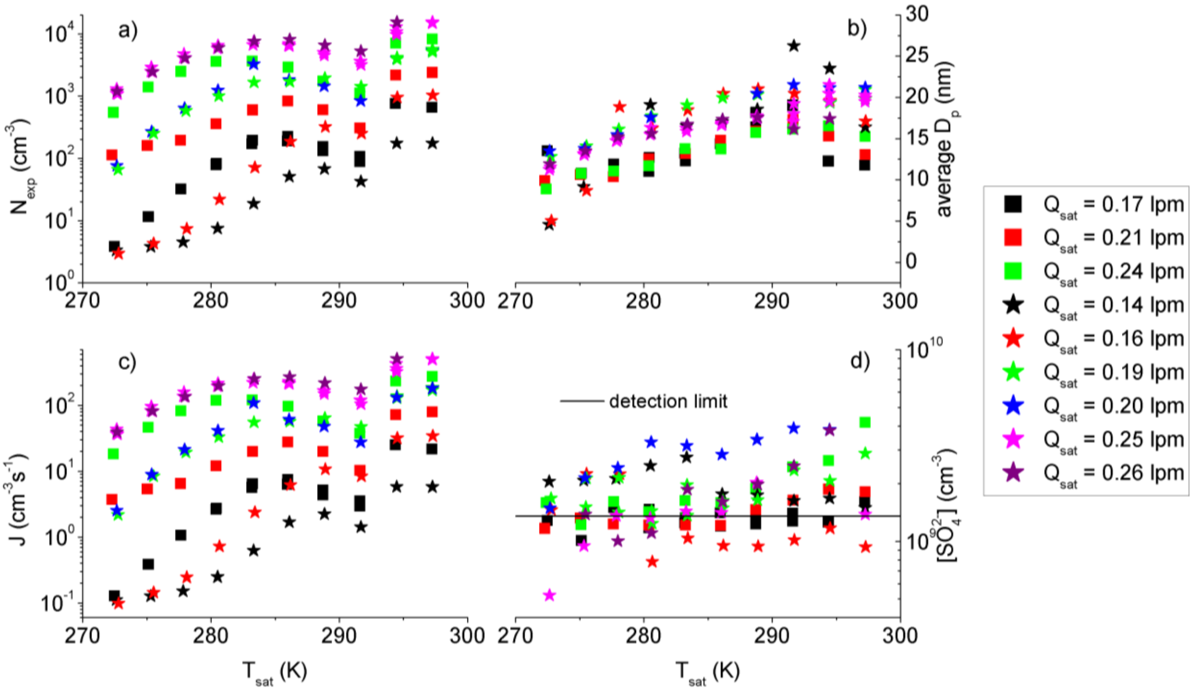

Figure 7. Number concentration N_{exp} (~~left upper~~ panel~~)~~ a)) measured with TSI 3776, geometric mean diameter D_p (~~right upper~~ panel~~),~~ b)), formation rate J (~~left lower~~ panel~~)~~ c)) of the freshly nucleated particles and total~~-~~-sulphate concentration from MARGA (~~right lower~~ panel~~)~~ d)) with detection limit of MARGA with several different saturator ~~flow rates~~flowrates as a function of saturator temperature. Squares represent~~s~~ measurements at dry conditions, stars are measured with RH of ~30 %. All data ~~is~~are averaged over ~~time~~a period of constant saturator temperature (± 0.05 K) extracting first hour.

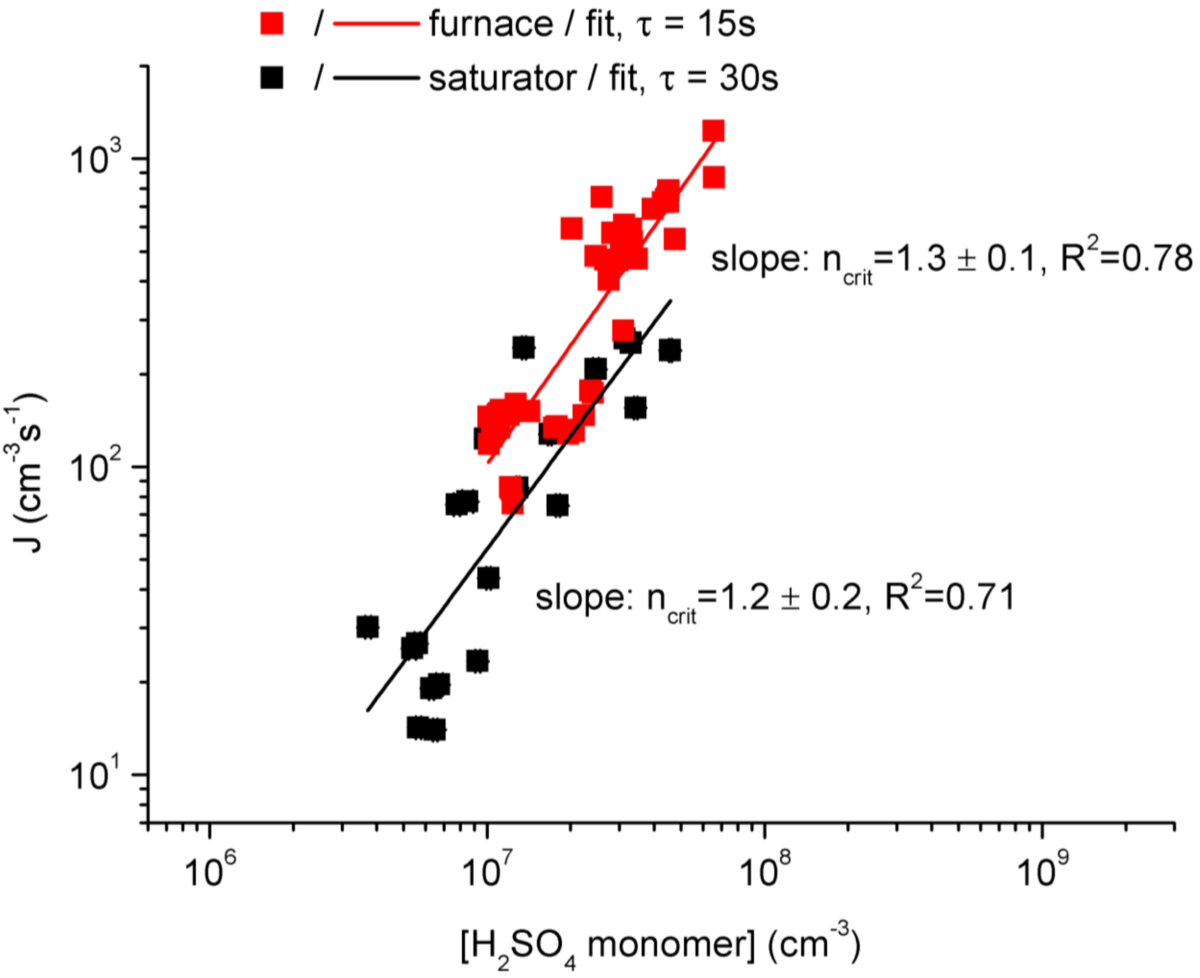

Figure 8. Formation rates *J* as a function of residual sulphuric acid monomer concentration [H_2SO_4 monomer] at *T* = 298 K and RH ~ 30 % measured using CIMS. In the first ~~data set~~dataset (red squares) sulphuric~~-~~-acid vapour was produced with the furnace method and the residence time was defined to be 15 s (Brus et al., 2011).

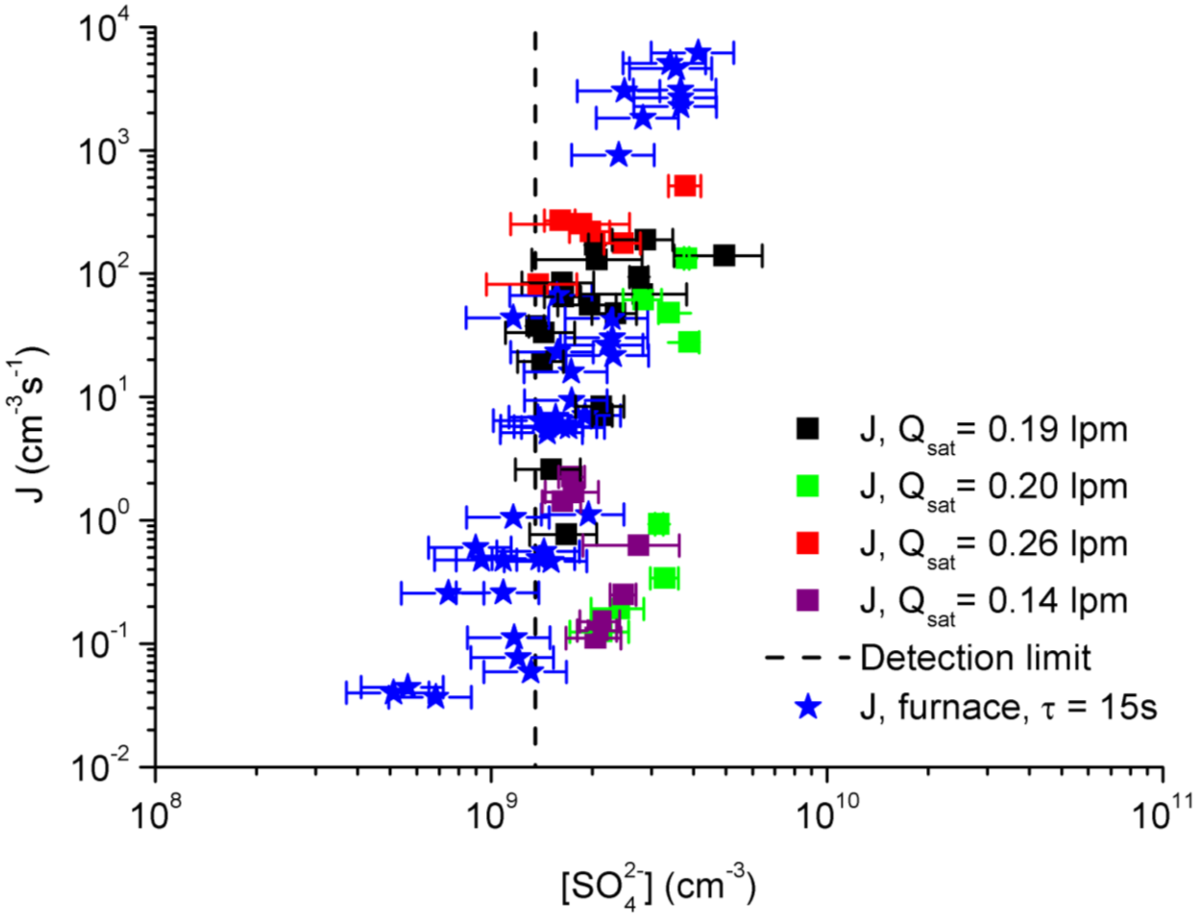

Figure 9. Formation rates *J* as a function of total~~-~~-sulphate concentration [SO_4^{2-}] measured with MARGA or bubbler with different saturator ~~flow rates~~flowrates. MARGA's detection limit is marked with the dashed line. Relative humidity RH ~30 % and nucleation temperature *T* = 298 K. Sulphuric~~-~~-acid vapour was produced with the furnace method (Brus et al., 2010) for bubbler measurements and with the saturator method for MARGA.

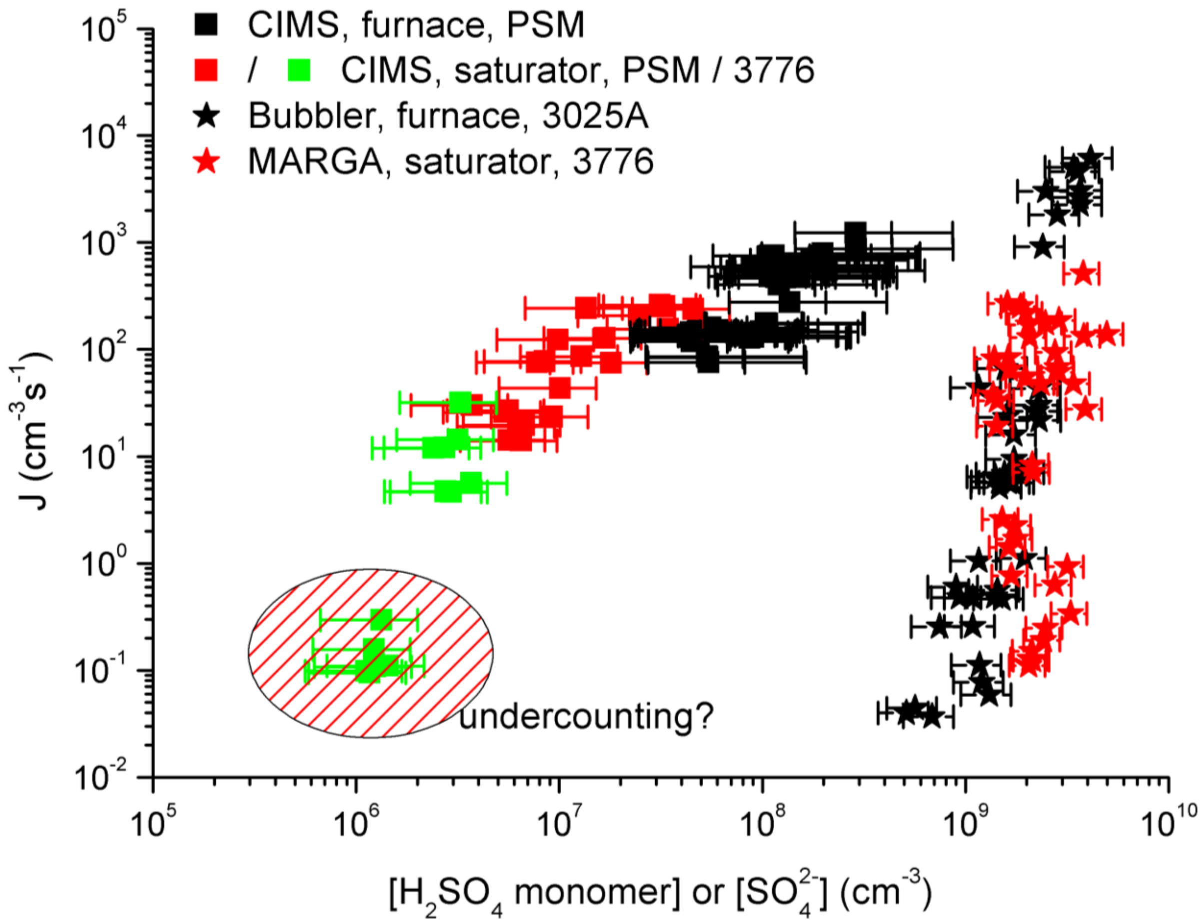

Figure 10. Comparison of formation rates J as a function of residual sulphuric-acid monomer concentration [H_2SO_4] or total-sulphate concentration [SO_4^{2-}] to our previous results. Conditions are similar (T =298 K, RH ~30 %). Note the factor-of-two difference between the residence times between furnace and saturator measurements. Sulphuric-acid vapour was previously produced with the furnace method and total sulphate concentration measured with the bubbler method (Brus et al., 2010).