Total sulphate vs. sulphuric acid monomer in nucleation studies

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Abstract

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

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

1 Introduction

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

Significant effort has been made by field measurements and laboratory studies, together with computer simulations, to understand the particle-formation mechanism itself and the

atmospheric conditions involved in the gas-to-liquid conversion. Despite such effort and numerous results, the underlying mechanism is not yet found.

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

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

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

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

Applying the saturator as the source of the sulphuric-acid vapour made it possible to compare the saturator to the furnace, which was used as the source of the sulphuric acid previously (Brus et al., 2010 and 2011) and eliminate the production method as a reason for the discrepancy. The flow-tube measurements with the saturator and the two sulphuric-acid or total-sulphate detection methods were conducted to check reproducibility of particle formation rates between the saturator and the furnace, with similar observed sulphuric-acid or total-sulphate concentrations. The measured sulphuric-acid or total-sulphate concentrations were compared and the total losses of sulphuric acid or sulphate were determined for both mass spectrometers and the ion chromatograph. The level of ammonia contaminant in the system was determined with the ion-chromatograph method.

2 Experimental

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

detection methods is described. The instrumentation for sulphuric-acid or total-sulphate and freshly-formed-particle detection is shortly presented.

2.1 Saturator

The saturator was a horizontally placed cylinder made of iron with Teflon insert inside the cylinder (inner diameter, I.D., of 5 cm). It was thermally controlled with a liquid-circulating bath (LAUDA RC 6) and the temperature was measured just above the liquid surface with a calibrated PT100 probe (accuracy ± 0.05 K) inserted from the outlet side of the saturator (Fig. 1). The saturator was filled with 150-200 ml of pure sulphuric acid (~97 % wt., Baker analyzed). H_2SO_4 vapour was produced by flowing purified, dry, particle-free carrier gas through the saturator in the range of 0.05-1 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:

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

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 ΔH_v (T_0) / R = 10156. See Kulmala and Laaksonen (1990) for more details. Here the predicted sulphuric-acid concentration depends only on saturator temperature, flowrate through the saturator and mixing flow. Measured sulphuric-acid or total-sulphate concentration is compared also to empirical fit by Richardson et al. (1986):

$$\ln p = 20.70 - \frac{9360}{T} \ . \quad (2)$$

The fit is made to their measurement data in the temperature range of 263.15-303.15 K, which suits the temperature range of 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-Api-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 (Fig. 1). The flow from the saturator (0.5 lpm) was mixed with another flow of 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-Api-TOF) in order to increase the sulphuric-acid concentration. The temperature was kept constant from 2 to 8 hours in order to achieve a steady state. The measured sulphuric-acid monomer and total-sulphate concentrations were compared to theoretical values calculated from the vapour pressure of sulphuric acid using Eq. (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 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 inside the saturator are lost in the 1-m long, thermally controlled Teflon tube (I.D. 4 mm) before the mixer, by diffusion and by the turbulent mixing in the mixer. After the mixing unit, nucleation and subsequent growth take place in the laminar flow chamber. The flow chamber 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 thermally controlled with a liquid circulating bath (LAUDA RC 6). One of the 100-cm-long parts of the flow chamber has four holes on the sides every 20 cm from the beginning of the chamber. The 3.5-cm Teflon connector between the two 100-cm flow-tube pieces has also a hole (see Fig. 2). These holes are used to continuously measure temperature in the flow tube with PT100 probes to ensure constant desired nucleation temperature. The RH of the mixing flow is controlled by 2 or 3 Nafion humidifiers. RH and temperature are measured also at the end of the tube with Vaisala HMP37E and humidity data processor Vaisala HMI38. Both saturator and mixing flow of the tube are controlled by a mass flowrate controller (MKS type 250) with an accuracy of ± 3 %. Flowrates through the saturator for nucleation measurements were kept at 0.13-0.27 lpm. The mixing flow was kept at approximately 11 lpm.

2.4 H_2SO_4 monomer, sulphate and particle detection

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

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

The monomer concentration is determined by the ratio of the resulting ion signals (HSO_4^- and $HSO_4^-\cdot HNO_3$) and the reagent ion signals (NO_3^-, $HNO_3\cdot NO_3^-$ and $(HNO_3)_2\cdot NO_3^-$). This ratio is then multiplied by the instrument-dependent calibration factor in both instruments. The calibration factor used here was $5\cdot10^9$ for both instruments. Neither CIMS nor CI-Api-TOF was calibrated using the saturator setup, but instead before the experiments using the standard calibration procedure of oxidation of SO_2 with OH (Kürten et al., 2012). For more information about the calibration of CIMS, see Berresheim et al. (2000), Petäjä et al. (2009), Zheng et al.

(2010) and Kürten et al. (2012). The nominal sample flowrate of these instruments is ~10 lpm. We considered only the monomer concentration, although detection of dimers and even larger clusters of pure sulphuric acid is possible with CI-Api-TOF. This was done because the dimer concentration was always in the magnitude of ~1 % of monomer concentration and the trimer concentration was in the magnitude of ~1 % of the dimer concentration and so on (e.g. Jokinen et al. 2012). The charging efficiency might not be the same for these clusters as it is for monomer. This would cause the calibration factor to change and the calculated concentration to be erroneous. The uncertainty in the resulting monomer concentration is estimated to be a factor of ~2. The nominal lower detection limit of CIMS and CI-Api-TOF is estimated to be $5 \cdot 10^4$ cm^{-3}, and the upper limit is approximately 10^9 cm^{-3} for both instruments. At this high concentration, the primary ions start to deplete causing the calibration factor to change.

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

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

The total-particle number concentration was measured with a Particle Size Magnifier (PSM, Airmodus Oy, Finland, Vanhanen et al., 2011, coupled with CPC TSI model 3772) and with Ultra-Fine CPC's (UFCPC, TSI models 3776, 3025A) with cut-off mobility diameters of ~1.5

nm and ~3 nm, respectively. Differential Mobility Particle Sizer (DMPS) was used to measure particle number size distribution from 3 to ~250 nm in a closed-loop arrangement (Jokinen and Mäkelä, 1997) using a blower to measure the wet size of the particles. The DMPS was run with a sheath flow of ~11 lpm and sample flow of 1.5 lpm in the short HAUKE-type Differential Mobility Analyzer (DMA). The DMA was coupled with UFCPC (TSI model 3025A) and with a bipolar radioactive (^{63}Ni) neutralizer. The charging efficiencies were calculated following the parameterization of Wiedensohler and Fissan (1991). The RH of the sheath flow was monitored to ensure that it was same as the RH in the chamber.

3 Results

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

3.1 Test of the saturator

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

two inlet flowrates (6 lpm for RH 29 % and 10 lpm for RH 15 %). MARGA experiments were conducted in dry conditions.

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

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

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

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

Extra saturator tests with mass spectrometers were done using three different carrier gas purities (N_2 6.0, N_2 5.0 and pressurized air) to check if the carrier gas used in our experiments (pressurized air) was more dirty than the most pure commercial ones. Two different purity sulphuric acids (~97 % and 100 %) were tested also to check if the purity of the acid itself has an influence. Changing the carrier gas or the sulphuric acid purity did not affect the observed

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

3.2 Losses of sulphuric acid and sulphate in the flow tube

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

Figure 4 presents the measured sulphuric-acid-monomer and total-sulphate concentration from the saturator tests (squares) and nucleation measurements (stars) as a function of the saturator

temperature. Saturator tests were done in dry conditions and nucleation measurements in RH 30 %. An inlet pipe is used to connect the mass spectrometer to the flow tube. Brus et al. (2011) state that the Wall Loss Factor (*WLF*) in the inlet pipe of length 100 + 22 cm is WLF_{inlet} = ~4. This factor, together with the mixing ratios, was accounted for to make the data sets directly comparable.

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

From Fig. 4, it is evident that wall losses are not the only losses affecting the measured concentrations since the trends in the fits for nucleation measurements are less steep than the ones from saturator tests. The losses to the particle phase also affect the situation. The maximum losses of sulphuric acid to particle phase are calculated using the DMPS data measured at the end of the nucleation chamber only. The total volume of the particles is calculated within the size distribution assuming that the particles are composed only of pure sulphuric acid with density of 1.84 g cm^{-3}. The losses of sulphuric acid to particles range from 0 % (dry conditions, T_{sat} = 273 K) up to maximum of 1.4 % (RH = 30 %, T_{sat} = 292 K) of the total sulphate concentration. Higher saturator temperature increases the number and the diameter of the particles, and relative humidity increases the diameter of the particles. The losses to the particle phase are substantial at the highest values of saturator temperature but this estimate is the maximum limit since the particles are not composed only of pure sulphuric-acid molecules. Contaminants from the flow condense to the particle phase or bond with sulphuric acid. When using humid conditions, sulphuric-acid particles uptake water since sulphuric acid is very hygroscopic. At the highest temperature of the saturator, the size distribution unfortunately extends out of the DMPS range (3-250 nm), thus conversely underestimating the losses. Losses to the clusters smaller than the cut-off size of the particle counters are substantial. The maximum losses to the particle phase have been calculated for each of the saturator temperature values and plotted with the measured monomer and total sulphate concentrations together with the prediction from Eq. (1) in Fig. S1 in supplementary material. Even summing up the measured monomer concentration and the losses to the particle phase leaves the summed total

concentration at least one order of magnitude lower than the measured total sulphate and the prediction by Eq. (1).

3.3 Nucleation measurements

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

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

Figures 6 and 7 present the number concentration N_{exp} (panel a)), geometric mean diameter D_p (panel b)) and apparent formation rate J (panel c)) of freshly nucleated particles with sulphuric-acid monomer concentration [H_2SO_4 monomer] or total sulphate [SO_4^{2-}] (panel d)) as a function of saturator temperature T_{sat} for nucleation temperature of 298 K with several different relative

humidity values (Fig. 6) and saturator flowrates (Fig. 7). The formation rate is reported the observed particle concentration N_{exp} divided by the residence time τ.

From Fig. 6, it is evident that all measured variables behave as expected as a function of the saturator temperature, except for the apparent saturation of the observed particle concentration (and hence, the formation rate). PSM was coupled with the TSI model 3772 CPC's, which has an upper limit of 10^4 cm^{-3} for the particle concentration. This caused the observed particle concentration to saturate in Fig. 6, even though the particle concentration was confirmed to increase to higher values by DMPS data (not shown in the Fig. 6). Coagulation has a minor effect on the particle number due to a short residence time (τ = 30 s) and relatively low particle concentration. The relative humidity affects mostly the diameter of the particles, but also decreasing RH decreases the formation rate if similar sulphuric acid concentration is considered. A lower formation rate with decreased RH might be caused by the diminishing of the particle diameter below the detection limit of the UFCPC (TSI model 3776).In Fig. 7, the squares present measurements during dry conditions and stars during RH of 30 %. Panel d) shows also the detection limit of MARGA for total sulphate concentration. The detection limit was determined from 20 hours of measurements with saturator flowrate set to zero and averaged over the time period. The detection limit was $1.35 \cdot 10^9$ cm^{-3}. All the total sulphate concentrations measured below this detection limit were considered as erroneous and rejected from further analysis, even though these values are presented in Fig. 7. MARGA can be used with concentration columns to measure lower concentrations of species but it was not available in this study.

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

The main difference between Fig. 6 and 7 is the maximum diameter reached. Due to the greater maximum saturator temperature (315 K) in the experiment with the mass spectrometers, the maximum diameter reached up to ~130 nm compared to the ~23 nm with the experiment with MARGA. The residence times in the flow tube are the same in both experiments (~30 s). The measured sulphuric-acid monomer concentration is at typical atmospheric levels, but the growth rates are much higher: indicating higher concentration of sulphuric-acid-containing

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

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

3.4 Formation rates and comparison to our previous results

Figure 8 presents formation rates J of the H_2SO_4-H_2O system as a function of sulphuric-acid monomer concentration measured with CIMS at nucleation temperature of T = 298 K and RH of ~30 %. Sulphuric acid was produced with the method of furnace (red squares, Brus et al., 2011) and with saturator (the black squares, present study). The sulphuric-acid concentration for data from Brus et al. (2011) is presented here as residual concentration (i.e. at the end of the flow tube) so that these two measurements would be comparable. Brus et al. (2011) present their data as the initial concentration. Both datasets have almost identical slopes (1.3 and 1.2) and the formation rates J have a difference of a factor of 2. For the dataset measured with the production method of the furnace, the residence time (τ = 15 s) is defined as the time that the particles spend in the flow tube after the nucleation zone. The nucleation zone was experimentally determined (Brus et al., 2010) and confirmed with CFD model (Herrmann et al., 2010) to be in the middle of the flow tube in the measurements with the furnace, where a thermal gradient was present. For the saturator measurements (present work), the residence time (τ = 30 s) was defined as the whole time the particles spend in the flow tube. The difference of

the residence time is exactly a factor of 2. Formation rate is defined as the number concentration divided by the residence time, so these two sets of data lie on top of each other if the same residence time would have been used for formation-rate determination.

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

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

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

The slope of the data measured using MARGA or bubblers is steeper than the slope of the results measured with mass spectrometers. There is a discrepancy of one-to-two orders-of-

magnitude between sulphuric-acid monomer and total-sulphate concentration for similar formation rates. The UFCPC 3776 (green squares) was probably undercounting at the lowest sulphuric acid concentrations. This can be seen in Fig. 10 where the lowest observed formation rates are not consistent with the rest of the data. This is probably caused by the small size of the particles at such low sulphuric-acid concentration ($1\text{-}2\cdot10^6$ cm^{-3}) (Sipilä et al., 2010).

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

3.5 Contaminants

In our previous study (Brus et al., 2011), an ion chromatograph was used to determine the background levels of ammonia and it was found that the background concentration was below the detection limit of the IC (500 pptv), accounting for the flowrates in the nucleation chamber. The concentration of background ammonia was measured with the MARGA system in this study. An average total concentration (gas and particle phase) of ammonia was 60 pptv for dry conditions and 126 pptv for RH 30 %, supporting our previous results. The concentration did not change as a function of saturator temperature, thus it is assumed to originate from the purified, particle-free air used as carrier gas in all measurements and the ultrapure water (Milli-Q, Millipore) used for humidification. The concentration for dry conditions is in the same order of magnitude as the concentration of total sulphate at the lowest (273 K) temperature of the saturator. When increasing the saturator temperature, ammonia to total sulphate-ratio decreases from ~1:1 to ~1:10 or less for dry conditions and from ~3:1 to ~1:5 for humid conditions. The extra saturator tests, mentioned in section 3.1 and found in supplementary material, showed that the carrier gas used in this experiment was at least as pure as the most pure gas available commercially (AGA, N_2, 6.0), which has impurities less than 1 ppm, including hydrocarbons less than 0.1 ppm. According to the results found in supplementary material, the actions taken to purify the carrier gas in these experiments were sufficient. Nevertheless, there were contaminants left in the carrier gas at levels which will affect the nucleation process.

4 Discussion and Conclusions

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

The characteristics of the freshly nucleated particles together with the conditions used for the nucleation has been identified and presented (Fig. 4-7). Total losses of sulphuric acid or total sulphate to the whole flow-tube setup have been determined for both methods to detect the concentration of sulphuric acid or total sulphate.

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

Formation rates of sulphuric acid-water system were compared to our previous studies (Brus et al., 2010 and 2011), where a method of the furnace was used (Fig. 8-10). Obtained apparent formation rates as a function of sulphuric-acid or total-sulphate concentrations were independent of the sulphuric-acid vapour-production method (furnace vs saturator). Conditions for these studies were similar (T = 298 K, RH ~30 %) but at similar formation rates, the sulphuric-acid monomer concentration is one-to-two orders-of-magnitude lower than the total sulphate. The slope of the fit to the formation-rate data as a function of sulphuric-acid monomer concentration (1.3 ± 0.2) is very similar as obtained in Brus et al. (2011) (1.2 ± 0.1). The comparison to our previous measurements was done to check reproducibility of the nucleation-experiment results between the sulphuric-acid vapour-production methods and to eliminate the production method as a possible reason for the discrepancy. The discussion and interpretation of the slopes (section 3.1) and comparison to the atmospheric data (section 3.5) can be found in Brus et al. (2011).

Average ammonia concentration of 60 pptv was found in the system for dry conditions and 126 pptv for RH 30 % as a contaminant and it was independent of the saturator temperature. It is assumed to originate from the purified, dry, particle-free air used as carrier gas and from the ultrapure water used for humidifying the mixing flow. Ammonia concentration is enough to affect the nucleation process itself substantially but the magnitude of this effect was not studied in this work. Ammonia can bind sulphuric acid by forming clusters, which might reduce the monomer concentration measured with CIMS and CI-Api-TOF slightly. Since the contaminant level was constant and saturator temperature was increased, reducing the contaminant to total sulphate-ratio from ~1:1 to ~1:10 for dry conditions and from ~3:1 to ~1:5 for humid conditions, does not explain the discrepancy between the two sulphuric-acid- or total-sulphate-detection methods. Even though the contaminant levels might sound high, those are still below the most-pure commercially available gases (AGA, N_2, 6.0).

Other possible reasons for the difference between sulphuric acid monomer and total sulphate is that sulphuric acid molecules are most probably bonded to some molecule(s) (e.g. amines, ammonia, organics) and not detected by CIMS or identified from the CI-Api-TOF spectra (Kulmala et al., 2013). As Kurten et al. (2011) state, base molecules can be only in minor importance due to the fact that nitrate ion (NO_3^-) will most probably substitute the base out in the CIMS charging process. Nevertheless, there is expected to be a substantial pool of clusters formed of sulphuric acid-base molecules in our system, which are too small to be detected by

current state-of-art particle counters such as PSM. These clusters are the main reason for the discrepancy between measured total-sulphate and the monomer concentrations. Same or similar clusters are most probably forming in all laboratory nucleation experiments involving sulphuric acid, as there are always contaminants present in carrier gases. Further analysis of the CI-Api-TOF mass spectra showed a large number of stick-unit masses correlating with sulphuric-acid monomer ion (HSO_4^-) suggesting a large number of clusters containing sulphuric acid which are not used for calculating the sulphuric-acid concentration measured by mass spectrometers (see supplementary material, section 6 and Fig. S6-S11). Sulphuric acid (measured here as sulphate) can contribute to the early growth of ultrafine particles to a much larger extent than currently thought, since most of the sulphuric acid remains undetected. Also the huge number of correlating masses with increasing sulphuric-acid concentration implies that there are numerous substances that can form stable clusters with sulphuric acid that may be the starting point for particle formation.

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

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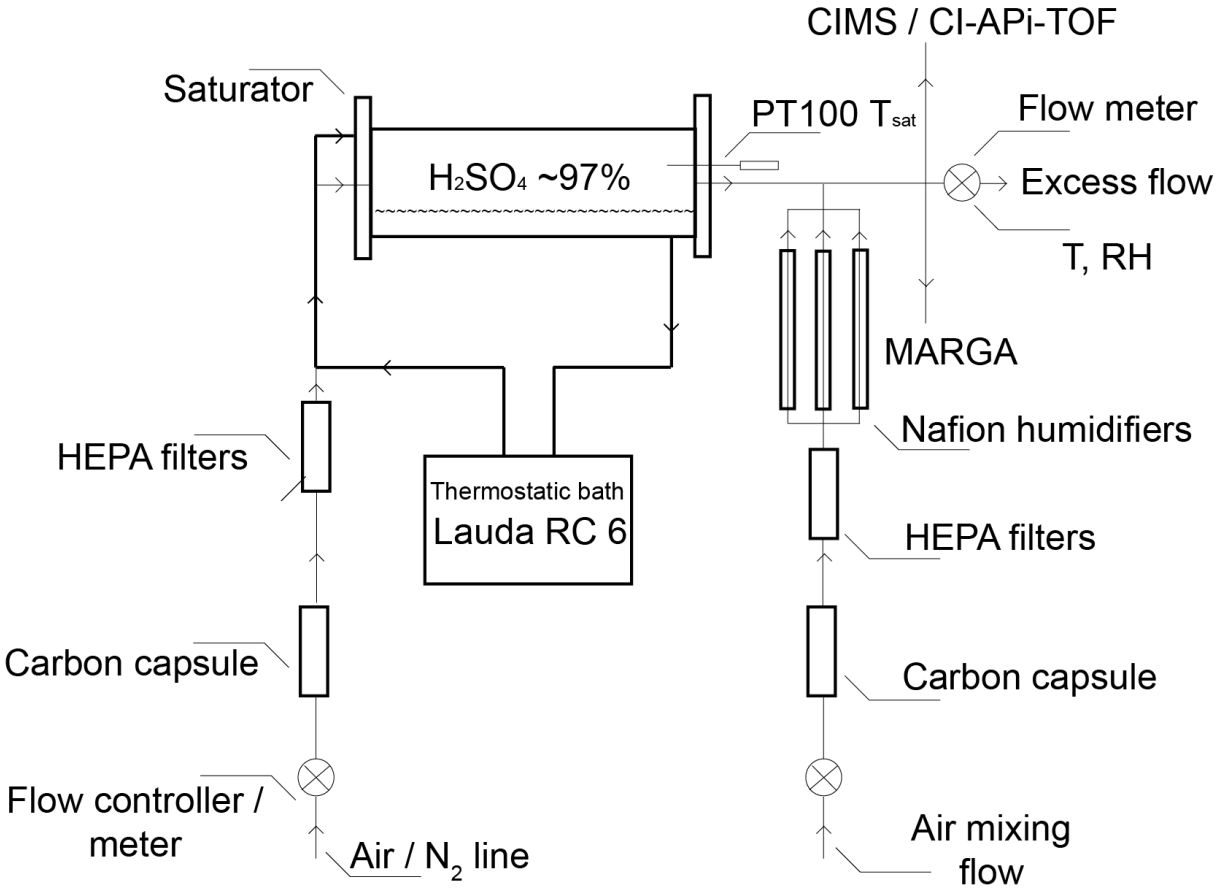

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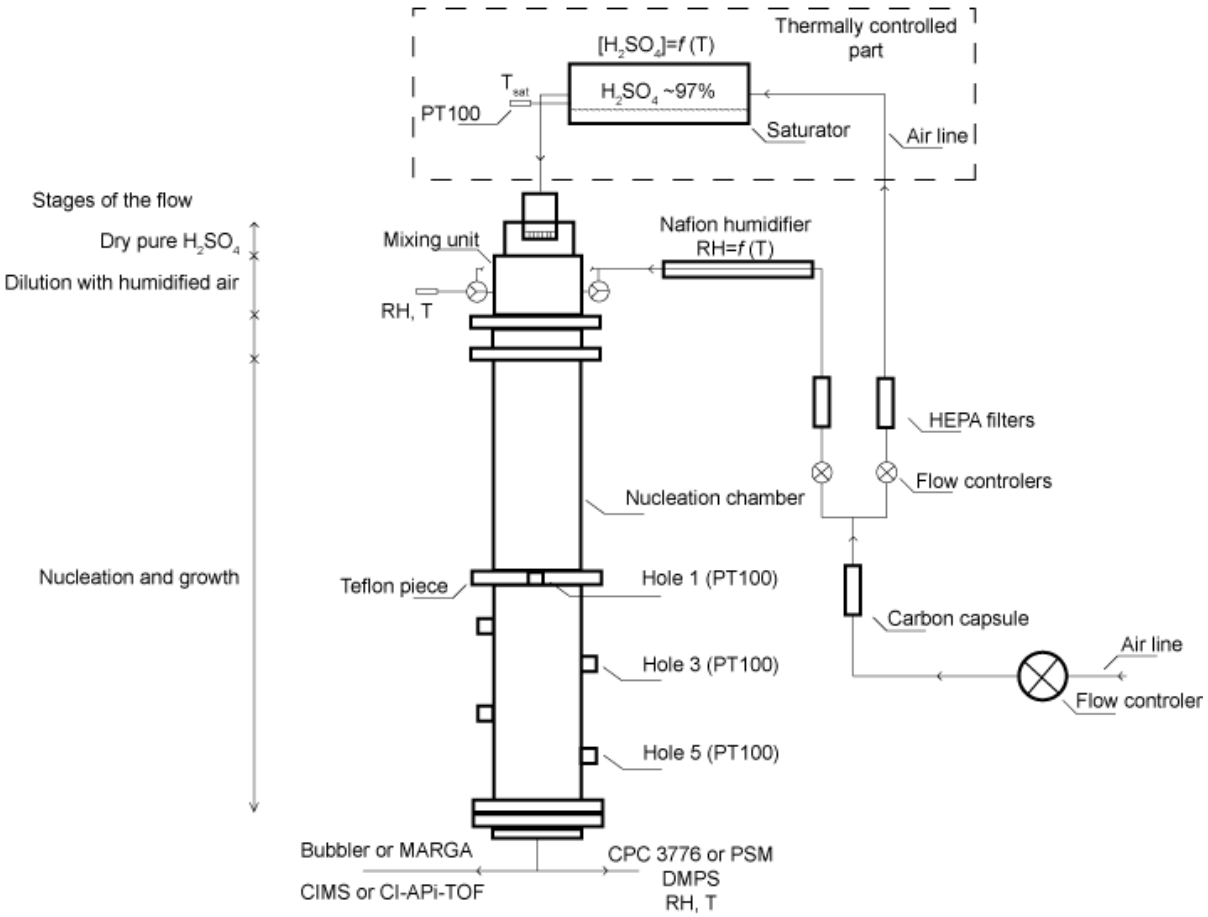
3 Figure 1. Sechematic figure of the setup for testing the saturator.



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3 Figure 2. Flow-tube setup.

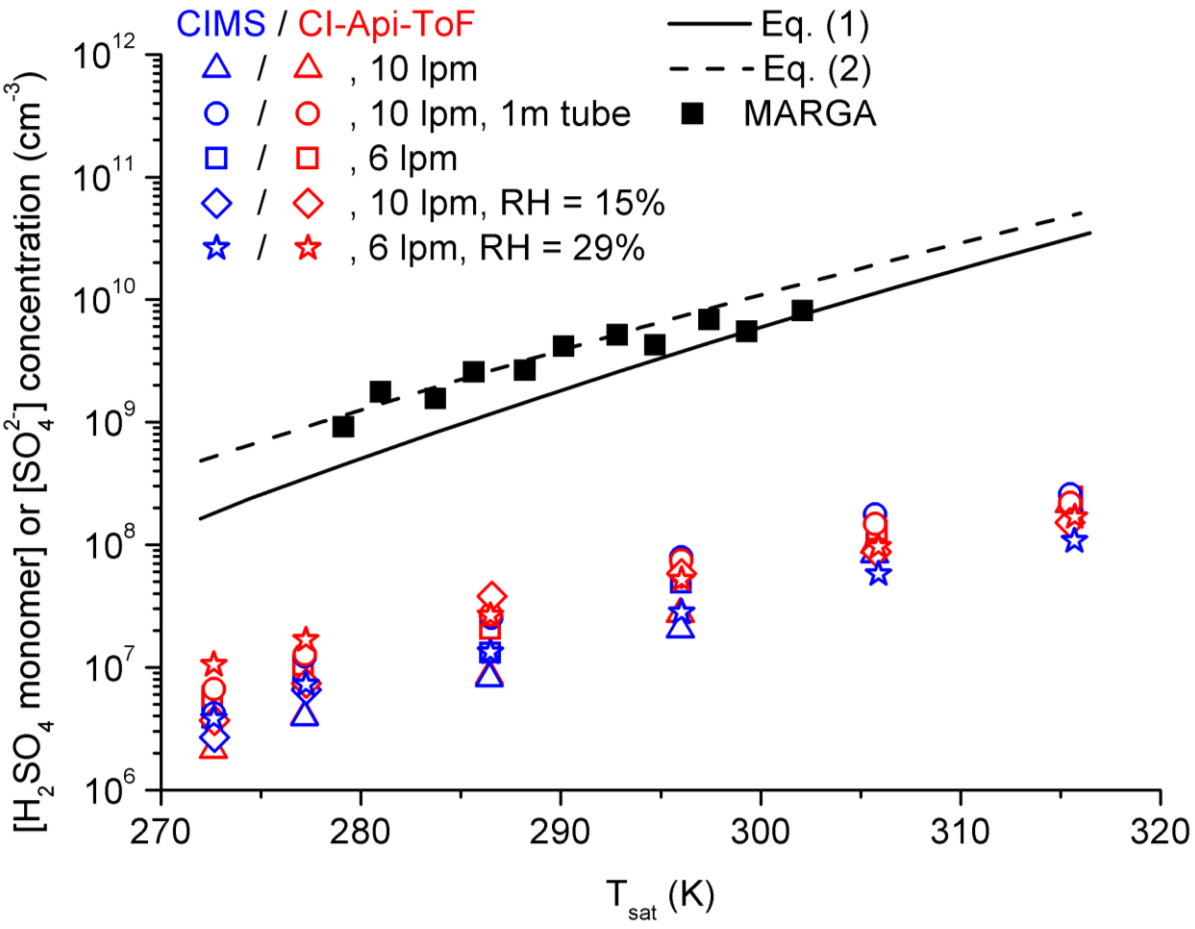
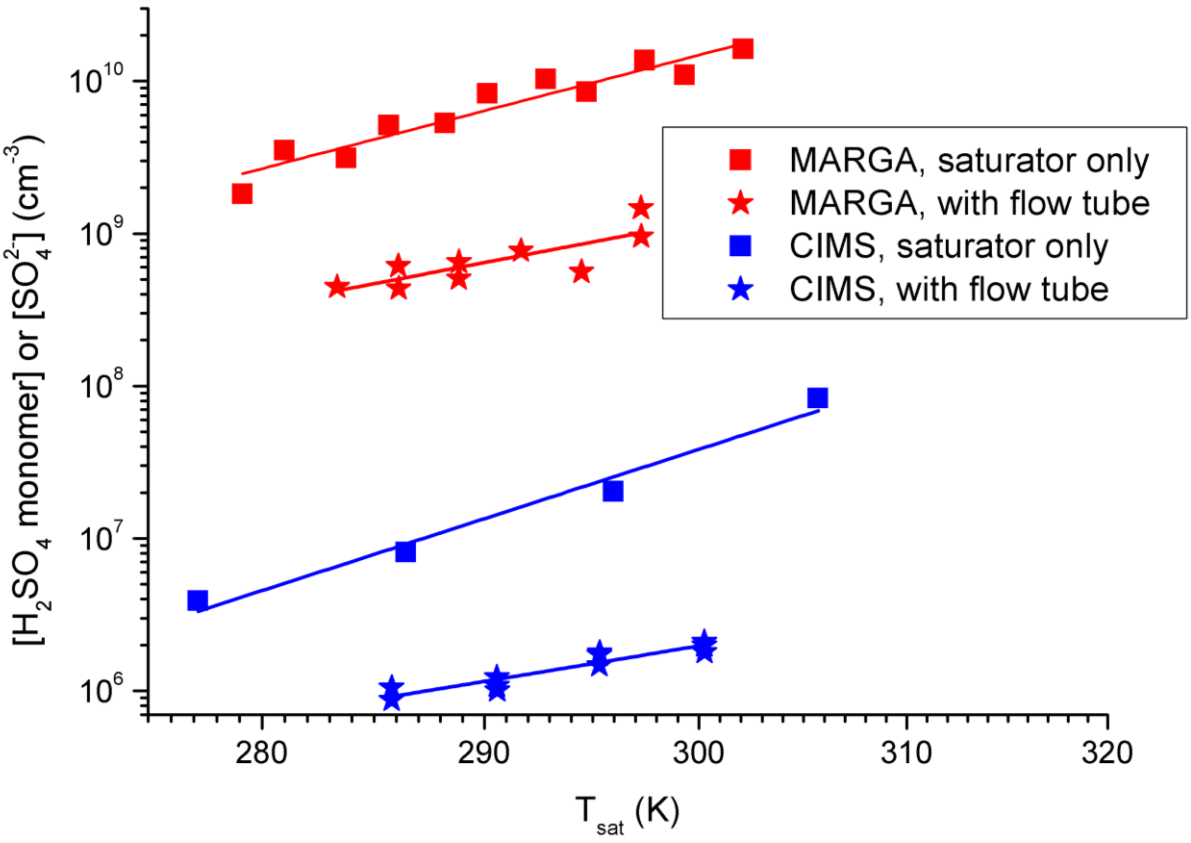


Figure 3. Measured sulphuric-acid monomer [H_2SO_4 monomer] and total-sulphate [SO_4^{2-}] (black squares) concentrations together with predicted values by Eq. (1) and (2) as a function of saturator temperature T_{sat}. Saturator flowrate is Q_{sat} = 0.5 lpm and mixing flowrates were 40 lpm (dry for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



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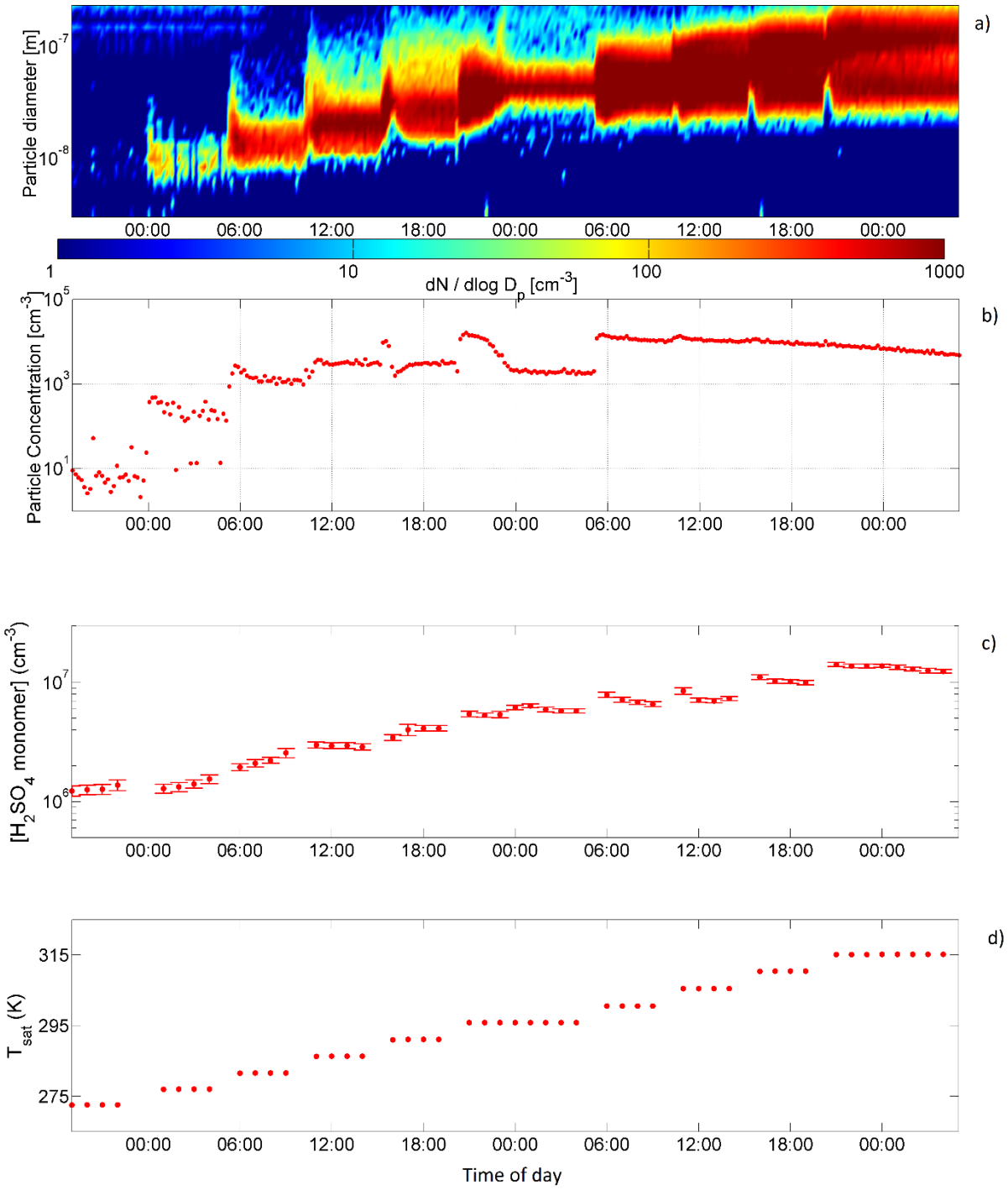
3 Figure 4. Comparison of MARGA and CIMS data between test with only saturator (dry
4 conditions, squares) and with saturator and flow tube (RH ~30 %, stars). Different flowrates
5 through saturator have been accounted for. Average total loss factors are TLF_{MARGA} = 10.0 ±
6 1.2 and TLF_{CIMS} = 14.2 ± 4.2. See text for details.



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

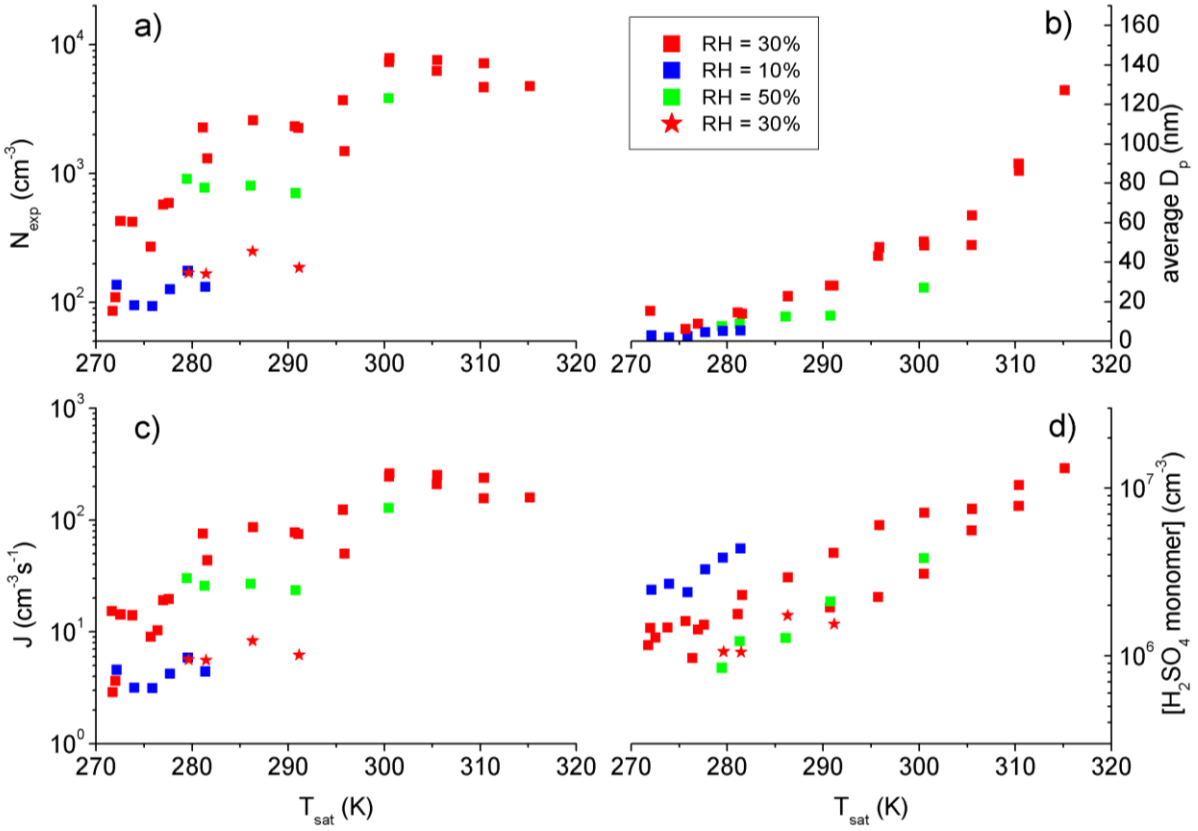

Figure 6. Number concentration N_{exp} (panel a)) measured with PSM and TSI 3776, geometric-mean diameter D_p (panel b)), apparent formation rate J (panel c)) of the freshly nucleated particles and sulphuric-acid monomer concentration measured (panel d)) with CIMS (squares) or CI-Api-TOF (stars) with several relative humidity as a function of saturator temperature with saturator flow of 0.1 lpm. All data are averaged over a period of constant saturator temperature excluding first hour to ensure steady-state. Stars are measured with CI-Api-TOF and squares with CIMS. All data are averaged over a period of constant saturator temperature (± 0.05 K) extracting first hour.

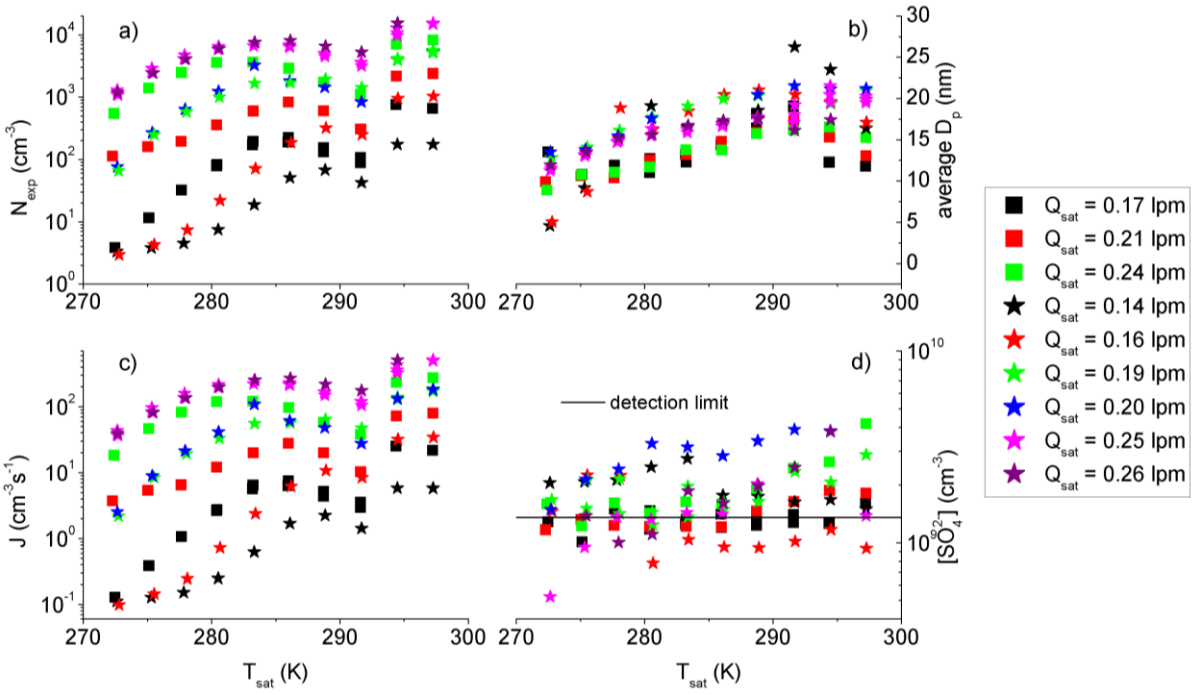

Figure 7. Number concentration N_{exp} (panel a)) measured with TSI 3776, geometric mean diameter D_p (panel b)), formation rate J (panel c)) of the freshly nucleated particles and total-sulphate concentration from MARGA (panel d)) with detection limit of MARGA with several different saturator flowrates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

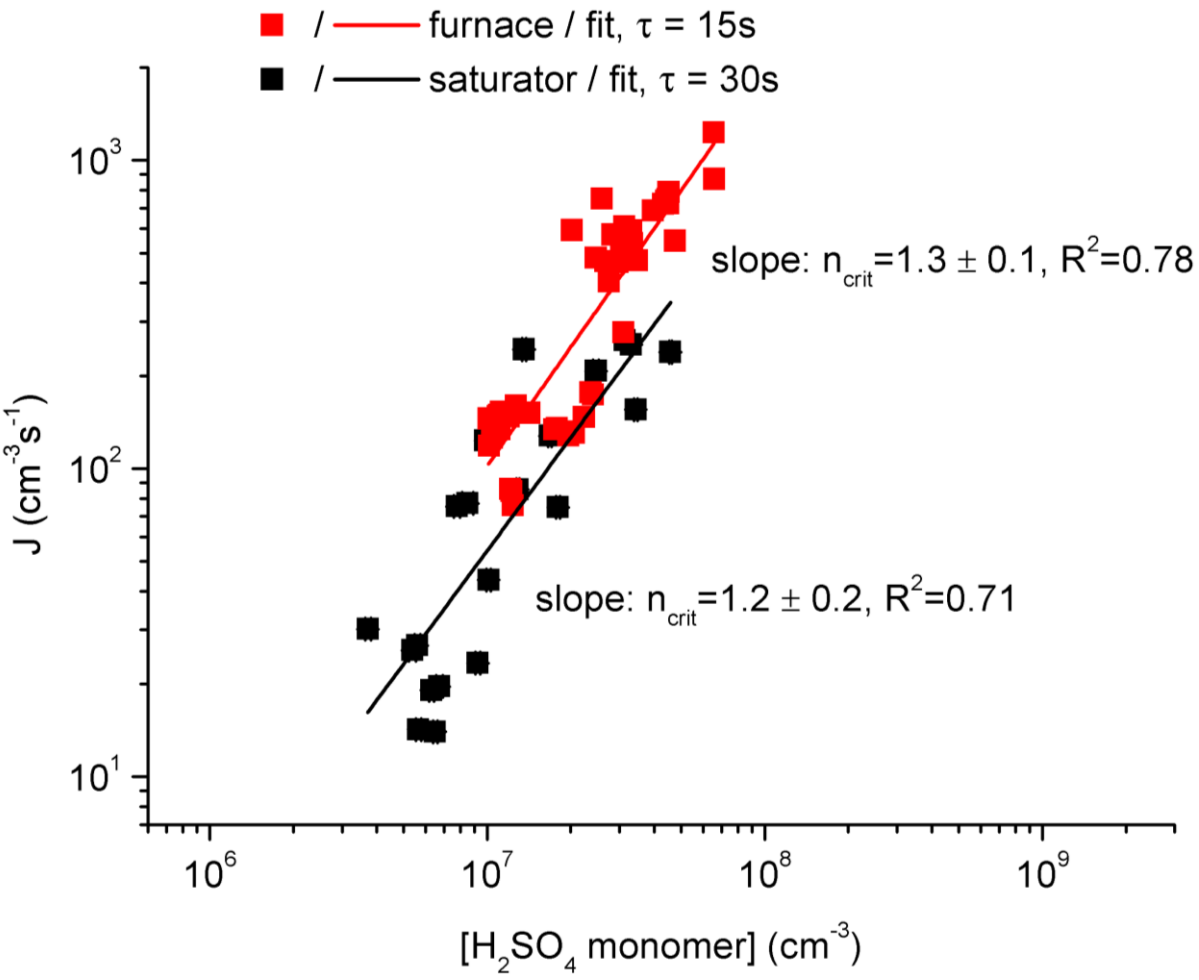

Figure 8. Formation rates *J* as a function of residual sulphuric acid monomer concentration [H_2SO_4 monomer] at *T* = 298 K and RH ~ 30 % measured using CIMS. In the first dataset (red squares) sulphuric-acid vapour was produced with the furnace method and the residence time was defined to be 15 s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

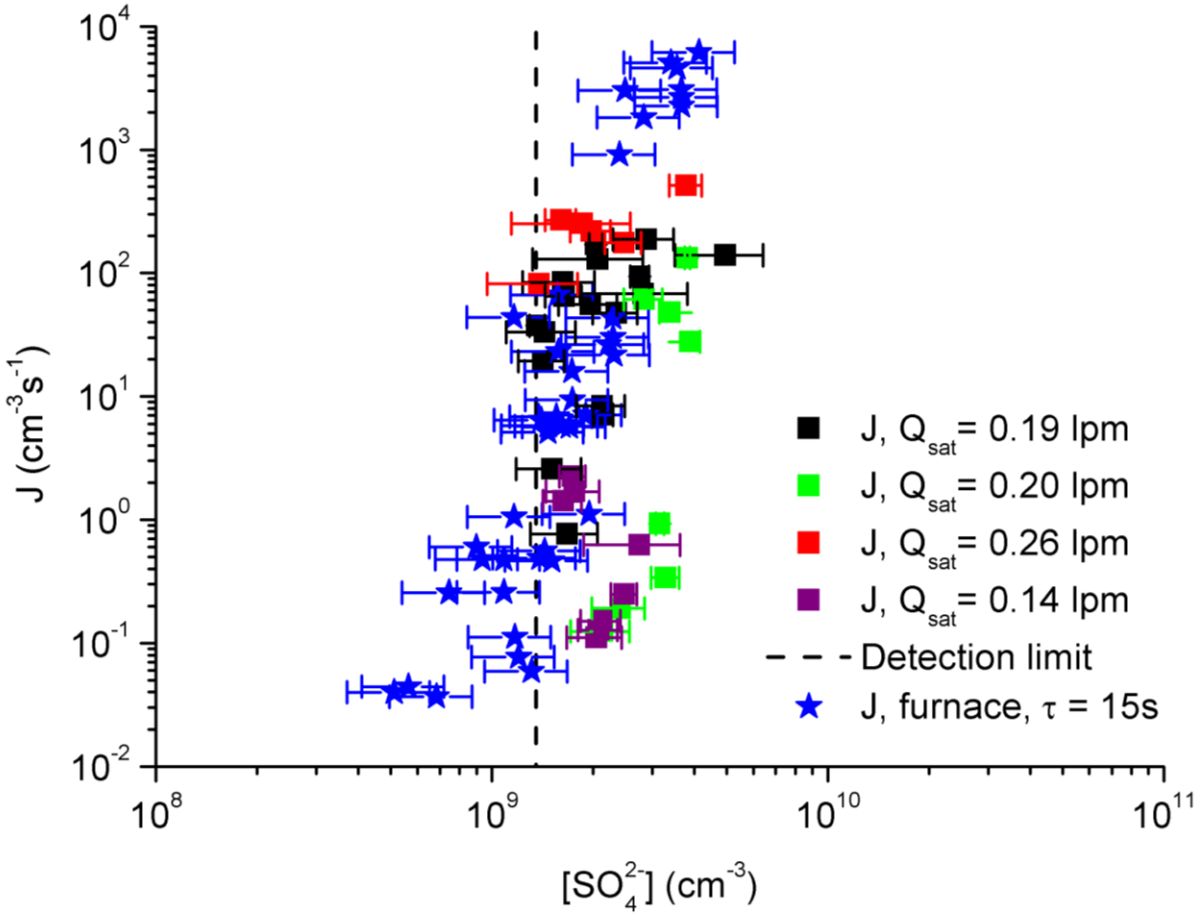

Figure 9. Formation rates *J* as a function of total-sulphate concentration *[SO_4^{2-}]* measured with MARGA or bubbler with different saturator flowrates. MARGA's detection limit is marked with the dashed line. Relative humidity RH ~30 % and nucleation temperature *T* = 298 K. Sulphuric-acid vapour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

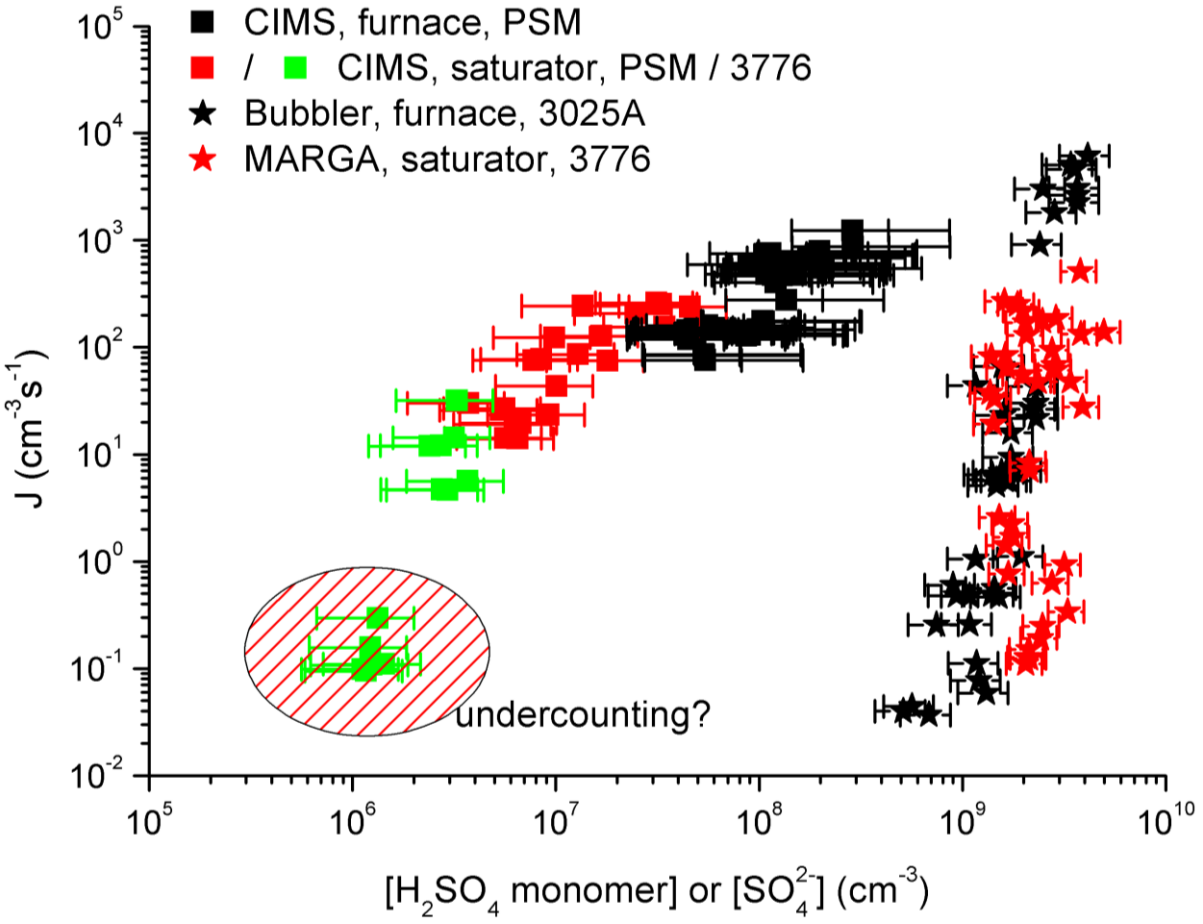

Figure 10. Comparison of formation rates J as a function of residual sulphuric-acid monomer concentration [H_2SO_4] or total-sulphate concentration [SO_4^{2-}] to our previous results. Conditions are similar (T =298 K, RH ~30 %). Note the factor-of-two difference between the residence times between furnace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