

1 **Author's response**

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

4

5 **Answer to referee #1.**

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

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

16 **Referee's main comment #1:**

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

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

29 "Possible reasons for the discrepancy are discussed and some suggestions include that the
30 missing sulphuric acid is in clusters, formed with contaminants found in most laboratory

1 experiments. One-to-two orders-of-magnitude higher sulphuric-acid concentrations (measured
2 as total sulphate in this study) would contribute to a higher fraction of particle growth rate
3 than assumed from the measurements by mass spectrometers (i.e. sulphuric-acid monomer).
4 However, the observed growth rates by sulphate-containing vapour in this study does not
5 directly imply similar situation on field, where the sources of sulphate are much more
6 diverse.”

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

16 “Extra saturator tests with mass spectrometers were done using three different carrier gas
17 purities (N₂ 6.0, N₂ 5.0 and pressurized air) to check if the carrier gas used in our experiments
18 (pressurized air) was more dirty than the most pure commercial ones. Two different purity
19 sulphuric acids (~97 % and 100 %) were tested also to check if the purity of the acid itself has
20 an influence. Changing the carrier gas or the sulphuric acid purity did not affect the observed
21 sulphuric-acid concentration (see supplementary material, Fig. S3 and S4). The measured
22 sulphuric-acid monomer concentration was one-to-two orders-of-magnitude lower than the
23 prediction by Eq. 1. Tests with different saturator flowrates (0.05-2 lpm) showed that with
24 flowrates below 0.1 lpm, diffusion losses dominated: causing the measured concentration to
25 decrease as a function of the saturator flowrate. Above 0.15 lpm, the observed results behaved
26 as expected. The measured cluster distributions (monomer, dimer and trimer) with different
27 carrier gas purity were constant through the measured saturator flowrate range (Fig. S5). The
28 ratios between monomer-to-dimer and dimer-to-trimer were between 1:10 and 1:100 with all
29 carrier gases. From these results it is evident that the carrier gas used in our studies does not
30 contain more contaminants than the most pure ones commercially available. CI-API-TOF
31 mass spectra observed with different carrier gases were investigated further to find the
32 missing sulphuric acid. A large number of peaks were found to correlate with mass 97

1 (HSO₄⁻), which is the ionized sulphuric-acid monomer, with all carrier gases. The number of
2 these peaks increased as a function of the saturator temperature, suggestive that the sulphuric
3 acid forms clusters with contaminant substances (Supplementary, section 6, Fig. S6-S8). The
4 correlating peaks in Fig. S6-S8 are stick masses (i.e. rounded to nearest integer), which means
5 that many of those peaks have actually several peaks within them. This is shown in Fig. S9-
6 S11 where the mass spectrum from CI-Api-TOF is zoomed in. Unfortunately, summing up all
7 of these correlating peaks to calculate the total sulphuric acid concentration is not feasible,
8 since these clusters are not identified (i.e. it is not known what molecules those clusters are
9 composed of) and the sheer number of these peaks is overwhelming. For more details and
10 discussion of the extra saturator tests, see supplementary material.”

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

12

13 **Referee’s main comment #2:**

14 The authors seem to have done a good job in performing their measurements and in
15 evaluating the importance of potentially important factors like e.g. relative humidity, wall
16 losses, and flow rates on measured concentrations. However, since the reason for the
17 discrepancy in the measured concentrations is not known there is no clear message in this
18 manuscript. The manuscript is generally unfocused, and it is unclear what the actual goal is of
19 the study. When introducing the study in the introduction the authors write: “Here we present
20 a way to produce sulphuric-acid vapour from thermally controlled saturator in a wide range of
21 sulphuric-acid concentrations”. Reviewer 2 from the review of this manuscript in ACPD in
22 2013 pointed out that the use of an H₂SO₄ saturator is not new” and the authors seemed to
23 agree on this in their response. Still one gets the feeling when reading both the introduction
24 and conclusions sections that this method of producing H₂SO₄ is one of the main points of
25 the paper. In addition, the language would have to be checked by a native English speaker.

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

1 “The saturator provided an independent vapour-production method, compared to our previous
2 method of the furnace (Brus et al., 2010 and 2011), to find out if the discrepancy is caused by
3 the production method itself. The saturator was used in a H₂SO₄—H₂O nucleation
4 experiment, using a laminar flow tube to check reproducibility of the nucleation results with
5 the saturator method, compared to the furnace.”

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

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

17

18 **Detailed comment #1:**

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

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

1 “The saturator provided an independent vapour-production method, compared to our previous
2 method of the furnace (Brus et al., 2010 and 2011), to find out if the discrepancy is caused by
3 the production method itself. The saturator was used in a $\text{H}_2\text{SO}_4\text{—H}_2\text{O}$ nucleation
4 experiment, using a laminar flow tube to check reproducibility of the nucleation results with
5 the saturator method, compared to the furnace.”

6 Introduction:

7 “Brus et al. (2011) found a discrepancy in sulphuric-acid mass-balance between a known
8 concentration of weak sulphuric-acid solution introduced to the experimental setup and a
9 measured sulphuric-acid concentration, even though correction for wall losses and losses to
10 particle-phase was applied, one-and-half orders-of-magnitude difference in sulphuric acid
11 concentration was found (see Fig. 5 in Brus et al., 2011). A large discrepancy between
12 measured sulphuric-acid monomer and total-sulphate concentration was observed in the
13 present study. To investigate the reason for this discrepancy, we applied a thermally
14 controlled saturator (e.g. Wyslouzil et al., 1991; Ball et al., 1999) to produce sulphuric-acid
15 vapour. The output of the saturator was tested with two independent detection methods (mass
16 spectrometry and ion chromatography) before using the saturator in a $\text{H}_2\text{SO}_4\text{—H}_2\text{O}$
17 nucleation study in a laminar flow tube.

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

25 as well as in the section 3.3:

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

29 and 3.4:

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

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

3

4 **Detailed comment #2:**

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

10 **Answer to detailed comment #2:** The referee has pointed out one of the possible
11 consequences arising from the discrepancy. If sulphuric-acid concentration in the flow tube is
12 between 10^6 and 10^7 cm^{-3} , the growth rate should not be as high as observed in the flow-tube
13 experiment. However, if the concentration is one-to-two orders-of-magnitude higher,
14 measured growth rates are consistent with the amount of sulphate containing vapour
15 available. We used the model described in Škrabalová et al. (2014) to calculate the particle
16 diameter (D_p) and growth rate (GR) of the particles accounting for the initial sulphuric-acid
17 monomer and total-sulphate concentrations as an input. Measured sulphuric-acid monomer
18 and total-sulphate concentrations (presented in Fig. 6 and 7, panel d)) were converted to initial
19 concentration (i.e. at the beginning of the flow tube) with the determined $TLFs$ (factor of 10
20 sulphate and 14.2 for SA monomer concentrations). Diameter of 1.5 nm was used as an initial
21 cluster size (Kulmala et al., 2007). Three different scenarios of particle neutralisation by
22 ammonia were used in the model: (0) no neutralisation, $\text{H}_2\text{SO}_4\text{—H}_2\text{O}$ particles, (1)
23 neutralisation to ammonium bisulphate-water particles and (2) neutralisation to ammonium
24 sulphate-water particles. Using the sulphuric-acid monomer concentration as an input resulted
25 in growth rates ranging from 1 to 15 nm h^{-1} , as the referee is stating. With these growth rates
26 the particles grew up to 2 nm only, which is well below the observed diameters (Fig. 6, panel
27 b)). Using total-sulphate as an input, the growth rates ranged from 1250 to 2300 nm h^{-1}
28 resulting in diameters fitting well with the observed diameters. The results of the model are
29 presented in supplementary material section 7 and Fig. S12. A paragraph was added in the
30 end of section 3.3:

31 “The measured sulphuric-acid monomer concentration is at typical atmospheric levels, but the
32 growth rates are much higher: indicating much larger concentration of condensing vapour

1 than the detected sulphuric-acid-monomer concentration by CIMS. The growth is rather
2 driven by the total sulphate, originating exclusively from the sulphuric acid inside the
3 saturator, than the sulphuric-acid-monomer concentration.

4 To show the contribution of the sulphate to the growth rate, the model from Škrabalová et al.
5 (2014) was used to calculate the diameter (D_p) and growth rate (GR) of the particles.
6 Measured sulphuric-acid monomer and total-sulphate concentrations (Fig. 6 and 7, panel d),
7 RH 30 %) were multiplied by the TLFs to obtain the initial concentrations at the beginning of
8 the flow tube. Diameter of 1.5 nm was chosen as the initial cluster size according to Kulmala
9 et al. (2007). The model was used with three scenarios of particle neutralization by ammonia:
10 (0) no neutralization, particles composed of sulphuric acid and water, (1) neutralization to
11 ammonium bisulphate-water particles and (2) neutralization to ammonium sulphate-water
12 particles. When accounting for the initial sulphuric-acid monomer concentration as an input,
13 the resulting diameter (D_p) was always below 2 nm with growth rates (GR) ranging
14 approximately from 1 to 15 nm h⁻¹ as a function of the sulphuric-acid concentration (i.e.
15 saturator temperature T_{sat}) with all scenarios. When total-sulphate concentration was used as
16 an input, the resulting particle diameters and growth rates fit well with the measured particle
17 diameters presented in Fig. 7 for all scenarios (see suppl. Material, section 7 and Fig. S12).”

18 **Detailed comment #3:**

19 Is there a reason for the total sulphate concentration measured by the MARGA (saturator
20 only) being higher in Fig. 4 ($2 \cdot 10^9$ at 280K) than in Fig. 3 ($1 \cdot 10^9$ at 280K)?

21 **Answer to detailed comment #3:** The values presented in Fig. 3 are the actual measured
22 values. In Fig. 4 the different mixing ratios of saturator flow and the mixing flow between
23 saturator tests and nucleation measurements has been taken into account to be able to
24 determine the Total Loss Factors (TLF) in the section 3.2. In the nucleation measurements,
25 the mixing flow was kept at appr. 11 lpm to have similar conditions as in our previous
26 experiments where the furnace was used, but the saturator flow rate was varying. To account
27 for the different mixing ratios, total-sulphate concentration (saturator only) was divided by a
28 factor of 1.9. The usage of the mixing ratios is mentioned in the section 3.2 (page 25798, line
29 17):

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

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

3 **Detailed comment #4:**

4 Some of the typing errors.

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

7 References:

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

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

15

16 **Answer to referee #2.**

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

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

27

28 **Referee's comment #1:**

1 In my view, the most interesting results are those from the saturator itself (Figure3). It is more
2 difficult for me to understand the purpose of the nucleation experiments. No reason for
3 performing these experiments is mentioned in the introduction, and it is not until Section 3,
4 Results and Discussion, that we see an overview of the study and an explanation for why
5 these nucleation experiments are presented. According to the authors, the purpose is to
6 compare their results with previous studies. My recommendation is to put a paragraph similar
7 to this (p2596, ln16) in the introduction (p25790).

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

10 “The saturator provided an independent vapour-production method, compared to our previous
11 method of the furnace (Brus et al., 2010 and 2011), to find out if the discrepancy is caused by
12 the production method itself. The saturator was used in a H₂SO₄—H₂O nucleation
13 experiment, using a laminar flow tube to check reproducibility of the nucleation results with
14 the saturator method, compared to the furnace.”

15 , Introduction:

16 “Brus et al. (2011) reported a discrepancy in sulphuric-acid mass-balance between a known
17 concentration of weak sulphuric-acid solution introduced to the experimental setup and a
18 measured sulphuric-acid concentration, even though correction for wall losses and losses to
19 particle-phase was applied, one-and-half orders-of-magnitude difference in sulphuric acid
20 concentration was found (see Fig. 5 in Brus et al., 2011). A large discrepancy between
21 measured sulphuric-acid monomer and total-sulphate concentration was observed in the
22 present study too. To investigate the reason for this discrepancy, we applied a thermally
23 controlled saturator (e.g. Wyslouzil et al., 1991; Ball et al., 1999) to produce sulphuric-acid
24 vapour. The output of the saturator was tested with two independent detection methods (mass
25 spectrometry and ion chromatography) before using the saturator in a H₂SO₄—H₂O
26 nucleation study in a laminar flow tube.

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

1 formation rates between the saturator and the furnace, with similar observed sulphuric-acid or
2 total-sulphate concentrations.”

3 as well as in the section 3.3:

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

7 and 3.4:

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

12

13

14

15 **Referee’s comment #2:**

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

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

1 concentration. The text within the manuscript is corrected to emphasize that the observed
2 formation rates are rather apparent formation rates and not actual nucleation rates.

3

4 **Referee's comment #3:**

5 Also, except for the comparison to the Brus et al study (Figure 10), no other comparisons are
6 made. Likely, it was because it would be difficult due to the above-mentioned problem with
7 nucleation rates (Item 3). This study would be a lot more useful to readers if you can place it
8 in context by comparing results to prior studies.

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

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

17

18 **Referee's comment #4:**

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

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

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

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

20

21 **Referee’s comment #5:**

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

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

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

4 From the comparison measurements among commercially available N₂ of different purity, it
5 is clear that contaminants of similar level were still present in the carrier gas (pressurized air)
6 used in our experiment. No extra denuders were used in this study.

7 **Referee’s comment #6:**

8 Section 3.5 provides important insights into the possible source of this discrepancy between
9 sulfuric monomer and sulfate. It may in fact be the most important section, since possible
10 contaminants in the flows provide an explanation for these observations. The authors just
11 refer to the supplemental information and state that the results and a discussion are provided
12 there, but I see very little discussion there about the effects of contaminants. Since 100ppt is
13 about 2.5×10^9 molecule cm³, or about the reported concentrations of the sulfuric acid
14 monomer, that and other contaminants are sufficient to neutralize the acid. Please provide a
15 summary of the results of your “extensive measurements” in the main article so the reader can
16 better interpret these results. For example, if dirty air was used then it could fully explain
17 most of these results . . . and of course make them inconsequential since most nucleation
18 experimenters go through great lengths to characterize and eliminate contaminants.

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

20 “Extra saturator tests with mass spectrometers were done using three different carrier gas
21 purities (N₂ 6.0, N₂ 5.0 and pressurized air) to check if the carrier gas used in our
22 experiments (pressurized air) was more dirty than the most pure commercial ones. Two
23 different purity sulphuric acids (~97 % and 100 %) were tested also to check if the purity of
24 the acid itself has an influence. Changing the carrier gas or the sulphuric acid purity did not
25 affect the observed sulphuric-acid concentration (see supplementary material, Fig. S3 and S4).
26 The measured sulphuric-acid monomer concentration was one-to-two orders-of-magnitude
27 lower than the prediction by Eq. 1. Tests with different saturator flowrates (0.05-2 lpm)
28 showed that with flowrates below 0.1 lpm, diffusion losses dominated: causing the measured
29 concentration to decrease as a function of the saturator flowrate. Above 0.15 lpm, the
30 observed results behaved as expected. The measured cluster distributions (monomer, dimer
31 and trimer) with different carrier gas purity were constant through the measured saturator
32 flowrate range (Fig. S5). The ratios between monomer-to-dimer and dimer-to-trimer were

1 between 1:10 and 1:100 with all carrier gases. From these results it is evident that the carrier
2 gas used in our studies does not contain more contaminants than the most pure ones
3 commercially available. CI-API-TOF mass spectra observed with different carrier gases were
4 investigated further to find the missing sulphuric acid. A large number of peaks were found
5 to correlate with mass 97 (HSO_4^-), which is the ionized sulphuric-acid monomer, with all
6 carrier gases. The number of these peaks increased as a function of the saturator temperature,
7 suggestive that the sulphuric acid forms clusters with contaminant substances
8 (Supplementary, section 6, Fig. S6-S8). The correlating peaks in Fig. S6-S8 are stick masses
9 (i.e. rounded to nearest integer), which means that many of those peaks have actually several
10 peaks within them. This is shown in Fig. S9-S11 where the mass spectrum from CI-API-TOF
11 is zoomed in. Unfortunately, summing up all of these correlating peaks to calculate the total
12 sulphuric acid concentration is not feasible, since these clusters are not identified (i.e. it is not
13 known what molecules those clusters are composed of) and the sheer number of these peaks is
14 overwhelming. For more details and discussion of the extra saturator tests, see supplementary
15 material.”

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

21 **Referee’s list of technical corrections.**

22 The manuscript was proof-read by a native speaker.

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

24 **Answer:** This is corrected throughout the manuscript.

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

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

31 **Answer:** The Fig. 2 is updated.

1

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

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

10

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

12 **Answer:** all is now corrected to UFCPC.

13

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

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

20

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

23 **Answer:** Figures have been updated accordingly.

24

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

27 **Answer:** CPC 3772 has lower limit of 10^4 cm^{-3} which is very low compared to other particle
28 counters used in the experiment (10^5 cm^{-3}). Total particle concentration was checked from

1 DMPS data to have a maximum of $1.2 \cdot 10^4 \text{ cm}^{-3}$. As there are no larger particles present,
2 coagulation can be considered to be marginal.

3

4 Škrabalová L., Brus, D., Anttila, T., Ždímal, V. and Lihavainen H.: Growth of sulphuric acid
5 nanoparticles under wet and dry conditions, *Atmos. Chem. Phys.* 14, 6461-6475, doi:
6 10.5194/acp-14-6461-2014, 2014.

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

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2 **Total sulphate vs. sulphuric acid monomer in nucleation** 3 **studies**

4

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17

18 **Abstract**

19 Sulphuric acid is known to be a key component for atmospheric nucleation. Precise
20 determination of sulphuric- acid concentration is a crucial factor for prediction of nucleation
21 rates and subsequent growth. In our study, we have noticed a substantial discrepancy between
22 sulphuric -acid monomer and total -sulphate concentrations measured from the same source of
23 sulphuric -acid vapour. The discrepancy of about one -to -two orders -of -magnitude was
24 found with similar **particle**-formation rates. To investigate this discrepancy, and its effect on
25 nucleation, a method of thermally controlled saturator filled with pure sulphuric acid (97 %
26 wt.) for production of sulphuric -acid vapour is **introduced****applied** and **rigorously** tested.
27 **Sulphuric**The saturator provided an independent vapour-production method, compared to our
28 **previous method of the furnace** (Brus et al., 2010 and 2011), to find out if the discrepancy is

1 caused by the production method itself. The saturator was used in a $\text{H}_2\text{SO}_4\text{—H}_2\text{O}$ sulphuric
2 acid-water nucleation experiment was done, using a laminar flow tube to check
3 reproducibility of the nucleation results with the saturator method, compared to the furnace.
4 Two independent methods of mass spectrometry and online ion chromatography were used
5 for detecting sulphuric acid or sulphate concentrations. The results are compared to our
6 previous results, where a method of furnace was used to produce sulphuric acid vapour (Brus
7 et al., 2010 and 2011). Measured sulphuric acid or total sulphate concentrations are
8 compared to theoretical predictions calculated using vapour pressure and a mixing law. The
9 calculated prediction of sulphuric acid concentrations agrees very well with the measured
10 values when total sulphate is considered. Sulphuric acid monomer concentration was found
11 to be about two orders of magnitude lower than the prediction theoretical predictions, but
12 with a similar temperature dependency as the predictions and the results obtained with the ion
13 chromatograph method. Formation rates agree well are reproducible when compared to our
14 previous results with both sulphuric acid or total sulphate detection and sulphuric acid
15 production methods separately, removing any doubts that the vapour-production method
16 would cause the discrepancy. Possible reasons for the discrepancy are discussed and some
17 suggestions include that the missing sulphuric acid is in clusters, formed with contaminants
18 found in most laboratory experiments. One-to-two orders-of-magnitude higher sulphuric acid
19 concentrations (measured as total sulphate in this study) would contribute to a higher fraction
20 of particle growth rate than assumed from the measurements by mass spectrometers (i.e.
21 sulphuric acid monomer). However, the observed growth rates by sulphate-containing vapour
22 in this study does not directly imply similar situation on in the field, where the sources of
23 sulphate are much more diverse.

25 1 Introduction

26 Secondary particle formation by gas to liquid conversion is widely recognized as an
27 important source of aerosol particles in the atmosphere worldwide (Weber et al., 1996;
28 Kulmala et al., 2004; Spracklen et al., 2006). These particles may grow to larger sizes and
29 affect the radiative balance of the Earth by scattering and absorbing the incoming radiation
30 (Feingold and Siebert, 2009). Aerosols can seriously reduce visibility and have also potential
31 health effects (Davidson et al., 2005). Model calculations and observations suggest that new
32 particle formation events with subsequent growth can contribute a significant substantial

1 amount to cCloud cCondensation nNuclei (CCN) concentrations, which can alter the lifetime
2 and albedo of clouds (Lihavainen et al., 2003 and 2009; Merikanto et al., 2009). Furthermore,
3 aerosols can reduce visibility and have potential health effects (Davidson et al., 2005).

4 Significant effort has been madone by field measurements and laboratory studies, together
5 with computer simulations, to understand the particle -formation mechanism itself and the
6 atmospheric conditions involved in the gas -to -liquid conversion. Despite thesuch effort and
7 numerous results, the underlying mechanism is not yet solvedfound.

8 It is widely accepted that sulphuric acid plays a key role in atmospheric nucleation (Kulmala
9 et al., 2006; Sipilä et al., 2010; Brus et al., 2011; Kirkby et al., 2011). Binary nucleation of
10 sulphuric acid and water (Vehkamäki et al., 2002; Yu, 2006; Kirkby et al., 2011), ternary
11 nucleation involving also ammonia and/or amines (Ball et al., 1999; Korhonen et al., 1999;
12 Napari et al., 2002; Benson et al., 2009; Berndt et al., 2010; Kirkby et al., 2011; Zollner at
13 al., 2012) and ion-induced nucleation (Lee et al., 2003; Lovejoy et al., 2004; Yu et al., 2008,
14 2010; Nieminen et al., 2011) have been suggested as possible mechanisms for the nucleation
15 to occur in the atmosphere. Ions have been shown to lower the thermodynamic potential of
16 nucleation (Arnold 1980; Winkler et al., 2008; Kirkby et al., 2011)), but the role of ions in
17 nucleation occurring in the atmospheric boundary layer nucleation havehas been shown to be
18 minor (Manninen et al., 2010; Paasonen, et al., 2010, Kerminen et al., 2010; Hirsikko et al.,
19 2011).

20 Recently several laboratory studies have been conducted concerning the role of sulphuric acid
21 in atmospheric nucleation (e.g. Benson et al., 2008, 2011; Young et al., 2008; Berndt et al.,
22 2008, 2010; Brus et al., 2010, 2011; Sipilä et al., 2010; Kirkby et al., 2011; Zollner et al.,
23 2012) with different methods of producing the gas -phase sulphuric acid: with their own
24 advantages and drawbacks.disadvantages. For example, the evaporation method of weak
25 sulphuric -acid solution used by Viisanen et al.,. (1997) and Brus et al. (2010 and 2011)
26 introduces a thermal gradient into the beginning of the flow tube.. Production of the sulphuric
27 acid with a SO₂ + OH reaction is used in most of the experiments, since it is similar to that
28 observed in atmosphere (e.g. Benson et al., 2008; Berndt et al., 2008, 2010; Sipilä et al., 2010;
29 Kirkby et al., 2011). The SO₂ oxidation method involves usagethe use of UV light to produce
30 OH radicals. The excess OH must be removed so that it woulddoes not disturb the nucleation
31 process itself (Berndt et al., 2010). OAnother way is to have excess of SO₂, so that all the OH
32 reacts rapidly with SO₂; but for the calculation of the produced H₂SO₄ concentration, the

1 exact concentration of OH produced must be known (Benson et al., 2008). Ball et al., (1999)
2 and Zollner et al., (2012) produced sulphuric acid vapour by saturating N₂ flow in a glass
3 saturator, containing pure (~96 % and ~98 %, respectively) sulphuric acid. Ball et al., (1999)
4 varied the temperature of the saturator as, whilst Zollner et al., (2012) kept the saturator at
5 constant temperature (303 K) and varied the carrier gas flow rate to change the
6 sulphuric acid concentration.

7 As stated by others in literature (e.g. Benson et al., 2011; Brus et al., 2011; Kirkby et al.,
8 2011), contaminants are most probably present in almost all of the laboratory nucleation
9 studies. These contaminants arise from different sources like, such as from the water used for
10 humidifying the carrier gas or from the carrier gas itself which contains some trace levels of
11 contaminants. It is almost impossible to get rid of these contaminants, which most
12 probably affect the nucleation process itself.

13 Here we Brus et al. (2011) reported a discrepancy in sulphuric acid mass-balance between a
14 known concentration of weak sulphuric acid solution introduced to the experimental setup
15 and a measured sulphuric acid concentration, even though correction for wall losses and
16 losses to particle-phase was applied, one-and-a-half orders-of-magnitude difference in sulphuric
17 acid concentration was found (see Fig. 5 in Brus et al., 2011). A similar, large discrepancy
18 between measured sulphuric acid monomer and total-sulphate concentration was observed in
19 the present study. To investigate the reason
20 for this discrepancy, we applied a thermally controlled saturator in a wide range of (e.g.
21 Wyslouzil et al., 1991; Ball et al., 1999) to produce sulphuric acid vapour. The
22 output of the saturator was tested with two independent detection methods (mass spectrometry
23 and ion chromatography) before using the saturator in a H₂SO₄—H₂O sulphuric acid-water
24 nucleation study in a laminar flow tube.

25 Applying the saturator as the source of the sulphuric acid vapour made it possible to compare
26 the saturator to the furnace, which was used as the source of the sulphuric acid previously
27 (Brus et al., 2010 and 2011) and eliminate the production method as a reason for
28 the discrepancy. The flow-tube measurements with the saturator and the two sulphuric acid or
29 total-sulphate detection methods were conducted to check reproducibility of particle
30 formation rates, between the saturator and the furnace, with similar
31 observed sulphuric acid vapour or total-sulphate concentrations of H₂SO₄-H₂O nucleation
32 experiment are presented. The measured sulphuric acid or total-sulphate concentrations

1 were compared to the results measured with previous setup where furnace was used to
2 produce sulphuric acid vapour (Brus et al., 2010 and 2011). The experimental setup, where
3 saturator is used, was tested with two independent analytical methods to measure sulphuric
4 acid concentration based on different principles. Total losses of sulphuric acid within the flow
5 tube and the total losses of sulphuric acid or sulphate were determined and for both analytical
6 methods of detecting sulphuric acid compared. mass spectrometers and the ion chromatograph.
7 The level of ammonia contaminant in the setup system was also determined. with the ion-
8 chromatograph method.

9 Introducing saturator as the source of sulphuric acid vapour reduces disadvantages associated
10 with other methods, like a temperature gradient arising from usage of furnace, or calculations
11 of OH concentration produced with UV light and removal of excess OH associated with the
12 oxidation of SO₂. The major disadvantage using this method is the handling of pure sulphuric
13 acid when filling the saturator. Luckily, the saturation vapour pressure of sulphuric acid is
14 very low and therefore, the sulphuric acid is consumed very slowly. Due to the high
15 hygroscopicity of sulphuric acid, the saturator should not be exposed to humid flow as the
16 pure liquid sulphuric acid would draw water vapour from the flow contaminating the
17 sulphuric acid. This would lead to a significant error in the predicted concentration due to a
18 much higher vapour pressure of water compared to sulphuric acid.

20 2 Experimental

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

27 2.1 Saturator

28 The saturator was a horizontally placed cylinder made of iron with Teflon insert inside the
29 cylinder (inner diameter, I.D., of 5 cm). It was thermally controlled with a liquid -circulating
30 bath (LAUDA RC 6) and the temperature was measured just above the liquid surface with a
31 calibrated PT100 probe (\pm (accuracy \pm 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). H₂SO₄ 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:

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

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

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 compared also to empirical fit by Richardson et al., (1986):

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

(2)

The fit is made to their measurement data in the temperature range of 263.15 K – 303.15 K, which fit well in 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-AP_{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). 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 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-AP_{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 Eqs. (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 unitsaturator 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

1 thermally controlled with a liquid circulating bath (LAUDA RC 6). One of the 100 -cm -long
2 parts of the flow chamber has four holes on the sides every 20 cm from the beginning of the
3 chamber with one hole in . The 3.5 -cm Teflon connector between the two 100 -cm flow-tube
4 pieces. has also a hole (see Fig. 2). These holes are used to continuously measure temperature
5 in the flow tube with PT100 probes to ensure constant desired nucleation temperature. The
6 RH of the mixing flow is controlled by 2 or 3 Nafion humidifiers. RH and temperature are
7 measured also at the end of the tube with Vaisala HMP37E and humidity data processor
8 Vaisala HMI38. Both saturator and mixing flow of the tube are controlled by a mass flow
9 rateflowrate controller (MKS type 250) with an accuracy of $\pm 3\%$. Flow ratesFlowrates
10 through the saturator for nucleation measurements were kept betweenat 0.13 lpm and -0.27
11 lpm. The mixing flow was kept at approximately 11 lpm. The line from the saturator to the
12 mixing unit was kept at the same temperature as the saturator to prevent condensation of
13 sulphuric acid.

14 2.4 H₂SO₄ monomer, sulphate and particle detection

15 Gas phase sulphuric -acid monomers were measured with CIMS or CI-APpi-TOF. The CI-
16 inlet used in both instruments works as follows: Tthe sulphuric -acid molecules are ionized in
17 ambient pressure via proton transfer between nitrate ions (NO₃⁻) and sulphuric acid molecules
18 (H₂SO₄). The nitrate ions are produced from nitric acid with radioactive ²⁴¹Am-source and
19 mixed in a controlled manner in a drift tube utilizing, using a concentric sheath and sample
20 flows together with electrostatic lenses.

21 After the ionization in the inlet, the instruments differ from each other. In the CIMS sample,
22 flow is dried using a nitrogen flow to dehydrate the molecules before entering the vacuum
23 system. and detection in the quadrupole mass spectrometer. In the CI-APpi-TOF, a flow
24 rateflowrate of 0.8 lpm is guided through a critical orifice. The ions are guided through the
25 differentially pumped APiAtmospheric pressure interface (Api) and finally to the TOF for
26 detection according to the ions' *m/z*-mass-to-charge ratio.

27 The monomer concentration is determined by the ratio of the resulting ion signals (HSO₄⁻ and
28 HSO₄⁻·HNO₃) and the reagent ion signals (NO₃⁻, HNO₃·NO₃⁻ and (HNO₃)₂·NO₃⁻). This ratio
29 is then multiplied withby the instrument -dependent calibration factor in both instruments.
30 CalibrationThe calibration factor used here was $5 \cdot 10^9$ for both instruments. Neither CIMS nor
31 CI-APpi-TOF was not calibrated using the saturator setup, but instead before the experiments

1 using the standard calibration procedure of oxidation of SO₂ with OH (Kürten et al., 2012).
2 For more information about the calibration of CIMS, see Berresheim et al., (2000), Petäjä et
3 al., (2009), Zheng et al., (2010) and Kürten et al., (2012). The nominal sample **flow**
4 **rateflowrate** of these instruments is ~10 lpm. We considered only the monomer concentration,
5 although detection of dimers and even larger clusters of pure sulphuric acid is possible with
6 CI-AP*pi*-TOF. This **is due to following reasons:was done because** the dimer concentration
7 was always in the magnitude of ~1 % of monomer concentration and **larger (the trimer**
8 **concentration was in the magnitude of ~1 % of the dimer concentration and tetramer) cluster**
9 **concentrations were even lowerso on (e.g. , continuing with similar concentration ratio**
10 **towards larger clusters (e.g. Jokinen et al. 2012).** The charging efficiency might not be the
11 same for these clusters as it is for monomer. This would cause the calibration factor to change
12 and the calculated concentration to be erroneous. The uncertainty in the resulting monomer
13 concentration is estimated to be a factor of ~2. The nominal lower detection limit of CIMS
14 and CI-AP*pi*-TOF is estimated to be 5 · 10⁴ cm⁻³, and the upper limit is approximately 10⁹ cm⁻³
15 for both instruments. At this high concentration, the primary **ion concentrationions** start to
16 deplete causing the calibration **constantfactor** to change.

17 The total -sulphate concentration was measured with an online ion chromatograph MARGA
18 2S ADI 2080. MARGA is able to detect 5 gases **fromin** the gas phase (HCl, HNO₃, HONO,
19 NH₃, SO₂) and 8 major inorganic species **fromin** aerosol phase (Cl⁻, NO₃⁻, SO₄²⁻, NH₄⁺, Na⁺,
20 K⁺, Mg²⁺, Ca²⁺). The sample flow is ~16.7 lpm. From the sample flow, all (more than 99.7 %)
21 of water -soluble gases are absorbed **in tointo** a wetted rotating denuder (WRD). Based on
22 different diffusion velocities, aerosols pass **the** WRD and enter **a Steam-jet-aerosol-**
23 **collectorJet-Aerosol-Collector** (SJAC) (Slanina et al., 2001). In the SJAC, conditions are
24 supersaturated with water vapour, which condenses **onto** particles and the particles **are**
25 **collected tothus collect at** the bottom of the SJAC. Sample solutions are drawn from the WRD
26 and the SJAC into syringes (25 ml) and are analysed one after another, once an hour. Samples
27 are injected in cation and anion chromatographs with an internal standard (LiBr). Components
28 are detected by conductivity measurements. The detection limits are 0.1 µg m⁻³**or³ or** better.
29 For more information about the instrument, see Makkonen et al., (2012).

30 In our previous study (Brus et al., 2010)), the total -sulphate concentration was measured
31 using **the** method of bubblers, **:** where a known **flow rateflowrate** from the flow tube was
32 bubbled through alkaline solution, thus trapping sulphate. This solution was then analysed

1 using offline ion chromatography. See Brus et al., (2010) for details. The method of bubbler is
2 analogous to the MARGA and the main difference is that MARGA is an online **asmethod**,
3 **whilst** bubbler is an offline method.

4 The total -particle number concentration was measured with a Particle Size Magnifier (PSM,
5 Airmodus Oy, Finland, Vanhanen et al., 2011, coupled with CPC TSI model 3772) and with
6 Ultra-Fine CPC's (UFCPC, TSI models 3776, 3025A) with cut-off mobility diameters of ~1.5
7 nm and ~3 nm, respectively. Differential Mobility Particle Sizer (DMPS) was used to measure
8 **the** particle number size distribution from 3 to ~250 nm in **a** closed -loop arrangement
9 (Jokinen and Mäkelä, 1997) using a blower to measure the wet size of the particles. The
10 DMPS was run with a sheath flow of ~11 lpm and sample flow of 1.5 lpm in the short
11 HAUKE-type Differential Mobility Analyzer (DMA). The DMA was coupled with UFCPC
12 (TSI model 3025A) and with a bipolar radioactive (⁶³Ni) neutralizer. The charging
13 efficiencies were calculated following the parameterization of Wiedensohler **and Fissan**
14 (1991). The RH of the sheath flow was monitored to ensure that it **iswas** same as the RH in
15 the chamber.

17 **3 Results and discussion**

18 To quantify the sulphuric acid input for flow -tube nucleation measurements, the saturator
19 output was tested in two experiments,; first with CIMS and CI-AP*pi*-TOF and **lattersecond**
20 with MARGA. After the tests, nucleation measurements of **H₂SO₄—H₂O** sulphuric acid-water
21 system were conducted. This enabled direct comparison **to**with the sulphuric -acid production
22 method used in our previous studies (Brus et al., 2010 and 2011).), **so that the production**
23 **method can be discounted as a reason for the discrepancy**. Presented values from CIMS, CI-
24 AP*pi*-TOF and MARGA measurements are residual, i.e. measured values at the end of the
25 flow tube accounting for dilutions, if not **otherwise** mentioned to be different.

26 **3.1 Test of the saturator**

27 Results of the saturator test are presented in **figure**Fig. 3 as measured sulphuric -acid **or total-**
28 **sulphate** concentrations and predicted values by Eqs. (1) and (2) as a function of temperature
29 of the saturator. The mixing flows were 40 (dry and RH 15 %) or 20 lpm (for RH 29 %) for
30 CIMS and AP*pi*-TOF and 20 lpm (only dry conditions) for MARGA measurements. **Tests**
31 **with MARGA were performed with dry conditions, since it was noticed that the RH did not**

1 have any influence on the results from the tests with mass spectrometers. MARGA uses
2 supersaturated conditions to grow the particles and collect them in the SJAC, hence initial RH
3 is not expected to have any influence. Saturator flow rate was 0.5 lpm. Mass
4 spectrometers were tested at dry and humid conditions. Dry experiments were run with two
5 mass spectrometer inlet flow rates (6 and 10 lpm) and with extra 1 m (I.D. 4 mm)
6 Teflon tubing between the saturator and the mixing unit, to test the effect of wall losses.
7 Humidified experiments were done with two inlet flow rates (6 lpm for RH 29 %
8 and 10 lpm for RH 15 %). MARGA experiments were conducted at dry conditions.

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

14 Sulphuric acid monomer concentration measured with CIMS and CI-APPI-TOF fit each
15 other very well, but they show one to two orders of magnitude lower concentrations than
16 predicted by Eq. (1) and (2) and measured total sulphate with MARGA. The slope is similar
17 to the predictions and to the points measured with MARGA. The dimer concentrations
18 were always approximately 1 to 10 % (increasing with increasing saturator
19 temperature) of the monomer concentration and trimer approximately 1 % of the dimer
20 concentration (see Supplementary Material, Fig. S5).

21 Relative humidity does not have any significant effect on the measured values
22 by CIMS and CI-APPI-TOF. RH can affect the wall losses by preventing the sulphuric acid to
23 evaporate from the inlet walls as, since the vapour pressure of water is
24 several orders of magnitude higher than that of the sulphuric acid. The predictions by Eqs. (1)
25 and (2) do not consider relative humidity as, since the flow through the saturator is always
26 dry. The relative humidity of the mixing flow causes the sulphuric acid molecules to get
27 hydrated as since sulphuric acid is very hygroscopic; but because the results from humid and
28 dry measurements are very similar, CIMS and CI-APPI-TOF can be considered measuring to
29 measure well in humid conditions also. The effect of RH is discussed in Eisele and Tanner
30 (1995) and our results agree with the discussion there.

31 A change of the nominal inlet flow rate of CIMS and CI-APPI-TOF did not
32 have large effect either. The inlet lines were short (~20 cm) in the saturator tests so the wall

1 losses due to lower inlet flow rate does flow rate did not play a big any significant role. Using
2 the instruments with a lower flow rate may flow rate might alter the measured concentration as
3 the calibration factor as it is acquired with inlet flow rate flow rate of 10 lpm.

4 Tests with different saturator flow rates (0.05 - 1 lpm) were conducted to estimate the limits
5 of the saturator flow (not shown in Fig. 3). With 0.05 lpm saturator flow rate diffusional
6 losses to the walls dominated causing the measured sulphuric acid concentrations decrease as
7 a function of the saturator temperature. In the saturator flow rate range from 0.2 up to at least
8 1 lpm, sulphuric acid concentrations behaved as expected. Results of different flow rate tests,
9 as well as results from tests with carrier gases with different purity, can be found in the
10 supplementary material (sections 3 and 4).

11 Extra saturator tests with mass spectrometers were done using three different carrier gas
12 purities (N₂ 6.0, N₂ 5.0 and pressurized air) to check if the carrier gas used in our experiments
13 (pressurized air) was more dirty than the most pure commercial ones. Two different purity
14 sulphuric acids (~97 % and 100 %) were tested also to check if the purity of the acid itself has
15 an influence. Changing the carrier gas or the sulphuric acid purity did not affect the observed
16 sulphuric-acid concentration (see Supplementary Material, Fig. S3 and S4). The measured
17 sulphuric-acid monomer concentration was one-to-two orders-of-magnitude lower than the
18 prediction by Eq. 1. Tests with different saturator flowrates (0.05–2 lpm) showed that with
19 flowrates below 0.1 lpm, diffusion losses dominated: causing the measured concentration to
20 decrease as a function of the saturator flowrate. Above 0.15 lpm, the observed results behaved
21 as expected. The measured cluster distributions (monomer, dimer and trimer) with different
22 carrier -gas purity were constant through the measured saturator flowrate range (Fig. S5). The
23 ratios between monomer-to-dimer and dimer-to-trimer were between 1:10 and 1:100 with all
24 carrier gases. From these results it is evident that the carrier gas used in our studies does not
25 contain more contaminants than the most pure ones commercially available. CI-API-TOF
26 mass spectra observed with different carrier gases were investigated further, to find the
27 missing sulphuric acid. A large number of peaks were found to correlate with mass 97
28 (HSO₄⁻), which is the ionized sulphuric-acid monomer, with all carrier gases. The number of
29 these peaks increased as a function of the saturator temperature, suggestive that the sulphuric
30 acid forms clusters with contaminant substances (Supplementary Material, section 6, Fig. S6-
31 -S8). The correlating peaks in Fig. S6–S8 are stick masses (i.e. rounded to nearest integer),
32 which means that many of those peaks have actually several peaks within them. This is shown

1 in Fig. S9–S11 where the mass spectrum from CI-API-TOF is zoomed in. Unfortunately,
2 summing up all of these correlating peaks to calculate the total sulphuric acid concentration is
3 not feasible, since these clusters are not identified (i.e. it is not known what molecules those
4 clusters are composed of) and the sheer number of these peaks is overwhelming. For more
5 details and discussion of the extra saturator tests, see Supplementary Material.

6 3.2 Losses of sulphuric acid and sulphate and sulphuric acid in the flow tube

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

14 Figure 4 presents the measured sulphuric acid monomer and total sulphate concentration
15 from the saturator tests (squares) and nucleation measurements (stars) as a function of the
16 saturator temperature. Saturator tests were done in dry conditions and nucleation
17 measurements in RH 30 %. An inlet pipe is used to connect the mass spectrometer to the
18 flow tube. Brus et al. (2011) state that the Wall Loss Factor (*WLF*) in the inlet pipe of length
19 $100 + 22$ cm is $WLF_{\text{inlet}} = \sim 4$. This factor, together with the mixing ratios, was used to
20 account for to make the data so that they would be directly comparable.

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

27 From Figure 4, it is evident that wall losses are not the only losses affecting the measured
28 concentrations since the trends in the fits for nucleation measurements are less steep than
29 the ones from saturator tests. The losses to the particle phase also affect the situation. The
30 maximum losses of sulphuric acid to particle phase are calculated using the DMPS data
31 measured at the end of the nucleation chamber only. The total volume of the particles is

1 calculated within the size distribution assuming that the particles are composed only of pure
2 sulphuric acid with density of 1.84 g cm^{-3} . The losses of sulphuric acid to particles range from
3 0 % (dry conditions, $T_{\text{sat}} = 273 \text{ K}$) up to maximum of 1.4 % (RH = 30 %, $T_{\text{sat}} = 292 \text{ K}$) of the
4 total sulphate concentration. Higher saturator temperature increases the number and the
5 diameter of the particles, and relative humidity increases the diameter of the particles. The
6 losses to the particle phase are **significant** at the highest values of saturator
7 temperature but this estimate is the maximum limit **since** the particles are not composed
8 only of pure sulphuric acid molecules. Contaminants from the flow condense to the particle
9 phase or **get** bond with sulphuric acid. **Also, when** When using humid conditions, sulphuric -
10 acid particles uptake water **since** sulphuric acid is very hygroscopic. At the highest
11 temperature of the saturator, the size distribution unfortunately extends out of the DMPS
12 range (3–250 nm) **and particles larger than 250 nm are not accounted for the losses to the**
13 **particle phase,** thus **on the other hand** **conversely** underestimating the losses. Losses to the
14 clusters smaller than the cut-off size of the particle counters are **probably significant**. For
15 **more details about the losses to the particle phase see supplementary material (Section**
16 **substantial**. The maximum losses to the particle phase have been calculated for each of the
17 saturator temperature values and plotted with the measured monomer and total sulphate
18 concentrations together with the prediction from Eq. (1) in Fig. S1 in **sSupplementary**
19 **mMaterial**. Even summing up the measured monomer concentration and the losses to the
20 particle phase leaves the summed total concentration at least one order -of -magnitude lower
21 **than the measured total sulphate and the prediction by Eq. (1).**

22 **3.3 Nucleation measurements**

23 Formation rates J of **$\text{H}_2\text{SO}_4\text{—H}_2\text{O}$ nucleation** **sulphuric acid-water** were measured in the range
24 from 0.1 to $\sim 300 \text{ cm}^{-3}\text{s}^{-1}$ with sulphuric acid monomer concentration approximately from
25 $5 \cdot 10^5$ to 10^7 cm^{-3} or in total sulphate concentration approximately from $4 \cdot 10^8$ to $3 \cdot 10^9 \text{ cm}^{-3}$
26 ³. Formation rates are usually reported as $J_{1.5}$ or J_3 (cut-off sizes of the particle counters are
27 1.5 nm for PSM and 3 nm for **UFCPC** TSI models 3776 and 3025) as discussed in Kulmala et
28 al., (2012). However, particles measured at the end of our flow tube were almost always in
29 the range of 8 – 20 nm, so we report formation rates as they were determined with our
30 particle counters. **The purpose of these nucleation measurements is to be able to compare the**
31 **formation rates and the sulphuric-acid or total-sulphate concentrations, between the two**
32 **sulphuric-acid vapour-production methods**. The results are discussed below.

1 Figure 5 presents DMPS and CIMS data for one cycle of saturator temperatures. The upper
2 most panel (Panel a) presents the number size distribution as a function of time, 2nd panel from
3 top (b) the total particle number concentration, 3rd panel from top (c) shows the hourly averaged
4 sulphuric acid monomer concentration with standard deviation as the error bars and the lower
5 most panel (d) shows hourly averaged saturator temperature. One can see from figure Fig. 5, 1st
6 and 2nd panels from the top (a) and b), that when the temperature of the saturator changes, the
7 number concentration and the number size distribution are not stable immediately. The
8 sulphuric acid concentration overshoots a bit slightly at the beginning as whilst the system is
9 stabilizing stabilizes to steady state. First The first hour from of averages from each of the
10 saturator temperatures were was excluded to ensure only stable steady-state data ($\text{std}(T) = \pm$
11 0.05 K) were included in the averages. When a new cycle started, the T_{sat} dropped from the
12 maximum value (~ 315 K) to the minimum (273 K) causing a long period of unstable data, and
13 the first two hours were excluded from the beginning of the cycle. In the upper most panel a)
14 in figure Fig. 5, nucleation is the main process below temperature of ~ 290 K and growth takes
15 over at higher temperatures. This can be seen as the bimodal distribution at highest saturator
16 temperatures.

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

24 From figure Fig. 6 one can see, it is evident that in the flow tube measurements with CIMS
25 and CI-API-TOF all the measured variables behave as expected to as a function of the
26 increasing saturator temperature. Increasing saturator temperature increases number
27 concentration and diameter of freshly nucleated particles. The number concentration and
28 formation rate seems to saturate at the highest temperatures but this, except for the apparent
29 saturation is due to the limits of the PSM (coupled with CPC, TSI model 3772). The upper
30 limit of observed particle concentration for CPC 3772 is (and hence, the formation rate). PSM
31 was coupled with the TSI model 3772 CPC's, which has an upper limit of 10^4 cm^{-3} , so higher
32 concentrations were still measured as 10^4 cm^{-3} . for the particle concentration. This is also

1 supported by DMPS data which shows higher total caused the observed particle concentration
2 to saturate in Fig. 6, even though the particle concentration than PSM. was confirmed to
3 increase to higher values by DMPS data (not shown in the Fig. 6). Coagulation has a minor
4 effect on the particle number due to a short residence time ($\tau = 30$ s) and relatively low
5 particle concentration. (maximum concentration of $1.2 \cdot 10^4 \text{ cm}^{-3}$ from DMPS data). The
6 relative humidity affects mostly the diameter of the particles, but also decreasing RH
7 decreases the formation rate if similar sulphuric acid concentration is considered. Lower
8 lower formation rate with decreased RH might be caused by the diminishing of the particle
9 diameter below the detection limit of UCPC the UFCPC (TSI model 3776).

10 In figure Fig. 7, the squares present measurements at during dry conditions and stars
11 with during RH of 30 %. The lower right panel Panel d) shows also the detection limit of
12 MARGA for total sulphate concentration. Detection The detection limit was determined from
13 20 hours of measurements with saturator flow rate flowrate set to zero and averaged over the
14 time period. Detection The detection limit was $1.35 \cdot 10^9 \text{ cm}^{-3}$. All the total sulphate
15 concentrations measured below this detection limit were considered as erroneous and rejected
16 from further analysis, even though these values are presented in figure Fig. 7. MARGA can be
17 used with concentration columns to measure lower concentrations of species but it was not
18 available in this study.

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

24 Main The main difference between figures Fig. 6 and 7 can be found in the mean diameter of
25 the particles. In the experiment with CIMS and CI-APi-TOF, the diameter ranges all the way
26 up to ~ 130 nm (Fig. 6, right upper panel) as in the experiment with MARGA, is the maximum
27 diameter is only approximately ~ 23 nm (Fig. 7 right upper panel). The main reason is that in
28 the CIMS and CI-APi-TOF experiment there reached. Due to the greater maximum saturator
29 temperature was increased 15 (315 K higher than in the MARGA experiment. This increases
30 sulphuric acid vapour concentration approximately order of magnitude which condenses on
31 the surface of the particles growing their diameter. At lower saturator temperatures (< 290 K)
32 the mean diameters are closer to each other at similar saturator temperatures and relative

1 **humidity.**) in the experiment with the mass spectrometers, the maximum diameter reached up
2 to ~130 nm compared to the ~23 nm with the experiment with MARGA. The residence times
3 in the flow tube are the same in both experiments (~30 s). The measured sulphuric-acid
4 monomer concentration is at typical atmospheric levels, but the growth rates are much higher:
5 indicating higher concentration of sulphuric-acid-containing condensing vapour than the
6 detected sulphuric-acid-monomer concentration by CIMS. The growth is rather driven by the
7 total sulphate, originating exclusively from the sulphuric acid inside the saturator, than the
8 sulphuric-acid-monomer concentration.

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

24 **3.4 Formation rates and comparison to our previous results**

25 Figure 8 presents formation rates J of the H₂SO₄—H₂O system as a function of sulphuric -
26 acid monomer concentration measured with CIMS at nucleation temperature of $T = 298$ K and
27 **relative humidity RH** of **RH ~30 %**. Sulphuric acid was produced with the method of furnace
28 (red squares, Brus et al., 2011) and with saturator (the black squares, **this present** study).
29 **Sulphuric** The sulphuric-acid concentration for data from Brus et al., (2011) is presented here
30 as residual concentration (i.e. at the end of the flow tube) so that these two measurements
31 would be comparable. Brus et al., (2011) present their data as the initial concentration. Both
32 **data sets** **datasets** have almost identical slopes (1.3 and 1.2) and the **data sets** **formation rates J**

1 have a difference of a factor of 2. For the **data set** measured with **the** production
2 method of **the** furnace, the residence time ($\tau = 15$ s) is defined as the time **that** the particles
3 spend in the flow tube after the nucleation zone. **Nucleation** **The nucleation** zone was
4 experimentally determined (Brus, et al., 2010) and confirmed with CFD model (Herrmann et
5 al., 2010) to be **at** the middle of the flow tube in the measurements with the furnace, where a
6 thermal gradient was present. For the saturator measurements (**this** **present** work), the
7 residence time ($\tau = 30$ s) was defined as the whole time the particles spend in the flow tube.
8 The difference of the residence time is exactly **a** factor of 2. Formation rate is defined as the
9 number concentration divided by the residence time, so these two sets of data lie on top of
10 each other if the same residence time would have been used for formation -rate determination.
11 Figure 9 presents formation rates J of $\text{H}_2\text{SO}_4\text{---H}_2\text{O}$ as a function of residual total sulphate
12 concentration $[\text{SO}_4^{2-}]$ at **relative humidity** **RH** of **RH** ~ 30 % and at nucleation temperature of
13 $T = 298$ K. Stars **present** **are** the data from measurements where sulphuric -acid vapour was
14 produced with **the** furnace and total sulphate measured with bubbler method (Brus et al.,
15 2010). The residence time used in there was $\tau = 15$ s. Squares **present** **are** total sulphate
16 measured with MARGA in this study with different **flow rates** **flow rates** through the saturator,
17 and the residence time was $\tau = 30$ s. All the points have **the** standard deviation as error bars.
18 The detection limit of MARGA is also marked as a dashed vertical line. Formation rates are
19 similar with both production methods. As **in** previously, the factor -of -two difference in the
20 residence time increases the scattering between the two **data sets** **datasets**.

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

29 Figure 10 shows comparison of **the** **apparent** formation rates J as a function of residual
30 sulphuric -acid monomer $[\text{H}_2\text{SO}_4 \text{ monomer}]$ or total sulphate concentration $[\text{SO}_4^{2-}]$ from
31 this study to our previous studies with **the** standard deviation as error bars. Note the **difference**
32 **of a** factor of two **difference** between the residence times. Squares show values measured

1 using mass spectrometers (PSM, red and black squares; TSI 3776, green squares). Stars
2 presents are data measured using ion chromatograph (i.e. total sulphate) methods with two
3 different UFCPC's (TSI 3025A, black stars and TSI 3776, red stars). Figure 10 shows that the
4 production method does not have significant substantial effect as since the results lie on same
5 line when comparing results obtained with mass spectrometers or MARGA and bubbler
6 method. The conditions for all the measurements were similar ($T = 298 \text{ K}$, $\text{RH} \sim 30 \%$).

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

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

19 3.5 Contaminants

20 In our previous study (Brus et al., 2011), an ion chromatograph was used to determine the
21 background levels of ammonia and it was found that the background concentration was below
22 the detection limit of the IC (500 pptv), accounting for the flow rates flowrates in the
23 nucleation chamber. The concentration of background ammonia was measured with the
24 MARGA system in this study. An average total concentration (gas and particle phase) of
25 ammonia was 60 pptv for dry conditions and 126 pptv for $\text{RH} 30 \%$, supporting our
26 previous results. The concentration did not change as a function of saturator temperature and,
27 thus, it is assumed to originate from the purified, particle-free air used as carrier gas in all
28 measurements and the ultrapure water (Milli-Q, Millipore) used for humidification. The
29 concentration for dry conditions is in of the same order of magnitude as the concentration of
30 total sulphate at the lowest (273 K) temperature of the saturator. With increasing the
31 saturator temperature, the ratio of ammonia to total sulphate-ratio decreases from $\sim 1:1$ to

1 ~1:10, or less, for dry conditions and from ~3:1 to ~1:5 for humid conditions. Results of
2 extensive measurements and discussion of the influence of several different carrier gases on
3 measured sulphuric acid concentration by mass spectrometers can be found in the
4 supplementary material (section 3). The extra saturator tests, mentioned in section 3.1 and
5 found in sSupplementary mMaterial, showed that the carrier gas used in this experiment was
6 at least as pure as the most pure gas available commercially (AGA, N₂, 6.0), which has
7 impurities less than 1 ppm, including hydrocarbons less than 0.1 ppm. According to the
8 results found in sSupplementary mMaterial, the actions taken to purify the carrier gas in these
9 experiments were sufficient. Nevertheless, there were contaminants left in the carrier gas at
10 levels which will affect the nucleation process.

12 4 Discussion and Conclusions

13 A method of saturator was used to produce sulphuric acid vapour from neat liquid sulphuric
14 acid for laboratory studies is presented. It was tested and shown to produce similar apparent
15 formation rates during similar conditions to our previous vapour-production method of the
16 furnace. The sulphuric acid or total-sulphate concentration was measured with two
17 independent methods and it was shown to produce exact concentrations as prediction from
18 Richardson et al., (1986) and slightly higher than the prediction from Kulmala and
19 Laaksonen (1990) when measured with MARGA (Fig. 3). Concentrations of sulphuric acid
20 monomer measured with CIMS and CI-APPI-TOF was one to two orders of magnitude
21 lower than the total sulphate values measured with MARGA and the prediction by Eqs. (1)
22 and (2). The only source of sulphuric acid (sulphate measured by MARGA) is the liquid
23 sulphuric acid inside the saturator as seen in Fig. 3. A possible reason for the
24 discrepancy is that the sulphuric acid is in particle phase since the saturator is a
25 significant substantial source of particles. However, these particles are lost in the way from
26 the saturator to the nucleation chamber due to two main reasons; The flow rate: (i) the
27 flowrate (0.5 lpm) in the tube (length: 1 m, I.D. 4 mm) from the saturator to the nucleation
28 chamber is relatively low (0.5 lpm) increasing diffusional losses and (ii) the highly turbulent
29 mixing of the saturator flow with the mixing flow ($Q_{sat} : Q_{mix} \approx 1:30$ or more) in transforms
30 the mixer which is into an effective trap for the particles. The loss of the particles is confirmed
31 with DMPS measurements which cannot explain the discrepancy (sSupplementary mMaterial,
32 Fig. S1). Maximum losses to the particle phase range from in the flow tube are 0 % up to -1.4

1 % with an average below 1 % of the total sulphuric acid sulphate. The discrepancy cannot be
2 explained by the formation of larger clusters containing solely sulphuric acid (dimer, trimer,
3 etc.) either, because the concentration of these clusters are in the order of a few percents
4 or lower than the monomer concentration (Supplementary Material, Fig. S5).

5 The saturator has been used in combination with a flow tube described earlier (Brus et al.,
6 2010) to measure characteristics of H₂SO₄-H₂O nucleation. It takes about 1 hour to stabilize
7 the sulphuric acid vapour concentration after changing the saturator temperature. The
8 characteristics of the freshly nucleated particles together with the conditions used for the
9 nucleation has been identified and presented (Figs. 4 to 7). Total losses of sulphuric acid or
10 total sulphate to the whole flow tube setup have been determined for both methods to detect
11 the concentration of sulphuric acid or total sulphate.

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

17 Formation rates of H₂SO₄-H₂O sulphuric acid-water system were compared to our previous
18 studies (Brus et al., 2010 and 2011), where a method of the furnace was used (Figs. 8-10).
19 Results obtained using mass spectrometers lie on the same line. Obtained apparent formation
20 rates as a function of sulphuric-acid or total-sulphate concentrations were independent of the
21 sulphuric acid vapour production method (furnace vs. saturator). At a lower sulphuric acid
22 monomer concentration ($1-2 \cdot 10^6 \text{ cm}^{-3}$) conditions for these studies were similar ($T = 298 \text{ K}$,
23 $\text{RH} \sim 30 \%$) but at similar formation rates, the UCPC used (TSI model 3776) was probably
24 undercounting compared to more efficient counter (PSM), which sulphuric-acid monomer
25 concentration is caused by one-to-two orders-of-magnitude lower than the small size total
26 sulphate. The slope of the particles. The slopes of the fits to the formation rate data as a
27 function of sulphuric acid monomer concentration are (1.3 ± 0.2) is very similar (1.3 and 1.2
28 for using furnace and saturator, respectively) as obtained in Brus et al., (2011). (1.2 ± 0.1).
29 The comparison to our previous measurements was done to check reproducibility of the
30 nucleation-experiment results between the sulphuric-acid vapour-production methods and to
31 eliminate the production method as a possible reason for the discrepancy. The discussion and
32 interpretation of the slopes (section 3.1) and comparison to the atmospheric data (section 3.5)

1 can be found in Brus et al., (2011). Nucleation results obtained using bubblers or MARGA
2 agree well when compared to each other. Conditions for these studies were similar ($T = 298$
3 K, RH ~30 %) but at similar formation rates, the sulphuric acid monomer concentration is one
4 to two orders of magnitude lower than the total sulphate.. (2011).

5 Other possible reasons for this difference between sulphuric acid monomer and total sulphate
6 is that sulphuric acid molecules are most probably bonded to some molecule(s) (e.g. amines,
7 ammonia, organics) and not been detected by CIMS or identified from the CI-APi-TOF
8 spectra (Kulmala et al., 2013). ~~As Kurten et al., (2011) state, base molecules can be only in~~
9 ~~minor importance due to the fact that nitrate ion (NO_3^-) will most probably substitute the base~~
10 ~~out in the CIMS charging process. Nevertheless, there is expected to be a substantial pool of~~
11 ~~clusters formed of sulphuric acid-base molecules in our system, which are too small to be~~
12 ~~detected by current state-of-art particle counters such as PSM. These clusters are the main~~
13 ~~reason for the discrepancy between measured total sulphate and the monomer concentrations.~~

14 Same or similar clusters are most probably forming in all laboratory nucleation experiments
15 involving sulphuric acid, as there are always contaminants present in the carrier gases (see
16 supplementary material, section 6 and Figs. S6 to S11). Average ammonia concentration of 60
17 pptv was found in the system for dry conditions and 126 pptv for RH 30 % as a contaminant
18 and it was independent of the saturator temperature. It is assumed to originate from the
19 purified, dry, particle -free air used as carrier gas and from the ultrapure water used for
20 humidifying the mixing flow. Ammonia concentration is enough to affect the nucleation
21 process itself **significantly** **substantially** but the magnitude of this effect was not studied in this
22 work. Ammonia can bind sulphuric acid by forming clusters, which might reduce the
23 monomer concentration measured with CIMS and CI-APi-TOF slightly **but as**. **Since** the
24 contaminant level was constant and saturator temperature was increased, reducing the
25 contaminant to total sulphate-ratio from ~1:1 to ~1:10 for dry conditions and from ~3:1 to
26 ~1:5 for humid conditions, **it** does not explain the discrepancy between the two sulphuric -
27 acid - or total-sulphate-detection methods. **Even though the contaminant levels might**
28 **sound** appear high to some, those are still below the most-pure commercially available gases
29 (AGA, N₂, 6.0).

30 Other possible reasons for the difference between sulphuric acid monomer and total sulphate
31 is that sulphuric acid molecules are most probably bonded to some molecule(s) (e.g. amines,
32 ammonia, organics) and not detected by CIMS or identified from the CI-Api-TOF spectra

1 (Kulmala et al., 2013). As Kurten et al. (2011) state, base molecules can be only in minor
2 importance due to the fact that nitrate ion (NO_3^-) will most probably substitute the base out in
3 the CIMS charging process. Nevertheless, there is expected to be a substantial pool of clusters
4 formed of sulphuric acid-base molecules in our system, which are too small to be detected by
5 current state-of-art particle counters such as PSM. These clusters are the main reason for the
6 discrepancy between measured total-sulphate and the monomer concentrations. Same or
7 similar clusters are most probably forming in all laboratory nucleation experiments involving
8 sulphuric acid, as there are always contaminants present in carrier gases. Further analysis of
9 the CI-API-TOF mass spectra showed a large number of stick-unit masses correlating with
10 sulphuric-acid monomer ion (HSO_4^-) suggesting a large number of clusters containing
11 sulphuric acid which are not used for calculating the sulphuric-acid concentration measured
12 by mass spectrometers (see sSupplementary mMaterial, section 6 and Fig. S6–S11).
13 Sulphuric acid (measured here as sulphate) can contribute to the early growth of ultrafine
14 particles to a much larger extent than currently thought, since most of the sulphuric acid
15 remains undetected. Also the huge number of correlating masses with increasing sulphuric-
16 acid concentration implies that there are numerous substances that can form stable clusters
17 with sulphuric acid that may be the starting point for particle formation.

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

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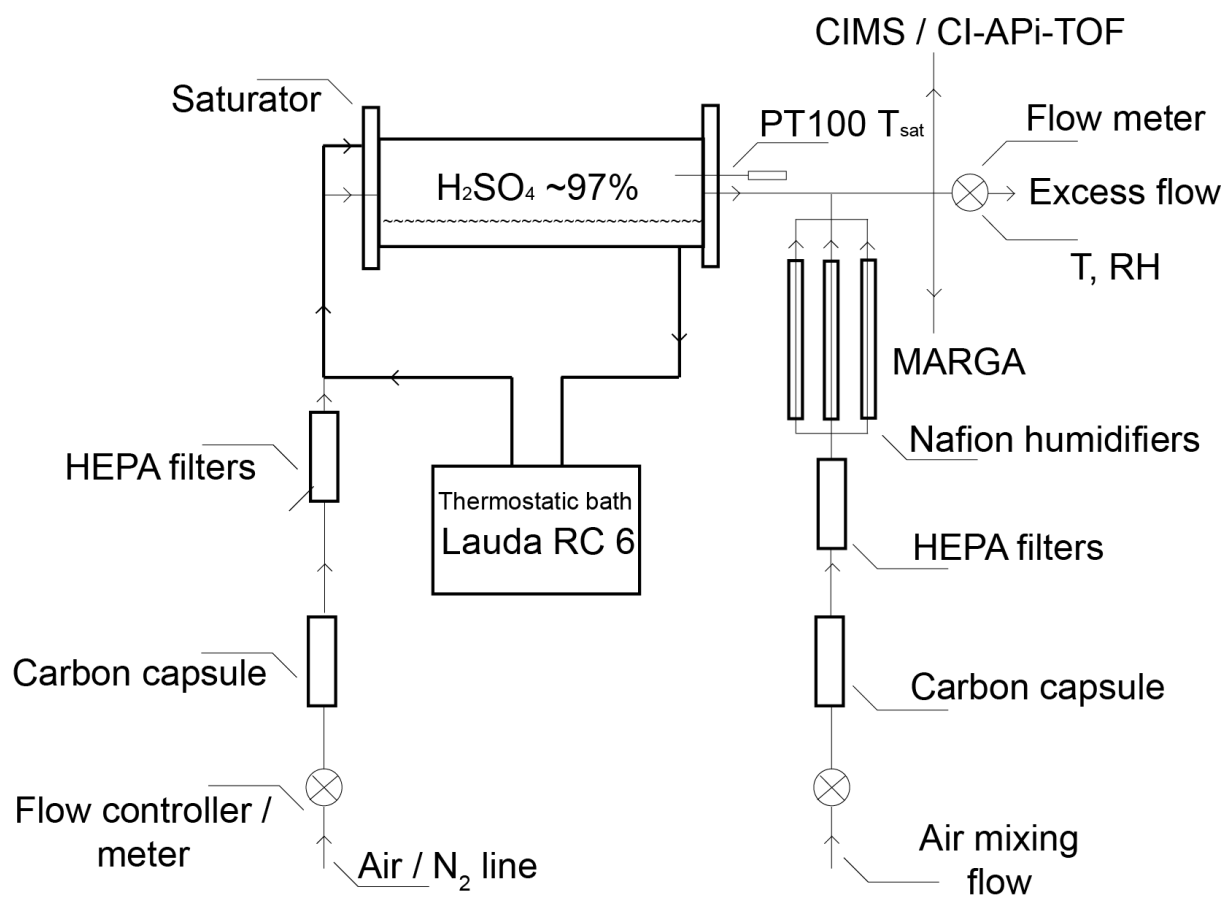
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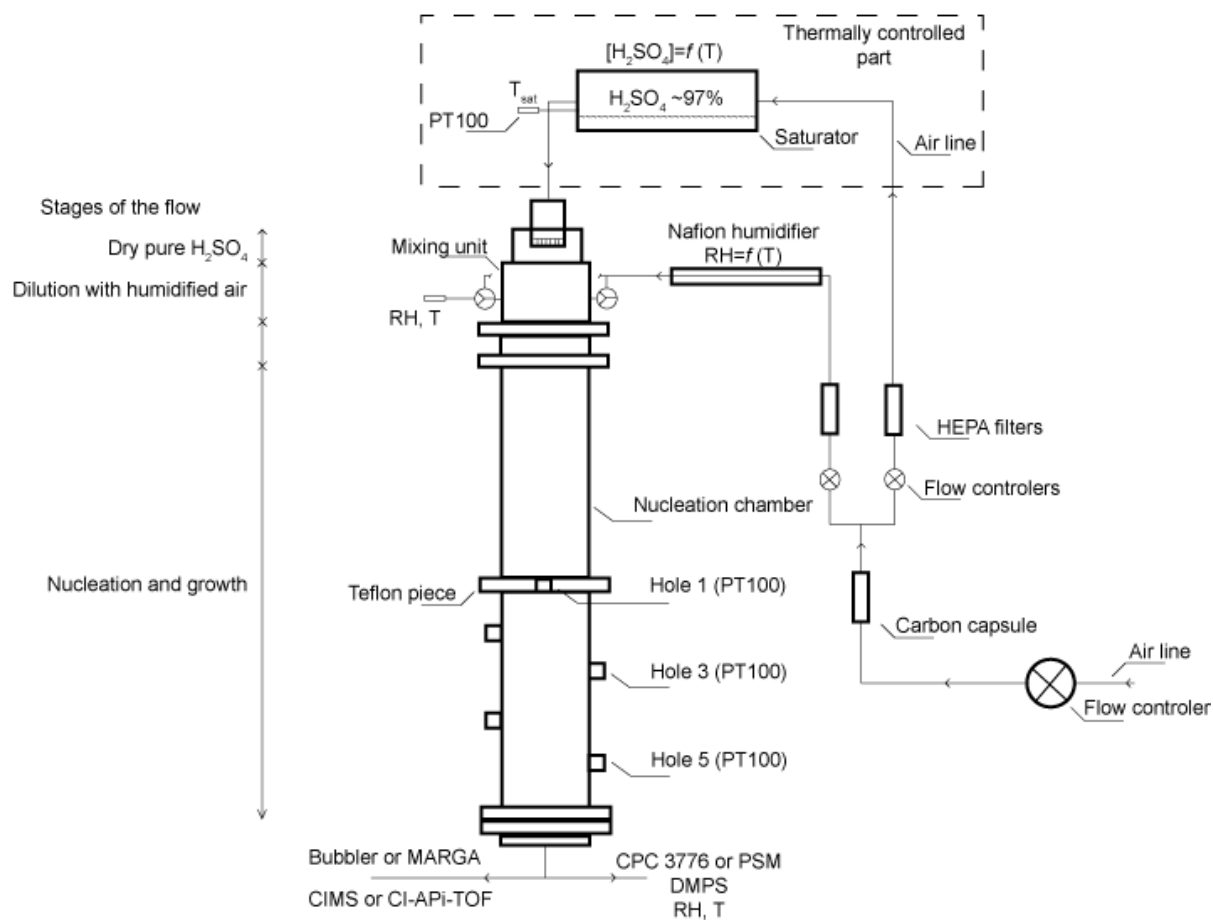
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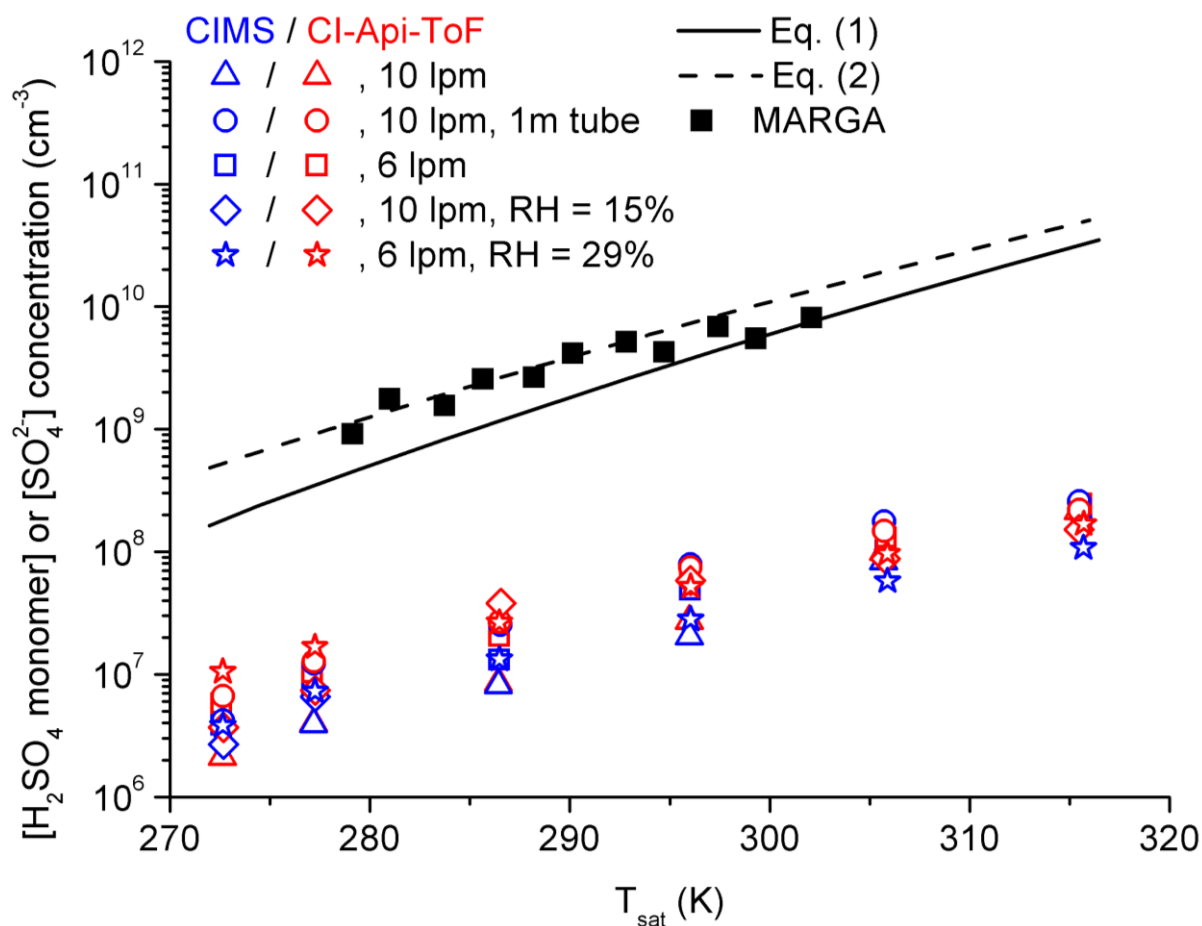
3 Figure 1. Schematic figure of the setup for testing the saturator.



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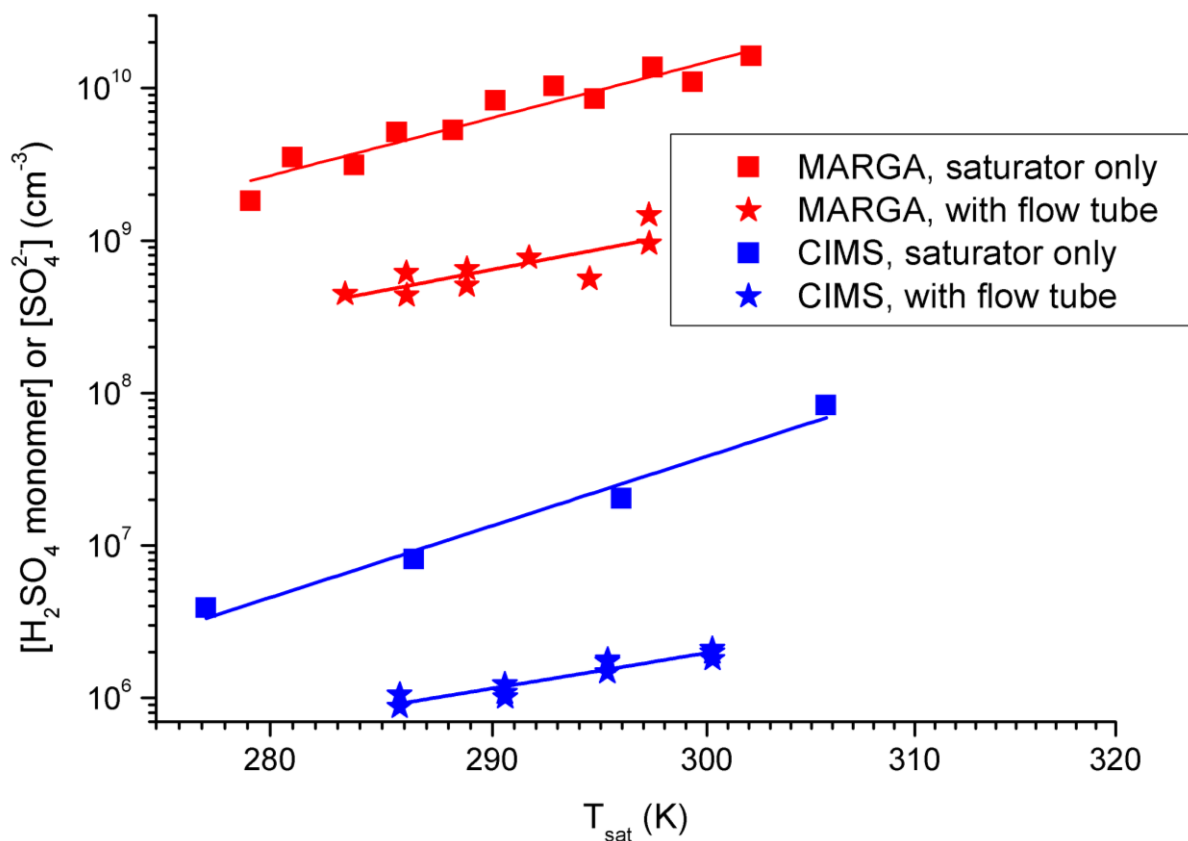
3 Figure 2. Flow -tube setup.



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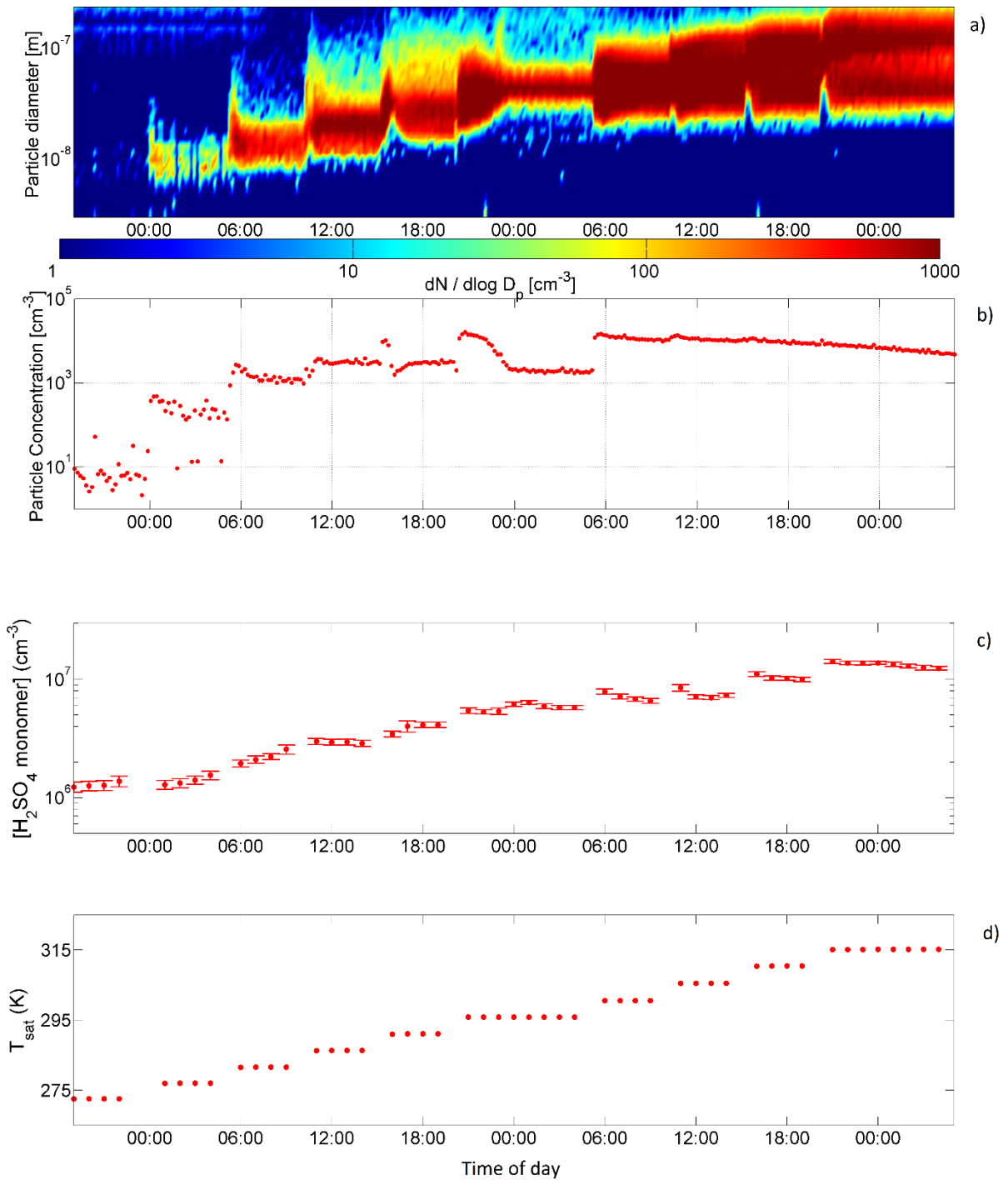
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3 Figure 3. Measured sulphuric acid monomer $[H_2SO_4 \text{ monomer}]$ and total sulphate $[SO_4^{2-}]$
 4 (black squares) concentrations together with predicted values by Eqs. (1) and (2) as a function
 5 of saturator temperature T_{sat} . Saturator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



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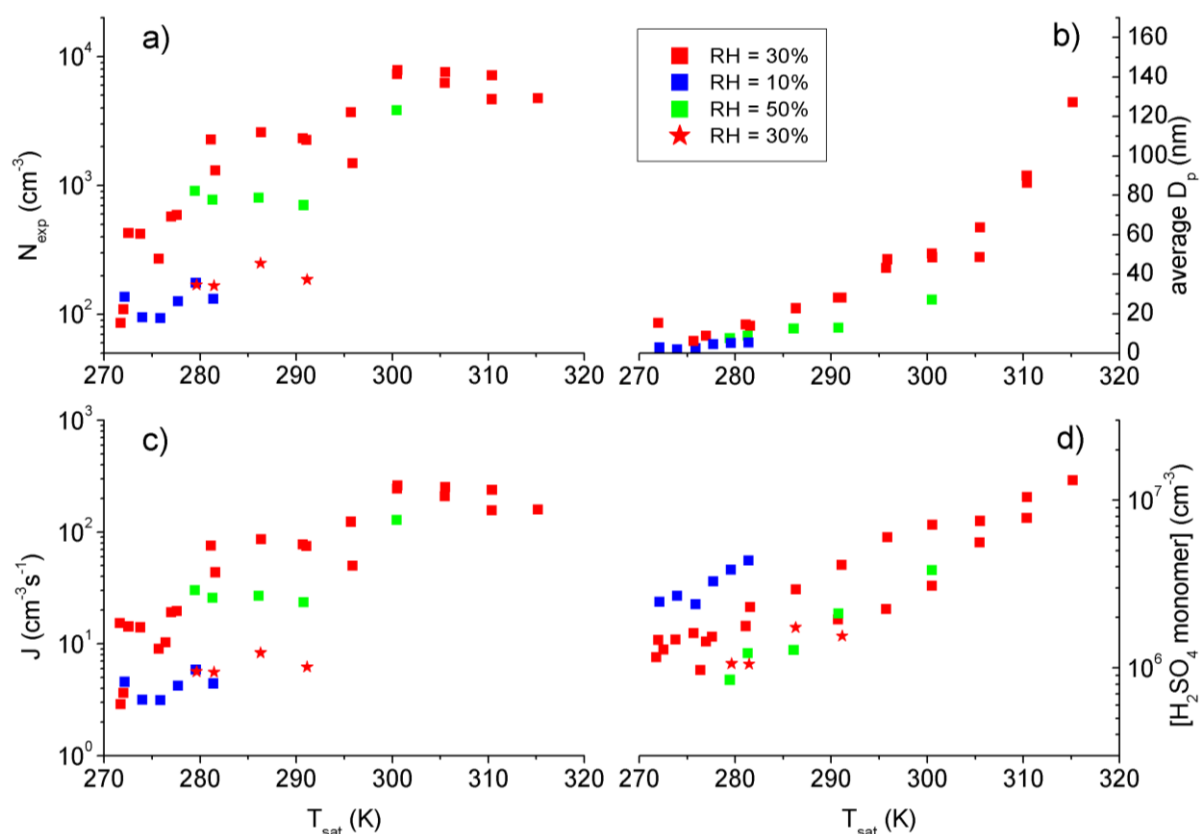
Figure 4. Comparison of MARGA and CIMS data between test with only saturator (dry conditions, squares) and with saturator and flow tube (RH ~30 %, stars). Different flow rates through saturator have been accounted for. Average total loss factors are $TLF_{\text{MARGA}} = 10.0 \pm 1.2$ and $TLF_{\text{CIMS}}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



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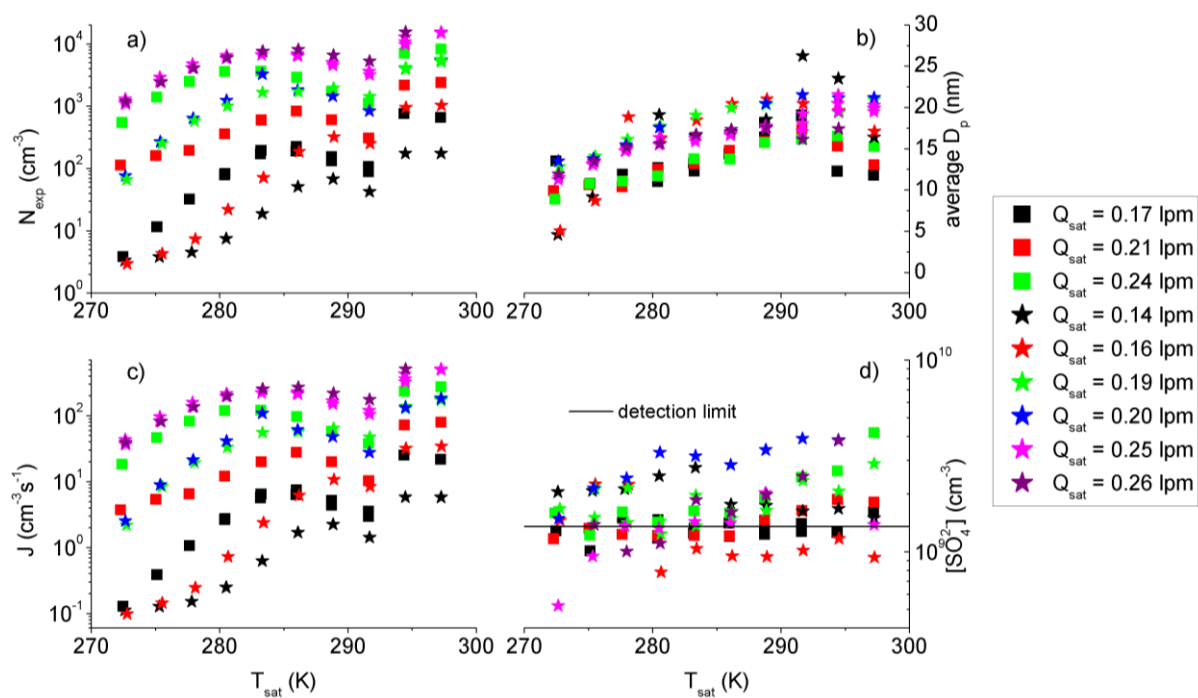
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3 Figure 5. DMPS and CIMS data from one T_{sat} cycle. Upper most panel Panel a) shows the
 4 number size distribution, 2nd panel from top b) shows the total number concentration from
 5 DMPS, 3rd panel presents c) shows the CIMS -measured sulphuric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



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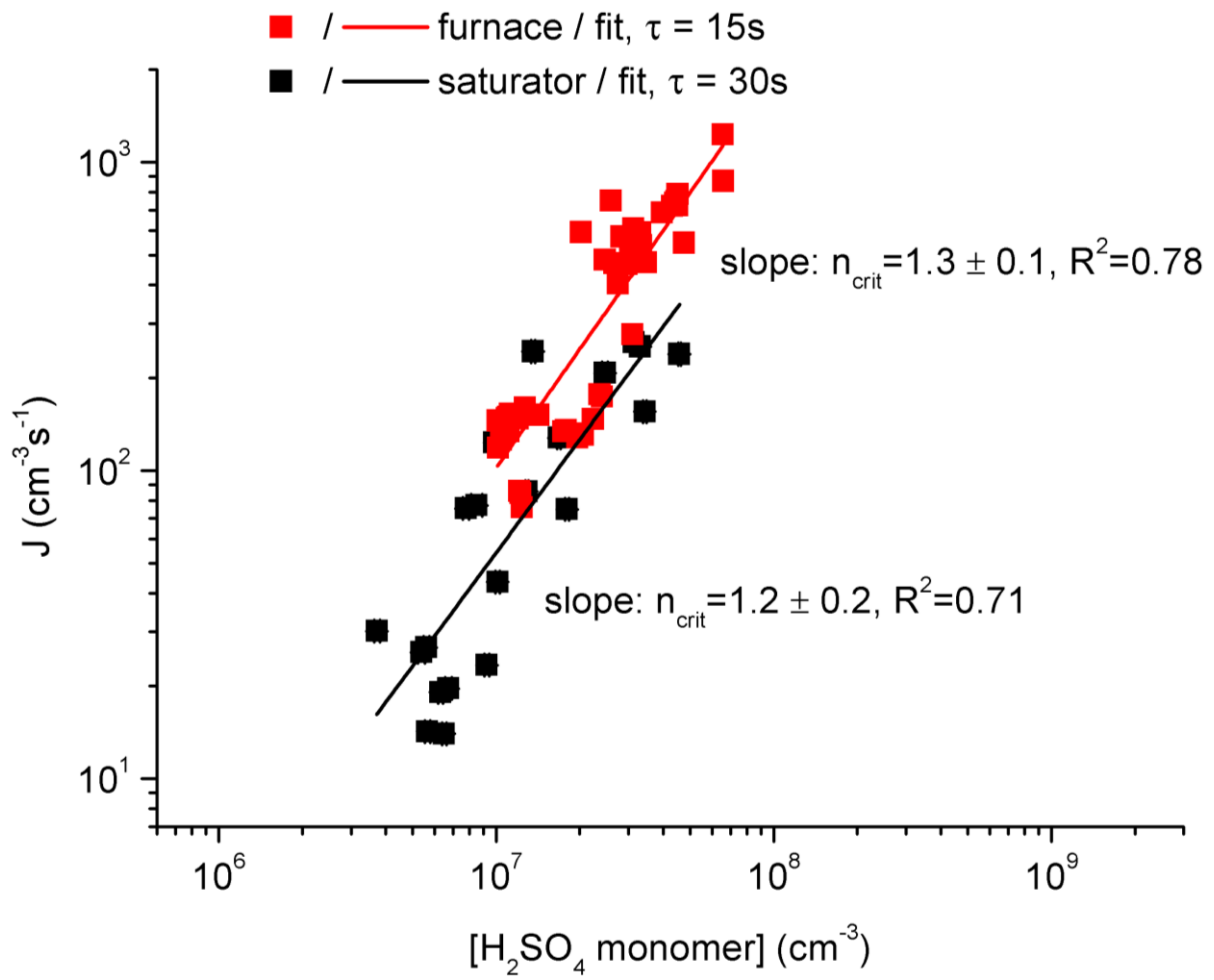
3 Figure 6. Number concentration N_{exp} (left upper panel) a)) measured with PSM and TSI 3776,
 4 geometric -mean diameter D_p (right upper panel), b)), apparent formation rate J (left lower
 5 panel) c)) of the freshly nucleated particles and sulphuric -acid monomer concentration
 6 measured (panel d)) with CIMS (squares) or CI-APpi-TOF (stars) with several relative
 7 humidities as a function of saturator temperature with saturator flow of 0.1 lpm. All data
 8 isare averaged over timea period of constant saturator temperature extractluding first hour. to
 9 ensure steady-state. Stars are measured with CI-APpi-TOF and squares with CIMS. All data
 10 isare averaged over timea period of constant saturator temperature (± 0.05 K) extracting first
 11 hour.



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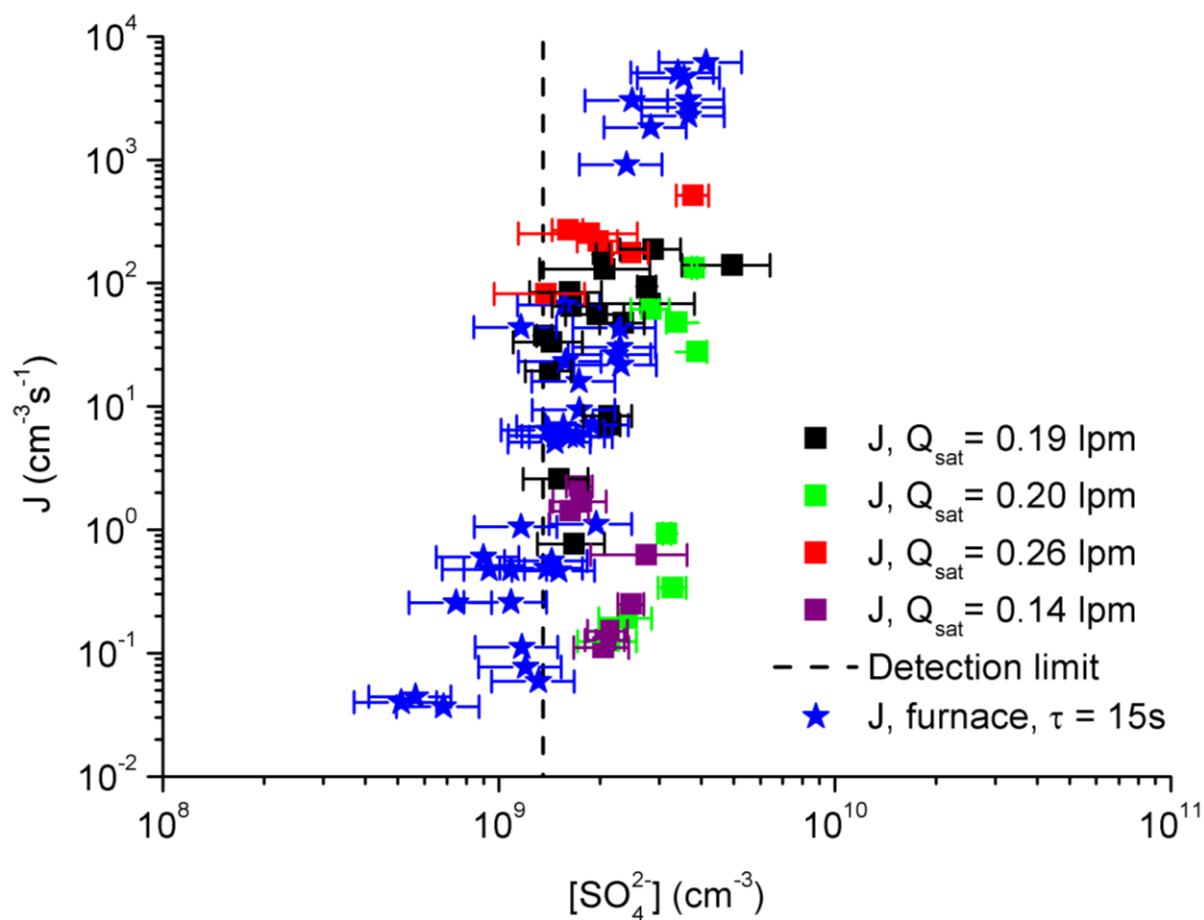
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3 Figure 7. Number concentration N_{exp} (left upper panel) a)) measured with TSI 3776,
 4 geometric mean diameter D_p (right upper panel), b)), formation rate J (left lower panel) c)) of
 5 the freshly nucleated particles and total -sulphate concentration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



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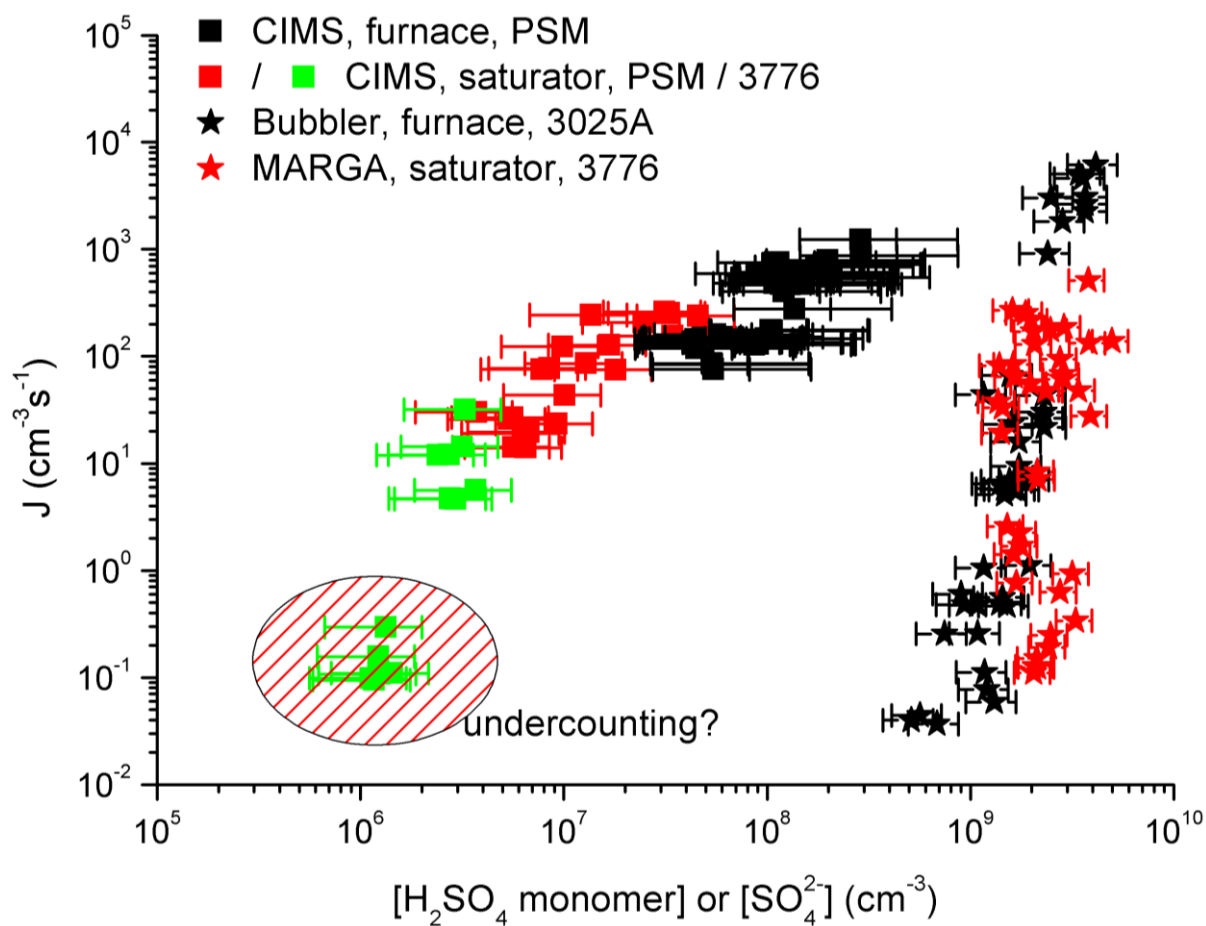
3 Figure 8. Formation rates J as a function of residual sulphuric acid monomer concentration
 4 $[\text{H}_2\text{SO}_4 \text{ monomer}]$ at $T = 298 \text{ K}$ and $\text{RH} \sim 30 \%$ measured using CIMS. In the first **data**
 5 **set** (red squares) sulphuric acid vapour was produced with the furnace method, and the
 6 residence time was defined to be 15 s (Brus et al., 2011).



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3 Figure 9. Formation rates J as a function of total sulphate concentration $[\text{SO}_4^{2-}]$ measured
 4 with MARGA or bubbler with different saturator flow rates. MARGA's detection
 5 limit is marked with the dashed line. Relative humidity RH $\sim 30\%$ and nucleation temperature
 6 $T = 298\text{ K}$. Sulphuric acid vapour was produced with the furnace method (Brus et al., 2010)
 7 for bubbler measurements and with the saturator method for MARGA.



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3 Figure 10. Comparison of formation rates J as a function of residual sulphuric acid monomer
 4 concentration $[\text{H}_2\text{SO}_4]$ or total sulphate concentration $[\text{SO}_4^{2-}]$ to our previous results.
 5 Conditions are similar ($T=298 \text{ K}$, $\text{RH} \sim 30 \%$). Note the factor-of-two difference between the
 6 residence times between furnace and saturator measurements. Sulphuric acid vapour was
 7 previously produced with the furnace method and total sulphate concentration measured with
 8 the bubbler method (Brus et al., 2010).